

Experimental Techniques

This chapter describes the sample preparation methods, different experimental techniques and basic principle of instruments used for characterizations of prepared materials, investigated in this thesis. Doped ceria electrolytes were synthesized by a single step chemical method, called as glycine nitrate auto combustion method, followed by subsequent calcination and sintering at elevated temperatures. A eutectic mixture of alkali carbonates and doped strontium ferrite based electrode materials have been also prepared by the well-known solid state ceramic route. After preparation, all the samples need to be characterized by different characterization techniques to evaluate their structure-property correlations. Thus, in order to explore the properties of materials, the characterization of all samples have been done by the use of some modern and sophisticated instruments in this thesis work. Structural, microstructural and compositional analysis of all the samples were done by X-ray diffractometer (XRD), Scanning Electron Microscope (SEM) and energy dispersive X-ray spectrometer (EDX), respectively. In order to get more insight into the microstructure of samples, transmission electron microscope (TEM) analysis is also done. Thermal characterization was carried out by TG-DTA (thermo-gravimetric-differential thermal analyzer) analysis. The formation of oxygen vacancies in the samples was investigated by Raman Spectroscopy. The electrical properties of prepared electrode and electrolyte samples were characterized by impedance analyser.

2.1 Sample Synthesis

2.1.1 Glycine-nitrate auto Combustion method

Auto Combustion method produces oxidized materials through a high temperature exothermic redox chemical reaction between chemical fuel and an oxidant. In this method, generally nitrates are used as starting materials and glycine is used as fuel, which produces energy from the exothermic decomposition of a redox mixture of

metal nitrates and glycine. The exothermic combustion reaction is controlled by the ratio of fuel (glycine) with reactant cations, such that, the oxidising and reducing valances in the mixture is balanced. The valances of cations and anions are taken with their sign e.g. +4 for 'Ce' and -2 for 'O', while nitrogen is given 0 valance, and carbon is assigned +4 valance, in calculating the balance of redox reaction, during combustion synthesis. Usually, in this synthesis method, the stoichiometric amounts of oxides of starting materials are first dissolved into nitric acid to get resultant nitrate solution, if reactants are not already in nitrate form. If nitrates are the starting materials then, they are dissolved in distilled water. After that, appropriate amount of glycine is dissolved using water in a separate beaker and then mixed to the previous reactant nitrate solution. The final solution is stirred continuously using magnetic stirrer under constant heating at 200-250°C for complete homogenization. As a result of continuous evaporation of solvent, the solution converts in to yellowish gel. The drying gel gets ignited after sometime with glowing flames and the evolution of large amount of gases. Within few seconds, the auto ignition is completed, giving rise to the fine ash powder. In order to further enhance the homogeneity of final product, the as-synthesized ash is then grounded in an agate mortar. A schematic flow chart of different steps in combustion synthesis is shown in Figure 2.1. The major advantages of this method over the others are:

- i. Final product having better purity and particle size homogeneity.
- ii. Cheap and low cost process.
- iii. Requires simpler equipment like glass beaker, magnetic stirrer, thermometer etc.
- iv. Requires lower temperatures for subsequent heat treatments.
- v. Agglomeration of powder remains limited.

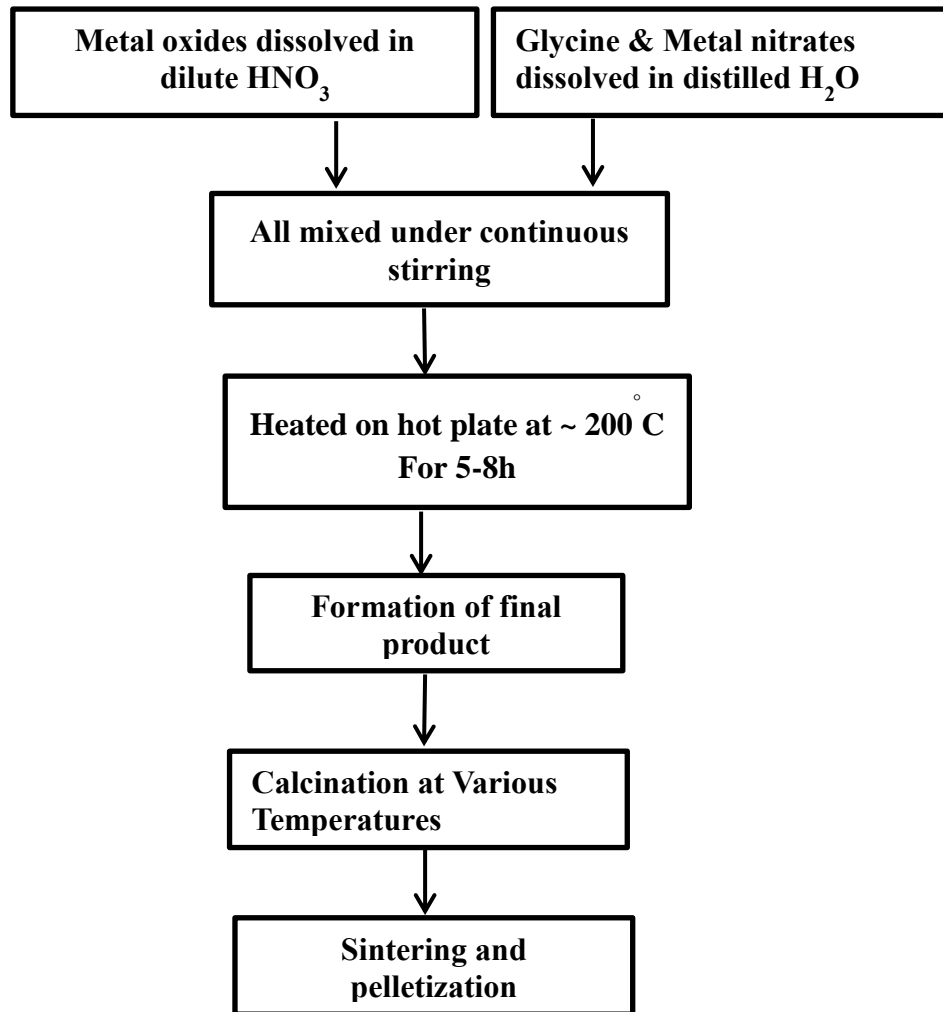


Figure 2.1 Flow chart of glycine-auto-combustion method.

2.1.2 Solid state reaction method

Solid state reaction method is very widespread method for the preparation of polycrystalline ceramics. This is the simplest procedure in many ways, the essential oxides are milled together and heated until they react and form the desired compound. In place of oxides the hydroxides and carbonates of precursor materials can also be used for this process. The ease of the procedure, though its main advantage, does get few disadvantages. The reactions among the constituent materials may occur at different temperature which combined through grain growth of the primarily formed phase that may not permit complete uniform homogenisation of the final product. The

agglomeration of final product is often occurring in this process which needs rigorous milling earlier to forming and calcination. In view of above shortcomings, an advanced milling method known as high energy ball milling is used, through which, oxide nanoparticles are prepared from the mixture of commercially available raw material by placing in the ball mill which generates energy through high collision from the balls inside the container. Usually, reaction between solids do not take place at room temperature, therefore it is essential to heat them in order to occur reaction at a significant rate. This point out that both thermal and kinetic factors play important role in solid state reactions. It is a well-controlled sample synthesis technique by which structural phase transformation can be occurred by energizing and dissociating of the starting raw materials. The mechanical alloying process can be carried out using different machine, specifically, attritor, horizontal ball mill, or a planetary ball mill. In this method starting materials, kept inside the tightly closed containers having balls of same material (ZrO_2) as that of containers, are rotated and vibrated at a particular rotation speed for predefined duration (see Figure 2.2). New phases and new compounds were formed after the starting materials were getting mixed, fractured, cold welded and energized during mechanical alloying. Finally, the nano powder was collected from the containers and calcined at various temperatures. Zirconium dioxide, Stainless steel, tungsten carbide etc. are the common materials of containers and balls. Flow chart of intermediated steps in solid state ceramic method is shown in Figure 2.3

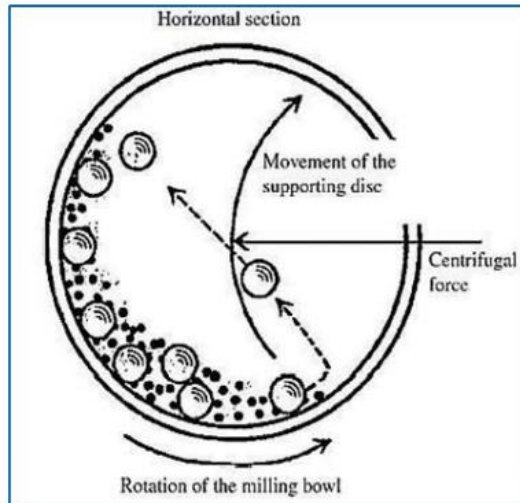


Figure 2.2 Mechanism and working principle of ball milling [Suryanarayana et al.,2001]

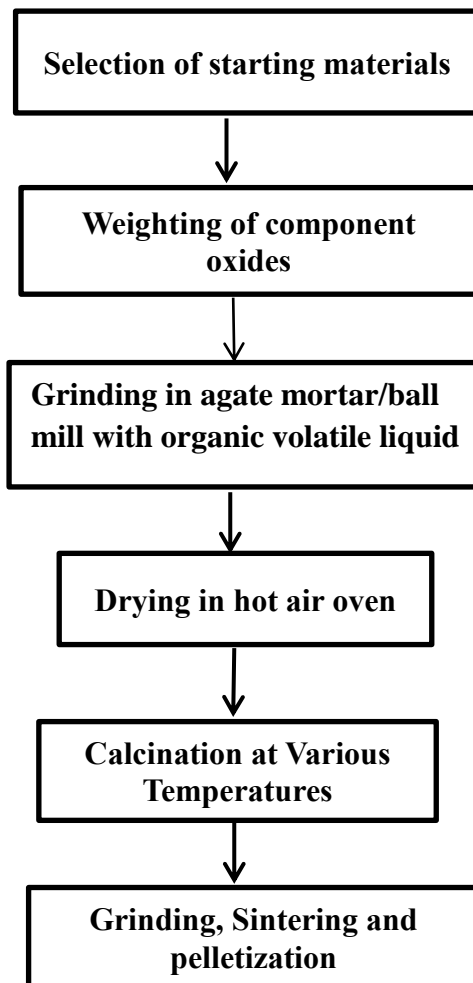


Figure 2.3 Flow chart of solid state reaction method

The major advantages of high energy ball milling method over the others are:

- (i) Low cost grinding medium and installation.
- (ii) One pot, facile one step mechanochemical synthesis.
- (iii) User defined speed of rotation, revolutions per minute (rpm) and sample milling time.
- (iv) Suitability of selecting milling atmosphere.
- (v) Appropriate for materials having all degrees of hardness.
- (vi) Control particle size of the final product.
- (vii) Formation of sample in nano dimension.

2.2 Characterization Techniques

2.2.1 Density measurement

The density of all sintered pellets was calculated by Archimedes principle. To measure the density, the pellet was weighted first in air followed by in an immersion liquid. Acetone (density ρ_{ace}) was used as immersion liquid. If the weight in air and acetone medium are measured as m_{air} and m_{ace} , respectively, then the actual density of the all pellet is calculated as Eq. 2.1

$$\rho = \frac{\rho_{ace} \times m_{air}}{m_{air} - m_{ace}} \quad \text{Eq. 2.1}$$

2.2.2 Powder X-ray diffraction (XRD)

Powder X-ray diffraction is a flexible non-destructive technique that provides in depth information about the crystallographic structure of materials in addition to some insight about the chemical composition of manufactured and natural materials. This method can be employed to determine the phase purity, crystal structure, crystallite size, preferred orientation of lattice planes, and size and shape distribution of a polycrystalline powder. The most commonly used X-ray radiation are from copper

$\text{CuK}_{\alpha 1}$ having characteristic wavelength (λ) = 1.5406 Å. The collimated X-ray beams are directed onto the sample surface followed by intensity of scattered X-ray recorded with a detector. It works on the principle that when a filtered monochromatic beam of X-rays is projected onto a sample at all possible incident angles θ , the strong diffracted intensity is obtained for only those angles which satisfies Bragg diffraction condition as illustrated below. The atoms in a crystalline materials lattice are in regular periodic order in such a manner that a series of parallel atomic planes are formed with separation from one another by a distance 'd', which varies according to the nature of the particular material and a particular set of parallel atomic planes. W. H. Bragg and W. L. Bragg established a relationship to describe the generalize explanation of X-ray diffraction patterns given by eq.2.2.

$$2d \sin\theta = n\lambda \quad \text{Eq. 2.2}$$

Where, d is the inter planer spacing of the parallel atomic layers, θ is the angle of incidence of the X-rays and λ is the wavelength of the incident X-rays and n is integer specifying order of reflection. In polycrystalline materials, Bragg's Law conditions are satisfied via changing angle θ for different inter planer d-spacing. The inter planner spacing d_{hkl} , refers the distance between the parallel planes of atoms. This observation generally known as X-ray diffraction is a case of X-ray wave interference and was direct evidence for the layered periodic atomic structure of crystals as shown schematically in Figure 2.4 [Barcikowski et al., 2016; Cullity et al., 1956].

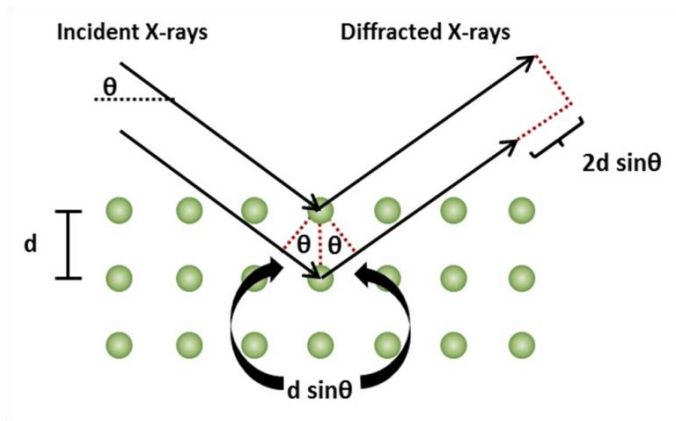


Figure 2.4 Schematic representation of X-ray beam incident on a crystal lattice plane of material [Barcikowski et al., 2016; Cullity et al., 1956].

The characteristic diffraction pattern of a particular sample is obtained by plotting diffracted intensities as a function of diffraction angles. When various phases are present, resultant diffractogram is the sum of individual diffracted intensities. By X-ray diffraction, chemical, physical and structural, information about material can be investigated. The X-ray diffraction pattern measured from atoms planes within the given material depends on both the length scale of periodic crystalline order as well as nature and relative position of atoms in the unit cell. So, it determines the spacing between lattice planes, crystalline phases, crystalline nature of materials, preferential ordering of atomic planes and epitaxial growth of crystallites.

In this thesis work, the prepared, finely grounded polycrystalline samples were characterized by using Rigaku Miniflex (see Figure 2.5) and SmartLab X-ray diffractometer equipped with Cu $K\alpha_1$ radiation of wavelength $\lambda = 1.5406 \text{ \AA}$. A standard Silicon sample was used for determination of instrumental parameters. For most of the samples, the scan range was $20^\circ - 80^\circ$ with step size 0.02° and scan rate 0.5 deg/minutes for Miniflex and 5 deg/minutes for SmartLab diffractometers.



Figure 2.5 X-Ray diffraction facility.

The Rietveld structure refinement was done to precisely determine the crystallographic parameters of the samples. The Rietveld method is described by International Union of Crystallography (IUCr) as *“Technique of analysing X-ray powder diffraction data from which crystallographic structural information is obtained via refining the complete profile of the observed diffraction pattern until it completely matches with calculated diffraction profile using a least-squares approach”*. This technique is extensively used for microstructural and quantitative phase information of any material [Rietveld et al., 1967; Rietveld et al., 1969]. In the initial step of this technique, crystalline phase(s) identification of the material is identified by ICDD (International Centre for Diffraction Data). Once the phase(s) is recognized, corresponding detailed crystal structure file named Crystallographic Information File (CIF) is taken either from ICSD (Inorganic Crystal Structure Database), or COD (Crystallographic Open Database) database, or from the reported literature, that closely matches with the experimental XRD pattern. Rietveld structure refinement software is employed to simulate theoretical XRD pattern with these CIF files. However, in order to obtain structure and microstructure information this data

must be provided: (i) instrumental correction factors (instrumental peak shift, peak broadening and peak asymmetry) for the used XRD with a certain setting which are acquired by studying the XRD pattern of a standard specimen like Silicon. (ii) approximate values of crystallite size and lattice strain. Keeping all instrumental correction parameters fixed, structural and microstructural parameters are refined via iterative mode to fit the experimental XRD pattern until all the parameters converge. The “best fit” between intensities of simulated (calculated) and the experimental (observed) XRD patterns is achieved by successive refinements of structural and microstructural parameters.

The Rietveld structural analysis of X-ray diffraction pattern is a cumbersome process needing lots of calculations containing many parameters. For this purpose, user friendly softwares are used which can correlate experimental and calculated pattern at each refinement step. There are a number of Rietveld softwares available free of charge and are being used by many researchers globally. In this thesis work, FullProf suite has been employed for Rietveld structure refinement analysis. This refinement software is proficient of estimating microstructural parameters as well with concerns of all current developments along with precise measure of structural parameters [Carvajal et al., 1993; Young et al., 1993]. A representative Rietveld fit for X-ray pattern at the initial stage of refinement (Figure 2.6 a) and after completion of the refinement (Figure 2.6 b) is shown in Figure 2.6.

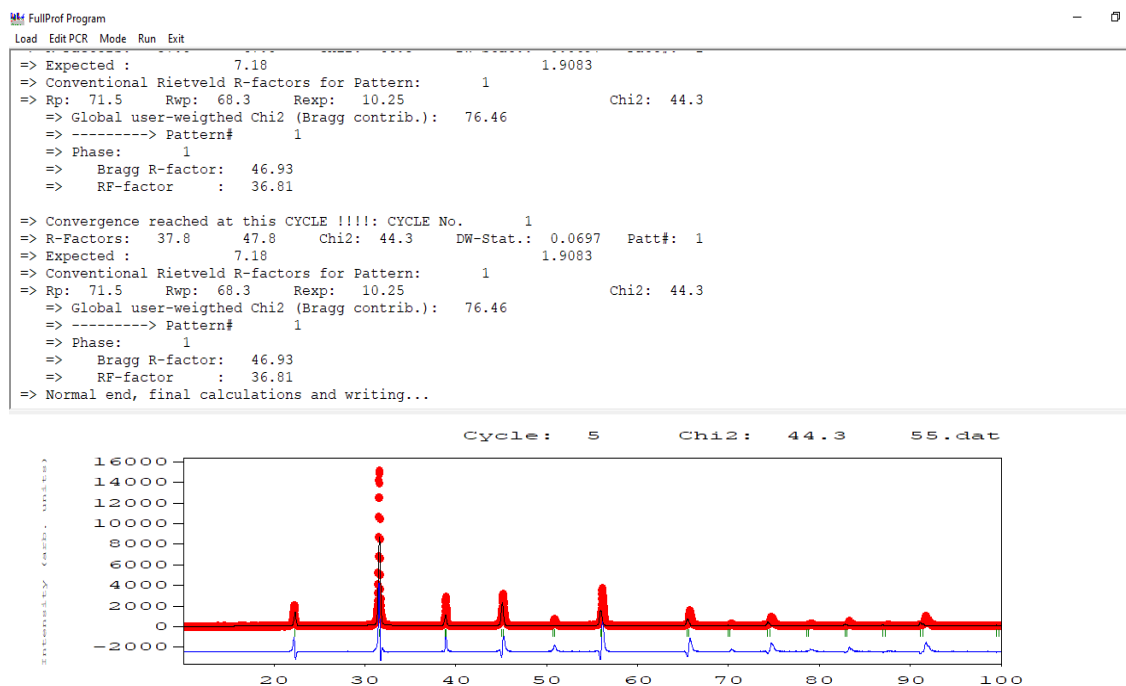


Figure 2.6(a) Representative image of structural refinement fit of XRD data using FullProf suite [Carvajal et al.,1993] at the initial stage of refinement.

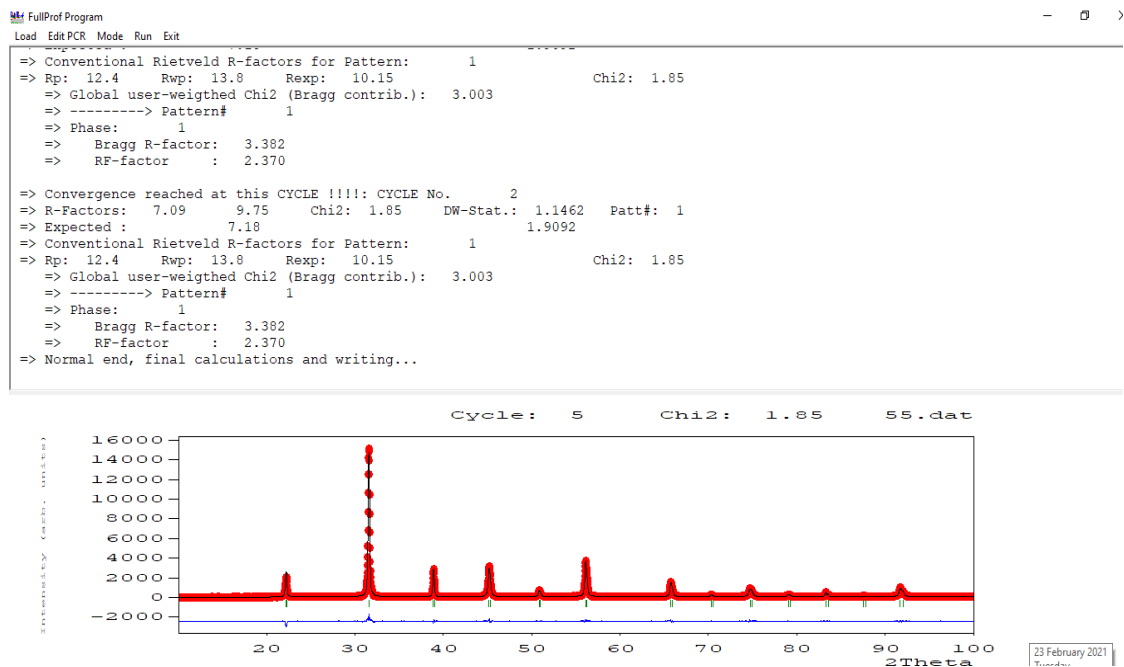


Figure 2.6(b) Representative image of structural refinement fit of XRD data using FullProf suite [Carvajal et al.,1993] after completion of the refinement.

The important features and benefits of this software are

- (i) Simultaneous quantitative phase analysis, crystal structure and microstructure refinement.
- (ii) Automatic structural refinement and quick parameter modification.
- (iii) Diffraction patterns obtained from powder, solid pellets, thin films or multilayers can also be refined.
- (iv) Various types of defect and texture models are included.
- (v) User friendly operation.
- (vi) More than one CIF data and different approaches of the program can be further added without recompiling the whole program.

2.2.3 Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM) is a microscope in which a beam of electrons is used to generate high resolution images of the sample surfaces by scanning it through the raster scan pattern. Lanthanum hexa boride (LaB_6) or heated tungsten filament single crystals generate electrons and produce a fine electron beam by magnetic lenses. A beam of electrons liberated from a tungsten filament or field emission source travel vertically through high vacuum column in a high electrical field gradient and is bombarded on to the sample surface. As a result, backscattered or secondary electrons collected by a detector above sample surface provide information of sample's morphology, particle size, defects and the distribution of elements at the surface [Skoog et al., 2010; Harvey et al., 1956]. A schematic representation of the entire process is shown in Figure 2.7. In this thesis, surface imaging of sintered pellets was performed by using scanning electron microscope from ZEISS EVO 18, as shown in Figure 2.8. This instrument gives new level of performance having high resolution

and excellent contrast at ultra-low, low and high voltage imaging with wide accelerating voltage range from 200V down to 30kV, extended magnification ranges up to 50K ~100K. For elemental analysis purposes i.e. qualitative and quantitative determination of elements in the samples, this SEM is equipped with an energy dispersive spectrophotometer (EDS). Measuring energy of emitted characteristic X-rays allows the spatial distribution of elements through mapping of sample.

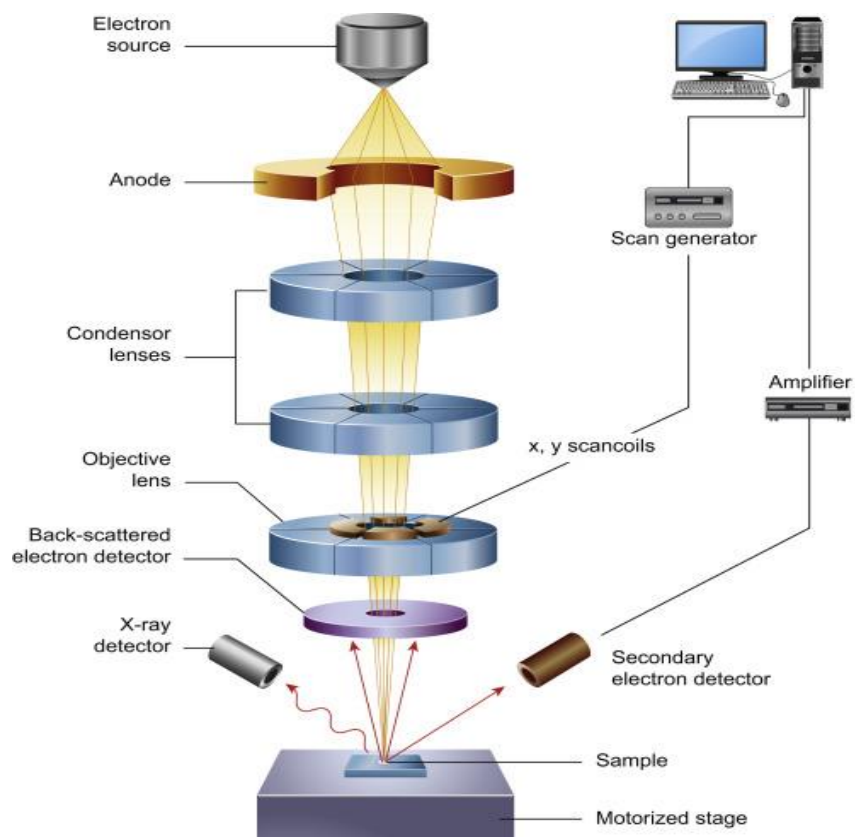


Figure 2.7 Schematic representation of image formation in SEM.



Figure 2.8 ZEISS EVO 18 SEM facility

2.2.4 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) is one of the most powerful methods to offers the atomic resolution imaging of materials in which lattice fringes are observed that refers the crystallographic planes. It provides method to examining sample's dimensions, defects, surface features, particle size, particle size distribution, crystal structure and crystalline phases of sample. The electron gun is used as emission source which emits electrons that travel within a column and focused through magnetic condenser lens into thin beam. An objective magnetic lens is used to focus transmitted electrons into an image, after that projective magnetic lens is used for magnification of image. The electron distribution of ultra-thin specimen is enlarged by using three/four stage magnetic lens arrangement and observed on fluorescent screen or a detector. The image can be acquired digitally by a CCD camera or direct introduction of photographic emulsion or an image plate.

TEM is able to yield crystallographic information of sample by means of selected area electron diffraction (SAED). The parallel beam of electrons having energy in the range of 100-400 KeV pass easily through the sample [Williams et al., 2010; Skoog et al., 2010]. For high energy electrons having wavelength of few thousands of nanometer, which is hundred times smaller than spacing between atoms in solid work as a diffraction grating for the electrons. Thus diffraction, at particular angle determined by crystal structure of the solid, will occur for some fraction of electrons while remaining continue to pass through sample without deflection (see Figure 2.9). Sharp diffraction spots in SAED pattern are observed due to projection of reciprocal lattice with lattice plane reflections.

In this thesis, we have employed Tecnai G2 20 TWIN for Transmission electron microscopy (see Figure 2.10). The microstructural characterizations of nanomaterials were carried out by placing the nano particles in formvar-carbon coated copper grid. The TEM micrograph were further analysed by using the ImageJ software.

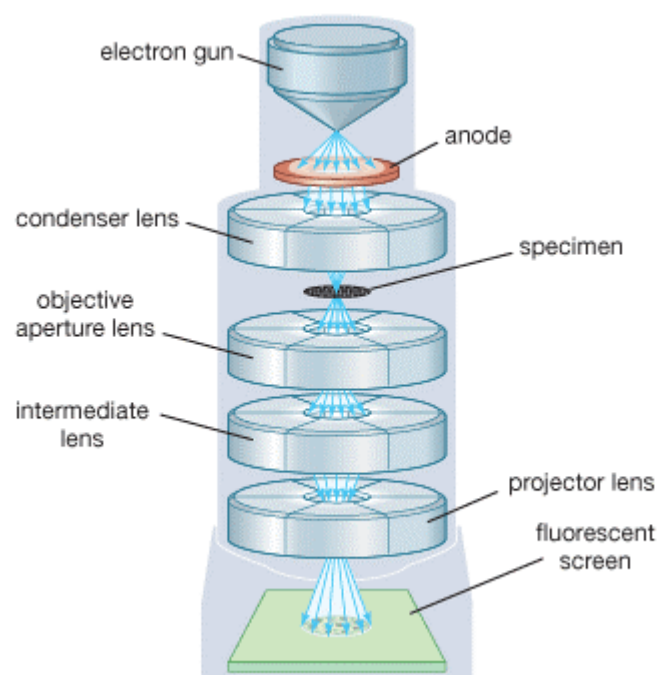


Figure 2.9 Schematic diagram of image formation in TEM.



Figure 2.10 Tecnai G2 20 TWIN TEM facility.

2.2.5 TG-DTA Thermal characterization

Thermal gravimetric analysis (TGA) is a technique to examine the thermal stability of as synthesized sample through which change in certain physical and chemical properties (like mass) of the as synthesized sample is analysed as a function of temperature. It is one of the foremost technique of thermal analysis that provides detailed information about phase transition, reduction/oxidation, solid state reactions, absorption, desorption etc. of the material under investigation. In TGA pattern, if no mass change is examined in a certain temperature range then the sample is considered as thermally stable material. TGA is widely used to know the phase transition, melting and degradation temperature of materials. The schematic diagram of TGA is represented in Figure 2.11 [West et al., 1999].

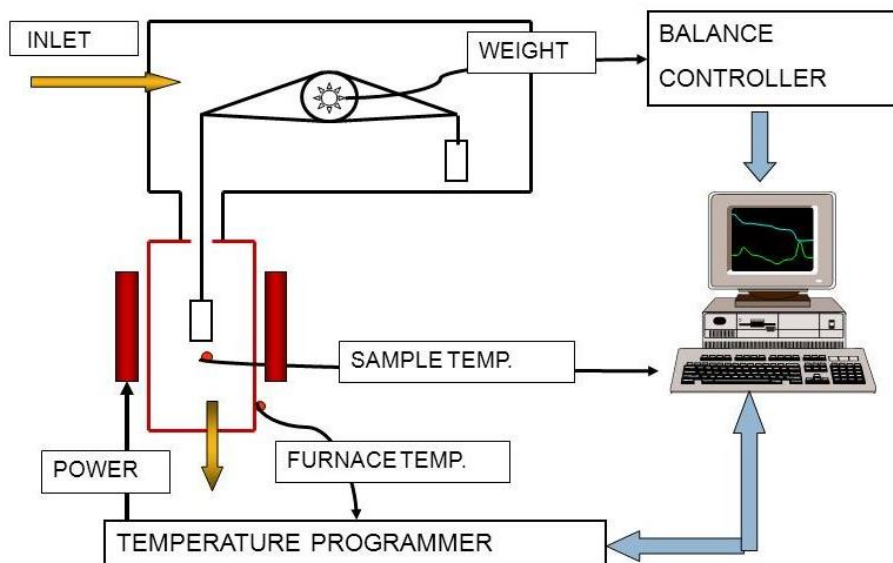


Figure 2.11 Schematic diagram of TGA

Differential thermal analysis, usually known as DTA determines the heat flow rate related with material transition as a function of temperature while throughout the experiment, the whole system i.e. sample as well as reference is maintained at nearly the similar temperatures. It also allows the detection of qualitative and quantitative data on exothermic (heat evolution) and endothermic (heat absorption) methods of samples during physical transitions that are occurring due to phase changes, adsorption, desorption, melting, crystallization, glass transitions, oxidation, and other heat associated changes. In the present thesis work, TG-DTA measurements were carried out using Mettler Toledo machine, operated in nitrogen atmosphere in the temperature range from RT to 800 °C (see Figure 2.12).



Figure 2.12 Mettler Toledo TG-DTA facility.

2.2.6 Raman Spectroscopy Study

Raman spectroscopy is an analytical technique in which the radiation scattered from a sample such that the structural phase, molecular bond structure, and different kind of defects can be studied based on vibrational (phonon) states transitions inside the material. In Raman spectroscopy, interaction of incident laser light with molecular vibrations causes the energy shift in a small fraction of the laser photons and these scattered laser radiations by the molecules produce a characteristic pattern (see Figure 2.13). It is also worthy to mention that the shifts in the energy of incident laser photons depends on the molecular structure of the system which is responsible for the scattering. The variation in Raman shifts give the information about different vibrational modes associated with the chemical groups of the structure. The Raman spectra of the samples in the present thesis work were recorded in a STR-300 system using a He-Ne laser at the 532 nm line as the excitation source in the wave-number range of $150\text{-}1000\text{ cm}^{-1}$ (see Figure 2.14).

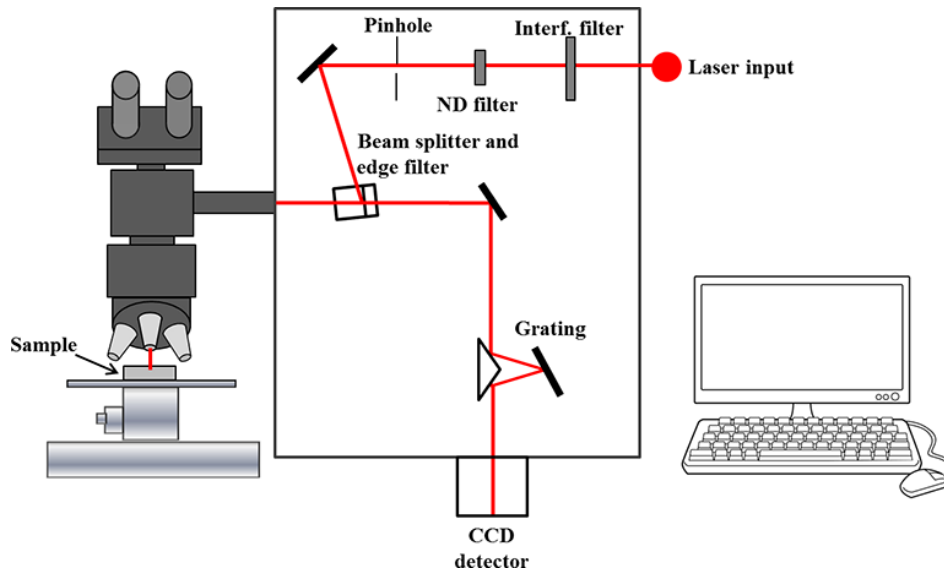


Figure 2.13 Graphical representation of the main apparatus of a Raman microspectrometer [Bonales et al., 2016]

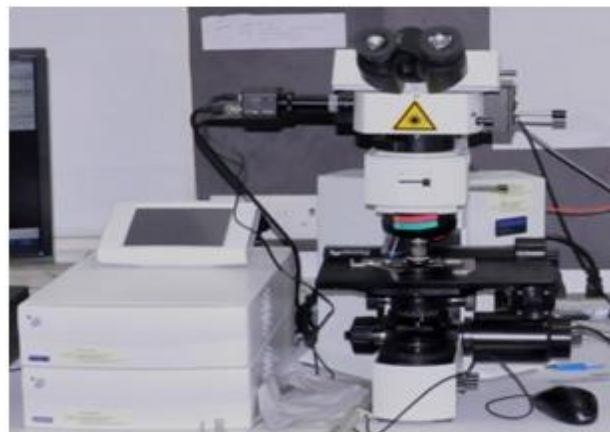


Figure 2.14 STR-300 Raman spectroscopy facility

2.2.7 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is a powerful testing technique for measuring the electrical behaviour of electro-ceramic materials by applying the small ac potential as perturbation. EIS is also used to observe the impedance, ac conductivity, dielectric and charge transport properties of the samples.

2.2.7.1 Sample preparation for EIS

In this thesis work, to measure the electrical properties, cylindrical pellets were made by uniaxial pressing [~ 70 MPa] with the help of a hydraulic press in a 10 mm diameter stainless steel die and using acetone as binder. The required electroding was done by applying high temperature conductive silver paste (Siltech) on both surfaces of the pellets. The electrical response in the presence of ac signal at different temperatures was recorded by mounting the pellet in a sample holder inside a tube furnace in air atmosphere using two probe method.

2.2.7.2 Set up for electrical measurement

The temperature and frequency dependence of various electrical responses such as impedance, dielectric loss, dielectric constant, etc. were measured by using an impedance analyser (KEYSIGHT-E4990A) in static ambient atmosphere in the frequency range 20Hz to 5MHz from RT to 700°C as illustrated in Figure 2.15. Through the help of these investigations the charge relaxation phenomena, the ion dynamics, etc. were facilitated in understanding the correlation between structure and electrical properties of the developed electrode and electrolyte materials. A thermocouple was placed inside the heating chamber and kept close to the sample for monitoring the temperature.

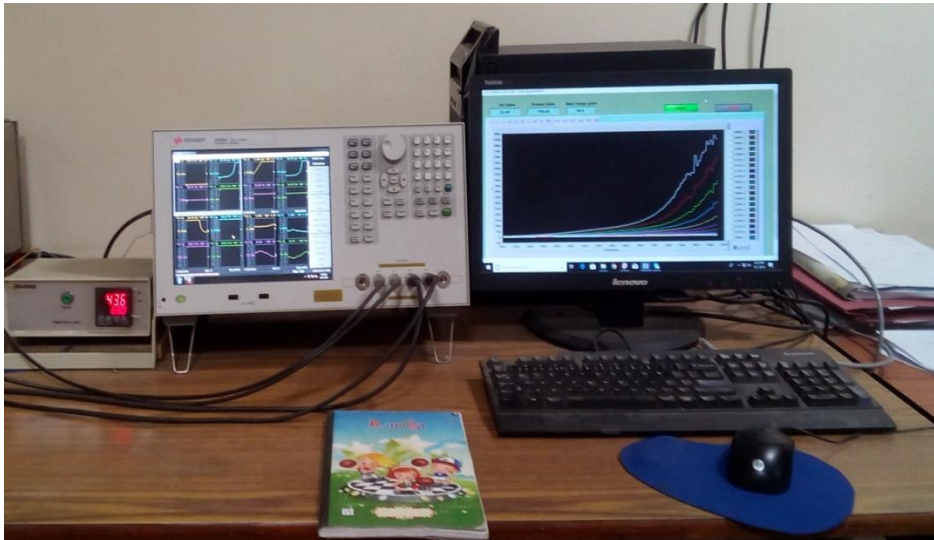


Figure 2.15 KEYSIGHT-E4990A ac impedance measurement facility.

2.2.7.3 Complex Impedance Spectroscopy Analysis

Electrochemical impedance spectroscopy (EIS) is established on applying to the system an external sinusoidal perturbation of current or voltage with variable frequency f but constant amplitude but and then after observing its response.

Typically, EIS data are represented as the plot of the real part of complex impedance (Z') against imaginary part of complex impedance (Z'') which is well known as Nyquist plots or Cole-Cole plots as shown in Figure 2.16. The advantage of Nyquist representation is that it provides a quick idea of the measured data and one can create some quantitative understanding about resistance therefore conductivity of the sample, at certain measuring temperature. Typically, one, two or three overlapping semicircular arcs are observed in the Nyquist plot of polycrystalline materials as shown in the Figure 2.8. Conductivity of a pellet samples can be calculated by using the Eq. 2.3

$$\sigma = L/RS \qquad \text{Eq. 2.3}$$

where, L denotes thickness and A denotes cross sectional area of the sample surface. R is the resistance associated with the bulk (R_b) and grain boundary (R_{gb}) contributions acquired from the impedance plots. The high, mid and low frequency semicircular arc determines the contribution of impedance from grain impedance (R_g), impedance from grain boundary (R_{gb}) and impedance from electrode-polarization (R_{el}) respectively [Irvine et al., 1990]. The equivalent circuit model is associated by all of these three contributions in the system, as represented in the inset of Figure 2.16. The Z-Simpwin software was used to calculate the total impedance, in view of the series arrangement of three parallel RQ circuit elements, equivalent to each of these, grain, grain boundary and electrode effect (see Figure 2.17).

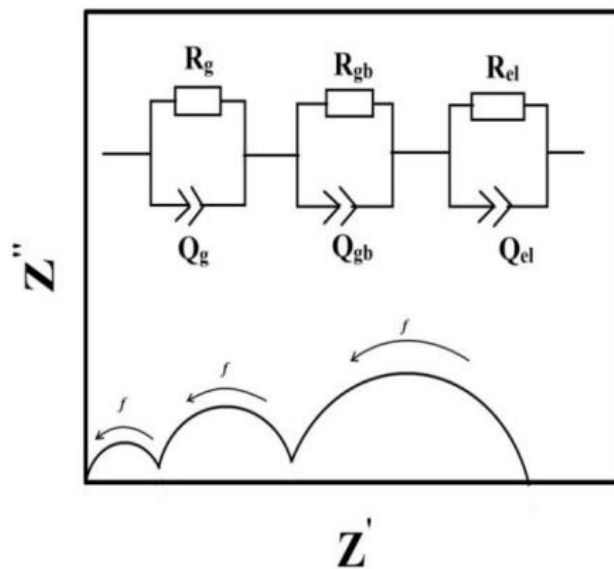


Figure 2.16 The typical Nyquist plot. The inset to figure denotes the equivalent electronic circuit mode [Pandey et al., 1995].

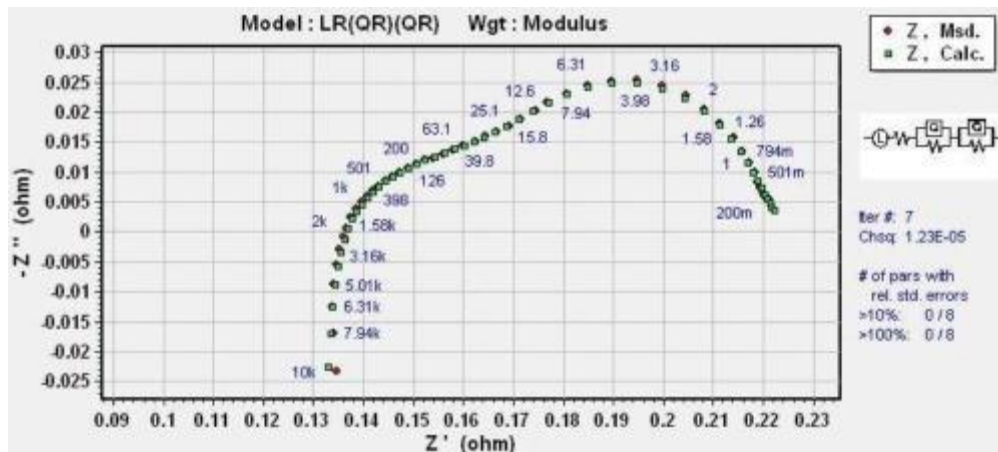


Figure 2.17 A representative fitted impedance data using Z-Simpwin software

2.3 Conclusions

In summary, this chapter gives detailed description about sample preparation procedures used in this thesis work. Various characterization techniques and analytical methods which are employed to analyze the samples and interpret the results throughout the present thesis work are given. The theoretical aspects of these characterizations are also discussed briefly.