

## CHAPTER – II

### Experimental Techniques

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*A theory is something nobody believes, except the person who made it. An experiment is something everybody believes, except the person who made it.*

*Albert Einstein*

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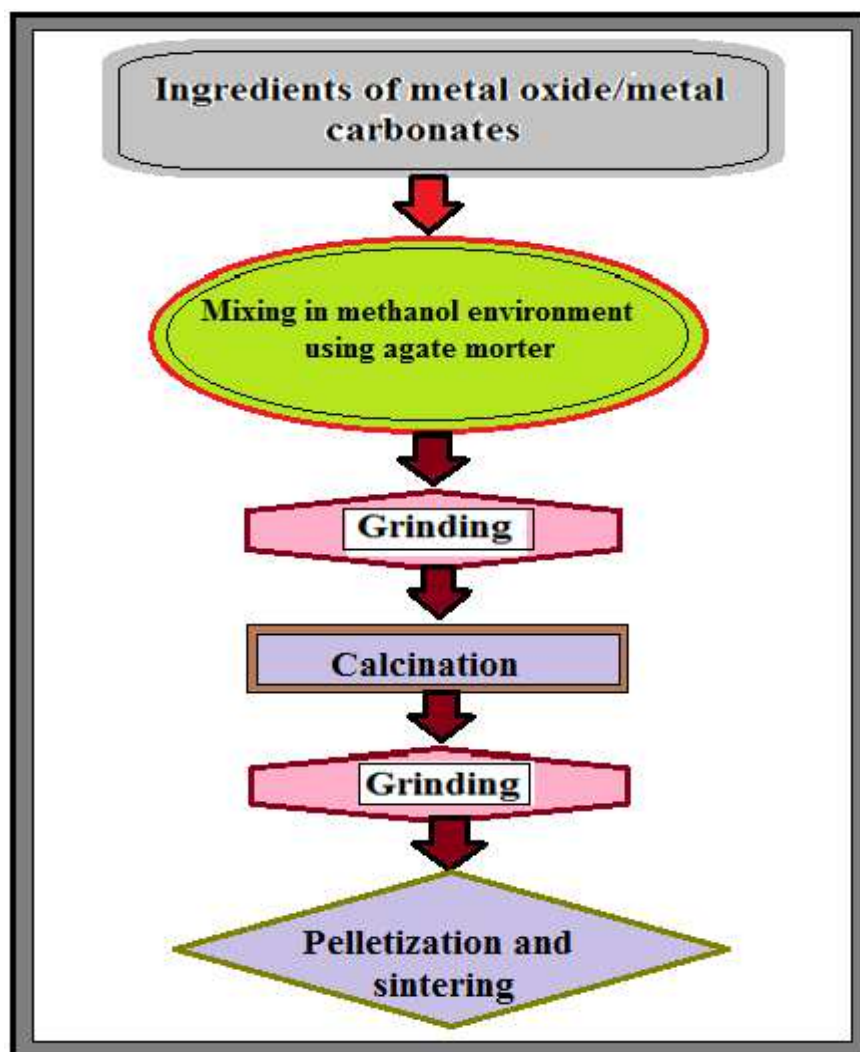
## 2.1 Introduction

The methods of preparation of samples from raw materials and characterization techniques are discussed in this chapter. The properties of electrochemical materials such as conductivity are highly dependent on synthesis techniques. The factors such as particle sizes, impurity content as well as density can vary a lot for different synthetic procedure and as a result affect the electrochemical properties of the substances. Brief details on the necessary heat treatment for the synthesis of compounds and thereafter preparation of pellets have been discussed. The prepared samples after sintering have been characterized by various techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), Fourier transformed infrared spectroscopy (FTIR) and complex impedance spectroscopy. For impedance spectroscopic measurements, the pellets were coated with conducting silver paste.

## 2.2 Synthesis

The electrochemical properties such as conductivity of oxide ion conducting ceramic materials are highly dependent on the method of synthesis. A lot of variation in particle sizes, impurity content as well as density of a sample can occur during different process of synthesis and might become the critical factors that affect the properties such as conductivity. Therefore, in order to obtain the desired materials proper method of synthesis should be chosen.

The samples were synthesized by using conventional solid state reaction technique. The flow sheet of the experimental procedure adopted is given in **Fig. 2.1**.



**Fig.2.1:** Flow chart depicting various steps of conventional Solid State Reaction Technique.

### 2.2.1 Calcination

In order to obtain required microstructures and proper reaction between the constituents of the compositions, the raw powders were usually subjected to heat treatment at certain temperatures with controlled procedures. The changes taking place in the process of firing could be quite complex which depends on the various parameters such as temperatures and atmospheres. Usually two terms are used to represent this heating process: calcination and sintering. Generally, the term calcination is used to the thermal treatment process applied to raw materials which causes a thermal decomposition, phase transition, or removal of a volatile substances

present within the composition. Usually the calcination process is carried out at temperatures below the melting point of the resulting composition.

### 2.2.2 Sintering

Sintering is a heat treatment process in which a compact powder is heated to an appropriate temperature just below the melting point of the material. During sintering the powder does not melt; instead the process of solid state atomic diffusion takes place and there by leads to joining the particles and reduce the porosity and as a result giving rise to higher densities.

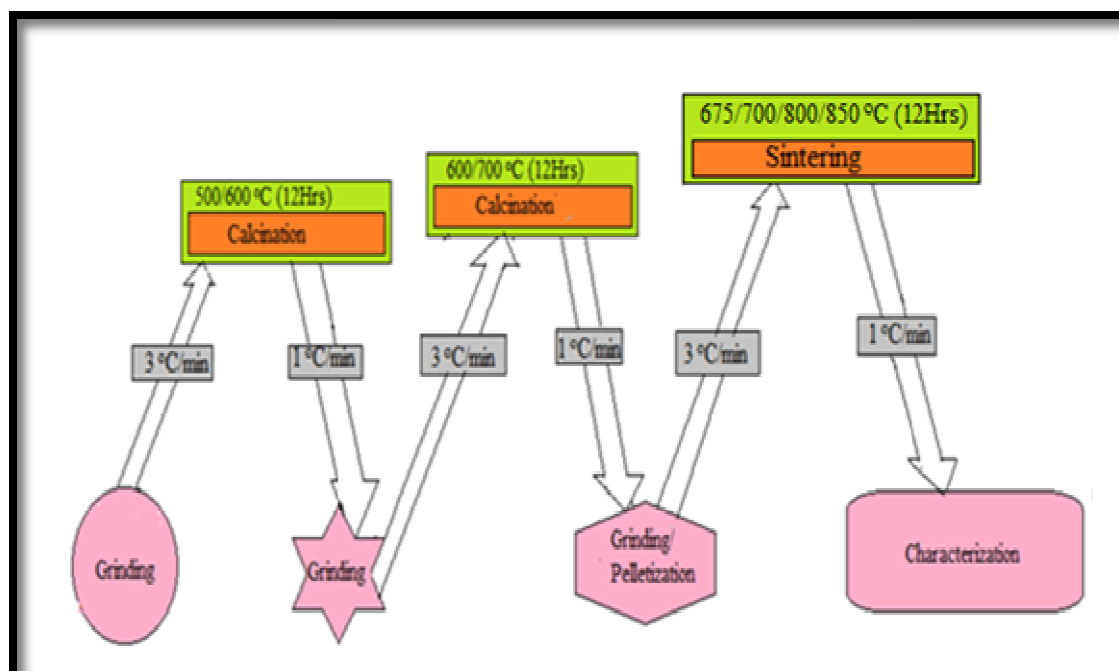
### 2.2.3 Sample preparation

Conventional solid state reactions technique were used to synthesize the compositions  $\text{Bi}_4\text{V}_2\text{O}_{11}$  and  $\text{Bi}_{4-x}\text{M}_x\text{V}_2\text{O}_{11-\delta}$  ( $\text{M}=\text{Li}, \text{Ca}, \text{Ba}$ ) from appropriate amounts of  $\text{Bi}_2\text{O}_3$  (99%, Loba chemie),  $\text{V}_2\text{O}_5$  (99%, Loba chemie),  $\text{Li}_2\text{CO}_3$  (99.99%, Loba chemie),  $\text{CaCO}_3$  (98.5%, Merck) and  $\text{BaCO}_3$  (99%, Merck). The composition selected for all the above mentioned systems were  $x=0.1$ ,  $x=0.2$ ,  $x=0.3$  and  $x=0.4$ . The details of the preparation of compositions from the constituent powders and different heat treatment cycles are given in **Table 2.1**.

**Table.2.1:** The samples with ingredients and their corresponding heat treatment.

Compositions	Ingredients	Calcination Temperature, Time ( $^{\circ}\text{C}$ , hour)		Sintering Temperature, Time ( $^{\circ}\text{C}$ , hour)
		I	II	
$\text{Bi}_4\text{V}_2\text{O}_{11}$	$\text{Bi}_2\text{O}_3, \text{V}_2\text{O}_5$	600, 12	700, 12	850, 12
$\text{Bi}_{4-x}\text{Li}_x\text{V}_2\text{O}_{11-\delta}$ ( $x=0-0.4$ )	$\text{Bi}_2\text{O}_3, \text{V}_2\text{O}_5,$ $\text{Li}_2\text{CO}_3$	500, 12	600, 12	700, 12 ( $x=0.1$ ) 675, 12 ( $x=0.2-0.3$ )
$\text{Bi}_{4-x}\text{Ca}_x\text{V}_2\text{O}_{11-\delta}$ ( $x=0-0.4$ )	$\text{Bi}_2\text{O}_3, \text{V}_2\text{O}_5,$ $\text{CaCO}_3$	600, 12	700, 12	800,12
$\text{Bi}_{4-x}\text{Ba}_x\text{V}_2\text{O}_{11-\delta}$ ( $x=0-0.4$ )	$\text{Bi}_2\text{O}_3, \text{V}_2\text{O}_5,$ $\text{BaCO}_3$	600, 12	700, 12	800,12

By taking stoichiometric amounts of constituent oxides/carbonates for each of the systems, the mixture of the starting powders was well mixed in methanol environment and continuously ground for 12 hours (manually) using an agate mortar. This length of time was required to achieve fully homogenous mixture of powders and to facilitate good reactions between the oxide/carbonate powders. The ground mixture obtained was then fired in a muffle furnace at temperature 500°C-600°C for 12 hours. To ensure complete reaction and avoid any large agglomeration, the resulting mixture was again ground for 6-7 hours and then heat treated at 600°C-700°C for 12 hours in air. The details of the heat treatment applied to the samples are explained in **Fig. 2.1**.



**Fig.2.2:** Details of the various steps of heat treatment.

The calcined powders were crushed again for 3-4 hours and mixed with polyvinyl butryal (PVA) which acts as binder and reduce the brittleness of the pellets. The mixture was then pelletized by applying a pressure of ~7 tons using die-punch in a hydraulic press. After waiting for 1-2 minutes, the pressure was released and the compacted pellet was ejected out. The dimensions of the pellets were of about 12-13 mm in diameter and 1-2 mm in thickness. The pellets obtained after compaction were sintered at different temperatures (as depicted in **Table 2.1**) for 12 hours in air in a calibrated resistance heating furnace. To optimize the processing conditions for

achieving better properties, the samples were sintered at different sintering temperatures (675-850 °C) depending upon their melting point.

### 2.3 Sample characterization

Characterization is the vital part of the study of a particular solid electrolyte which enables a better understanding of the different polymorphism possessed by the compound, evaluation of the structure, conductivity measurement and correlation between structure and conductivity. In order to investigate the above parameters, the sintered samples were characterized using X-ray diffraction (XRD), differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and conductivity, fourier transformed infrared spectroscopy (FTIR). The details of these characterization techniques are discussed below:

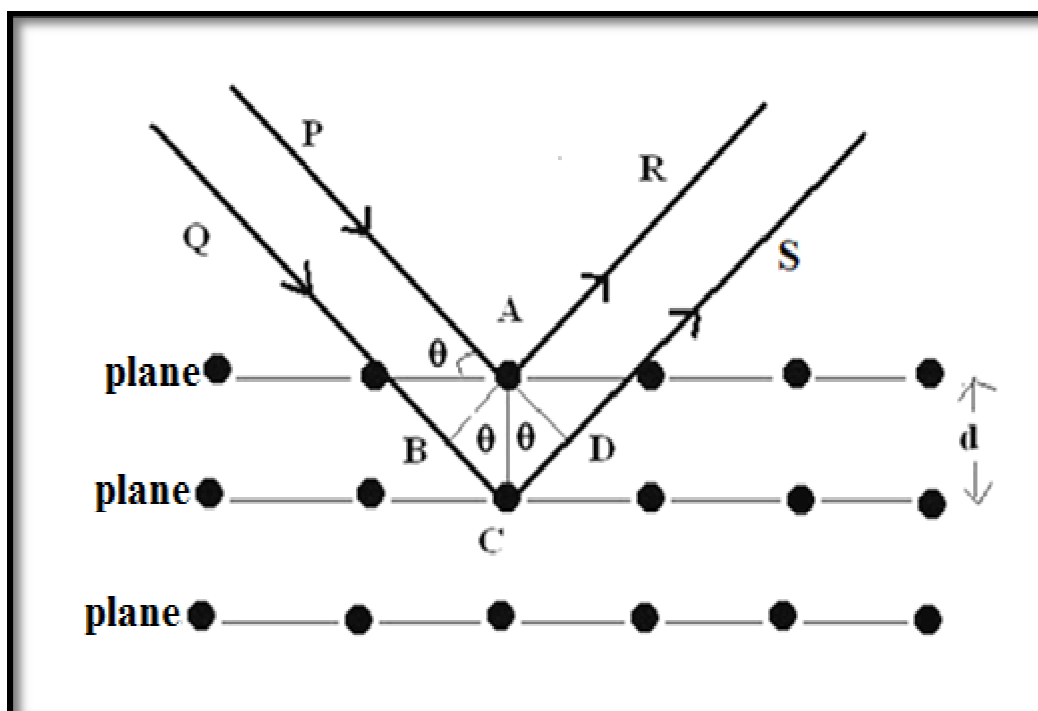
#### 2.3.1 X-ray diffraction

X-ray powder diffraction is a convenient and powerful tool for materials investigation and is used for the determination of crystal structure and examining purities. In a crystalline/polycrystalline material, the crystalline atoms cause a beam of X-rays to diffract into many specific directions and the structural information is obtained from the study of the diffraction pattern. Lattice parameters were calculated with the help of the diffractogram obtained for each sample using Bragg's law as described below:

Bragg's Law is the simple and straightforward way to describe x-ray diffraction. It treats one layer of atoms in crystal as a plane and the smallest unit to diffract incident light. If there is no phase difference between the emergent light AR and CS (**Fig.2.3**), the following equation must be satisfied:

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

Where  $d$  is the distance between adjacent atom planes,  $\theta$  is the incident angle and  $\lambda$  is the wavelength of the light. For a given set of planes, several solutions of Bragg's Law are usually possible, for  $n = 1, 2, 3$ , etc. It is customary to set  $n = 1$  since for  $n = 2$ , the  $d$ -spacing is instead halved by doubling up the number of planes in the set ( $2d \sin\theta = 2\lambda$  equals  $2(d/2) \sin\theta = \lambda$ ), so  $n$  is kept equal to 1 [**1-2**].



**Fig. 2.3:** Illustration of Bragg's law.

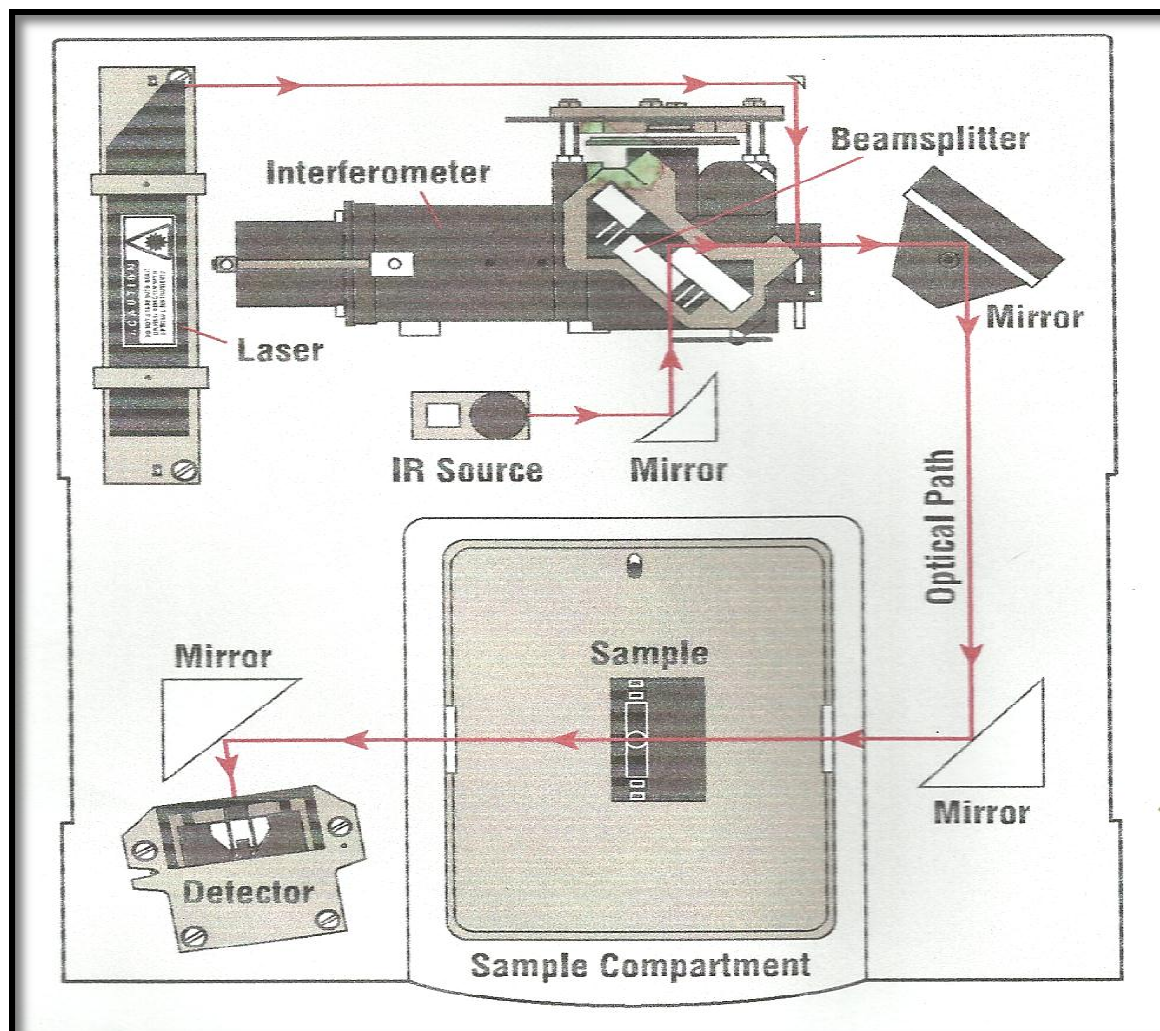
The X-ray powder diffraction data of the samples were recorded at room temperature by RIGAKU (Model, Miniflex) using  $\text{CuK}_\alpha$  radiation ( $\lambda=1.5418 \text{ \AA}$ ) in  $10^\circ$  to  $70^\circ$   $2\theta$  range at a scan speed of  $0.5^\circ$  per minute.

### 2.3.2. Fourier transformed infrared spectroscopy (FTIR)

Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used by organic and inorganic chemists. Simply, it is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam. The main goal of IR spectroscopic analysis is to determine the chemical functional groups in the sample. Different functional groups absorb characteristic frequencies of IR radiation. Using various sampling accessories, IR spectrometers can accept a wide range of sample types such as gases, liquids, and solids.

An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material [3-4]. In addition, the size of the peaks in the

spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis. The block diagram of a simple IR spectrometer is shown in **Fig. 2.5**.



**Fig. 2.4:** Block diagram of a simple spectrometer [3].

The normal instrumental process of a simple IR spectrometer is discussed as follows:

- 1. The Source:** Infrared energy is emitted from a glowing black-body source. The IR beam passes through an aperture which controls the amount of energy supplied to the sample (and ultimately to the detector).
- 2. The Interferometer:** The beam then enters the interferometer where the “spectral encoding” takes place. The resulting interferogram signal then exits the interferometer.



**3. The Sample:** The beam enters the sample compartment where it is transmitted through or reflected off of the surface of the sample, depending on the type of analysis being accomplished. This is where specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed.

**4. The Detector:** The beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal.

**5. The Computer:** The measured signal is digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation.

Because there needs to be a relative scale for the absorption intensity, a background spectrum must also be measured. This is normally a measurement with no sample in the beam. This can be compared to the measurement with the sample in the beam to determine the “percent transmittance.” This technique results in a spectrum which has all of the instrumental characteristics removed. Thus, all spectral features which are present are strictly due to the sample. A single background measurement can be used for many sample measurements because this spectrum is characteristic of the instrument itself. Electromagnetic waves used in infrared spectroscopy have frequencies ranging from  $1.9 \times 10^{13}$  to  $1.2 \times 10^{14}$  Hz, corresponding to photon energies ranging from 0.078 to 0.5eV from the Plank relation,

$$E = h\nu \quad (2.2)$$

Where  $h$  is the Planck constant and  $\nu$  the frequency.

This level of energy is inadequate to excite electrons but may induce vibrational excitation of covalently bonded atoms or groups. The frequencies that absorption happens are closely related to the structure of the molecules, i.e. atom species, bonding types and ways of possible vibration (stretching, scissoring, rocking and twisting). For a typical IR spectrum, studied samples are exposed to a beam of infrared light and transmitted light is collected which reveals the absorption of the samples. From their characteristic absorption frequencies, different functional groups can be quickly identified.

The vibrations of two covalently bonded atoms could be simplified and treated as a harmonic oscillator with 2 masses (atoms) linked by a spring (**Fig. 2.5**).



**Fig. 2.5:** A harmonic oscillator with two masses.

In this simple model, Hooke's Law could be used to approximate and understand stretching frequencies (equation 2.3),

$$\nu = \frac{1}{2\pi} \sqrt{k/\mu} \quad (2.3)$$

Where  $k$  is the force constant for the bond,  $\mu$  is the reduced mass of A-B systems and is given by the equation,

$$\mu = \frac{m_A m_B}{m_A + m_B} \quad (2.4)$$

$m_A$  and  $m_B$  are the masses of A and B atoms respectively.

In our system (bismuth vanadate), the atomic mass of Bismuth is much higher than Vanadium and gives a greater reduced mass for Bi-O systems. Therefore, the stretching frequencies of the Bi-O bonds are relatively low ( $\sim 420 \text{ cm}^{-1}$ ) with respect to V-O bond [5-6].

The FTIR spectra of the prepared samples were recorded in transmittance mode on an IR Affinity-1 spectrophotometer (**Fig. 2.4**) in the wave number region of  $4000\text{--}400 \text{ cm}^{-1}$ .



**Fig. 2.6:** Diagram of IR Affinity-1[3]

### 2.3.3 Scanning electron microscopy (SEM)

SEM of the samples is carried out by applying a beam of accelerated electrons which interact with the constituent atoms of the sample. The signals coming out of the specimen carry information about the sample's surface topography, composition and other properties such as electrical conductivity.

The Electron beams thermionically emitted from the Electron Gun are focused by passing through several condenser lenses to a spot around 0.4-5 nm in diameter. When the electron beams come in contact with the sample, a number of species are generated which are collected selectively by using different collectors and by transforming into signals form the whole image. Gold sputtering technique is used in case of a poorly conductive sample as the small gold particles cover the surface of the sample and give a better resolution.

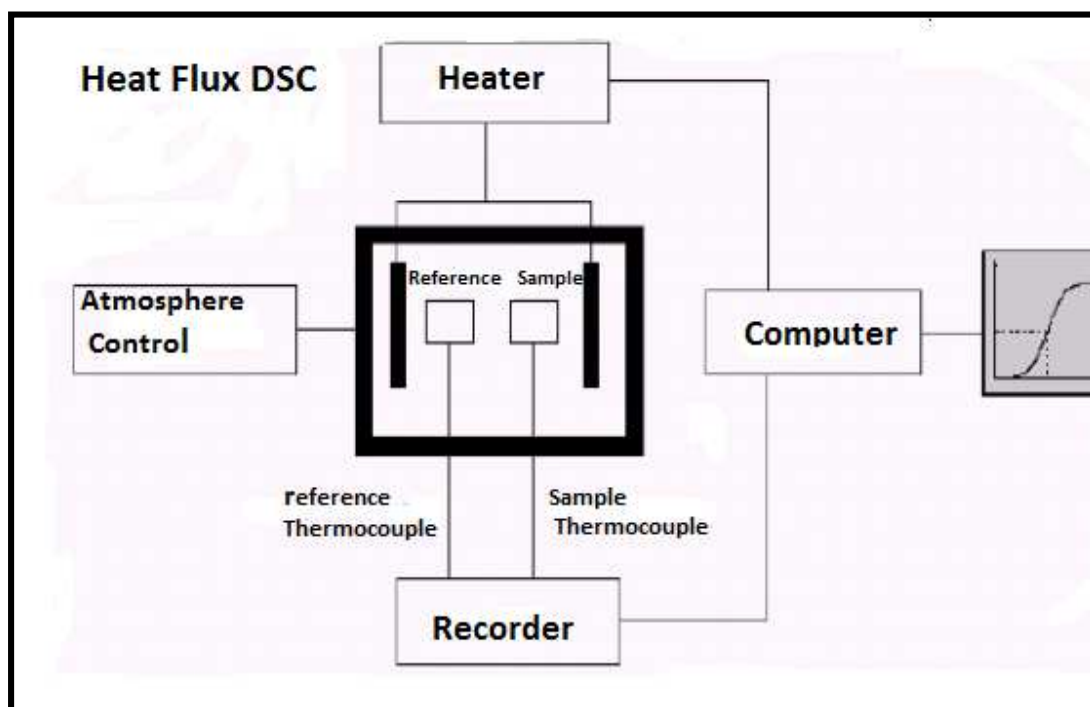
### 2.3.4 Energy-dispersive X-ray spectroscopy (EDS)

Energy-dispersive X-ray spectroscopy (EDS) is a powerful analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on the investigation of interactions between incident charged particles such as electrons and the sample. Its characterization capabilities are based on the fundamental principle that each element has a distinctive atomic structure represented by unique set of peaks on its X-ray spectrum [7]. At rest, an atom within the sample is in the ground state (unexcited) and the discrete energy levels or electron shells are bound to the nucleus. A high energy incident beam may knock out an electron in an inner shell creating an electron hole where the electron was. An outer electron from a higher energy shell will fill the hole and release the difference of energy between these two shells in the form of X-ray. The energy differences between the electron shells are closely related with the atomic structure of the element; hence the emitted X-rays contain the information with the help of which the elemental composition of the specimen could be found out [7].

### 2.3.5 Differential scanning calorimetry

In the field of solid state science, thermal analysis is a basic technique that allows to determine various useful parameters such as phase transition and the corresponding enthalpy, heat capacity, mass and coefficient of thermal expansion etc. The commonly used thermal analysis techniques are the thermogravimetry analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). TGA measures the change of mass as a function of either temperature or time where as the DTA measures the difference in temperature  $\Delta T$  between a sample and an inert reference material as a function of temperature. Differential scanning calorimetry (DSC) is a technique that is closely related to DTA which quantitatively measures the difference in the amount of heat required to increase the temperature of a sample and reference as a function of temperature and time. The term “differential” signifies the difference between the material under study and an inert reference material. The temperature of the sample and the reference continues to be same until some physical transformations occurs in the sample. With the sample undergoes a change in thermal state such as phase transition, order-disorder transitions and

chemical reactions etc., the temperature of the sample either leads (if the change is exothermic) or lags behind (if the change is endothermic) the reference material. The block diagram representing principle and working sketch of a DSC 60 is shown in Fig.2.7.



**Fig. 2.7:** Block diagram of a DSC 60 [8].

With the supply of power to the heater, the heating block (Heater) attains the temperature ( $T_b$ ) and is controlled according to the preset program. Heat flow from heating block to both the sample and reference section and as a result the sample temperature  $T_s$  and reference temperature  $T_r$  rise or fall in accordance with the programmed temperature  $T_b$ . During this process, the difference of the sample section temperature and the reference section temperature  $\Delta T = T_s - T_r$  is recorded. If  $\Delta T$  is plotted against time or the sample temperature  $T_s$ , it traces a curve and is called the baseline. If the sample material undergoes a thermal change such as melting or crystalline phase transition, the sample temperature remains fairly constant while the reference material temperature continues to be increasing. Consequently, the value of  $\Delta T$  will deviate from the value before melting. As soon as the melting completed, a large amount of heat flows from the heating block to the sample section to facilitate quick resume of the equilibrium state and  $\Delta T$  returns to the baseline.

The DSC analysis of the samples studied in this work was carried out at a heating rate of 10°C/min. using DSC 60 (Shimadzu, Japan) in the temperature range room temperature to 570 °C. All the measurements were performed in air atmosphere by taking alumina as reference sample.

### 2.3.6 Electrical characterization: complex impedance measurement

Impedance spectroscopy is a most powerful technique for characterizing electrochemical properties of the superionic conductors and their interfaces [9, 14-15]. Generally, the electrical conductivity is measured in two ways, i.e. as dc and ac conductivity ( $\sigma_{dc}$  and  $\sigma_{ac}$  respectively). The dc conductivity gives less amount of information of the entire dynamic behaviour of the sample whereas the ac conductivity provides various information regarding the microscopic nature of the ionic transport process in the material [10]. Usually, conductivity measurements were performed by applying d.c. bias across the material. As a result the ionic current decreases with time due to the polarization process taking place at the electrode/electrolyte interface of the material. This problem can be overcome by using (i) four probe or two reversible electrodes dc technique and ii) ac technique. As compared to the ac technique, the dc measurements are much complicated and supply less information. Therefore, the ac technique have seen tremendous increase in popularity to investigate the material properties such as bulk conductivity, grain boundary effect, ionic transport and double layer formation at the electrode/electrolyte interfaces, etc [9, 11].

In recent years, Impedance Spectroscopy has been extensively used to study the ion transport mechanism in single/polycrystalline and amorphous/glassy fast ion conducting materials [1, 12]. Impedance Spectroscopy (IS) can also be called as Imittance Spectroscopy. The term “Imittance” is used for any of the four quantities complex impedance ( $Z^*$ ), complex admittance ( $Y^*$ ), complex dielectric permittivity ( $\epsilon^*$ ) and complex modulus ( $M^*$ ) [9, 13]. The presence of different resistive and capacitive components leads to various processes within the materials and as a result the materials possess different relaxation times. The electrical response of solid electrolytes can be analyzed by using the complex impedance and complex admittance plane representations. On the other hand the complex modulus and

complex permittivity spectra are used to investigate the dielectric response of solid electrolytes.

### Theory

Impedance spectroscopy studies the response of a system to an applied periodic signal of small amplitude. The measurements are performed at different ac frequencies and accordingly, the name impedance spectroscopy was adopted. The standard means to define impedance is the quotient of vector voltage and vector current occurring as a result of small single sinusoidal measurement. When an ac signal is applied to a system, the impedance of the system obeys Ohm's law and in the time domain the corresponding expressions for voltage and current will be [9],

$$V(t) = V_0 \exp(j\omega t) \quad (2.5)$$

$$\text{And} \quad I(t) = I_0 \exp(j\omega t - \theta) \quad (2.6)$$

The impedance is a complex quantity and possesses both magnitude  $|Z|$  and phase angle ( $\theta$ ) and is expressed as,

$$Z(\omega) = |Z| \exp(-j\theta) \quad (2.7)$$

$$Z(\omega) = |Z| \cos\theta - j|Z| \sin\theta \quad (2.8)$$

$$Z^* = Z' - jZ'' \quad (2.9)$$

where  $Z'$  and  $Z''$  represent the real and imaginary parts of complex impedance ( $Z^*$ ). The complex impedance can also be represented in the other three forms,

$$\text{Complex impedance} \quad Z^* = Z' - jZ'' \quad (2.10)$$

$$\text{Complex Admittance} \quad Y^* = Y' - jY'' = 1/Z^* \quad (2.11)$$

$$\text{Complex permittivity} \quad \varepsilon^* = \varepsilon' - j\varepsilon'' = 1/j\omega C_0 Z^* \quad (2.12)$$

$$\text{Complex modulus} \quad M^* = M' - jM'' = j\omega C_0 Z^* \quad (2.13)$$

Where  $j = \sqrt{-1}$ ,  $C_0$  is the vacuum capacitance and  $\omega = 2\pi f$  is the angular frequency [9].

**Dielectric permittivity**

Dielectric permittivity is a distinctive property of short-range electrical conduction of a material in presence of an applied electric field [9, 16-19]. Under the influence of an external electric field  $V$ , the charges within the material displace from its normal site and accumulate at the interface and as a result dipoles of moment  $p = Q\delta$  are formed, where  $\delta$  is the distance of separation between the charges and  $Q$  is the charge.

$$Q = CV \quad (2.14)$$

Where  $C$  is the capacitance of the dielectric and is given by,

$$C = C_0\epsilon/\epsilon_0 \quad (2.15)$$

Here  $C_0$  stands for vacuum capacitance and is given by  $C_0 = \epsilon_0 A/t$ , where  $\epsilon_0$  is the permittivity of the free space,  $A$  is the area of cross section and  $t$  is the thickness of the sample.

If the material is subjected to a time varying electric field  $V$ , the induced charge is given by,

$$Q = \epsilon^* V_0 \exp(j\omega t) \quad (2.16)$$

Where  $\epsilon^*$  is the complex dielectric constant and is defined as,

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (2.17)$$

The term  $\epsilon'$  is the real part of the complex dielectric constant and is called the real or relative permittivity or dielectric constant and  $\epsilon''$  is the imaginary part or the dielectric loss. The complex dielectric constant  $\epsilon^*$  and the complex impedance  $Z^*$  are related by the equations [19-21],

$$\epsilon^* = \frac{1}{j\omega C_0 Z^*} \quad (2.18)$$

$$\epsilon' = \frac{1}{A\omega\epsilon_0} \left[ \frac{Z''}{Z'^2 + Z''^2} \right] \quad (2.19)$$

$$\epsilon'' = \frac{1}{A\omega\epsilon_0} \left[ \frac{Z'}{Z'^2 + Z''^2} \right] \quad (2.20)$$



Where,  $\omega$  is the angular frequency and  $C_o$  is the capacitance of free space.

And also, 
$$\tan \delta = \varepsilon'' / \varepsilon' \quad (2.21)$$

### Electric modulus

The complex electric modulus  $M^*$  is defined as the reciprocal of the complex permittivity  $\varepsilon^*$  [9],

$$M^* = 1 / \varepsilon^* \quad (2.22)$$

In terms of complex impedance, it can be represented by,

$$M^* = \frac{1}{\varepsilon^*} = j\omega C_o Z^* \quad (2.23)$$

$$M^* = M' + jM'' = j\omega C_o (Z' - jZ'')$$

$$M' = Z''\omega C_o \quad (2.24)$$

$$\text{and } M'' = -Z'\omega C_o \quad (2.25)$$

Complex electric modulus formulism indicates the dynamics of the electrical phenomena or configurations in the structure in solid ionic conductors and describes the electrical relaxation and microscopic properties of ionic materials [22-23]. The modulus formulism suppresses the polarization effects at the electrode electrolyte interface and gives only the dynamic property of the material. The real and imaginary parts of the modulus are given by,

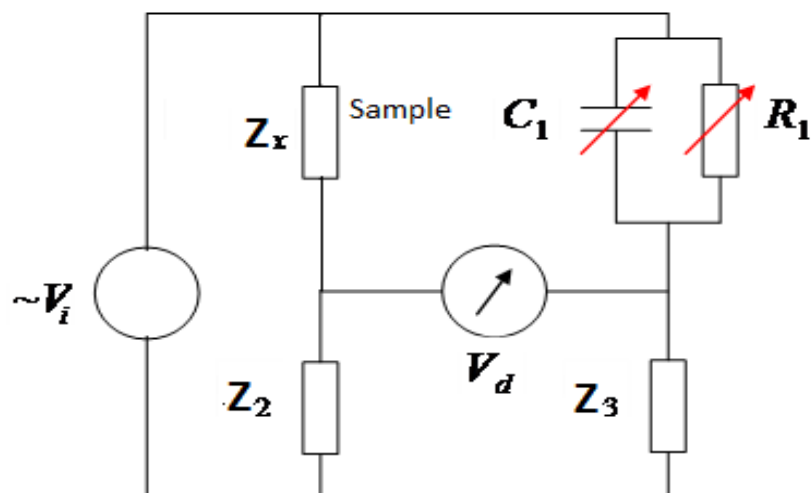
$$M' = \frac{R^2 C C_o \omega^2}{[1 + (\omega C R)^2]} \quad (2.26)$$

$$M'' = \frac{R C_o \omega}{[1 + (\omega C R)^2]} \quad (2.27)$$

### Conductivity measurement by AC method

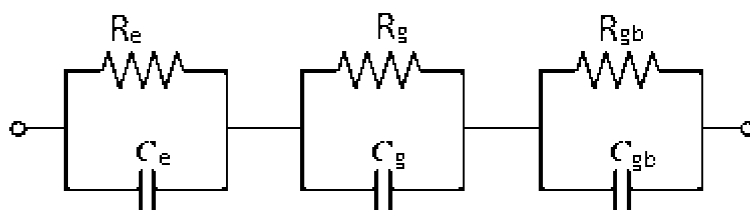
The different methods and techniques for measuring impedance are bridge method (ac coupled bridge and Lissajous figure), resonant method, I-V method, RF I-V method, network analysis method, and auto balancing bridge method [9, 24]. The most familiar is the Wheatstone bridge type of apparatus shown in **Figure 2.8**. The bridge is

balanced when the null detector voltage ( $V_d$ ) is adjusted to zero and hence the value of the unknown impedance  $Z_x$  of the sample (Resistance or Capacitance) is balanced against the variable resistor ( $R_1$ ) and capacitor ( $C_1$ ).



**Fig.2.8:** Measurement of R and C with Wheatstone bridge [24]

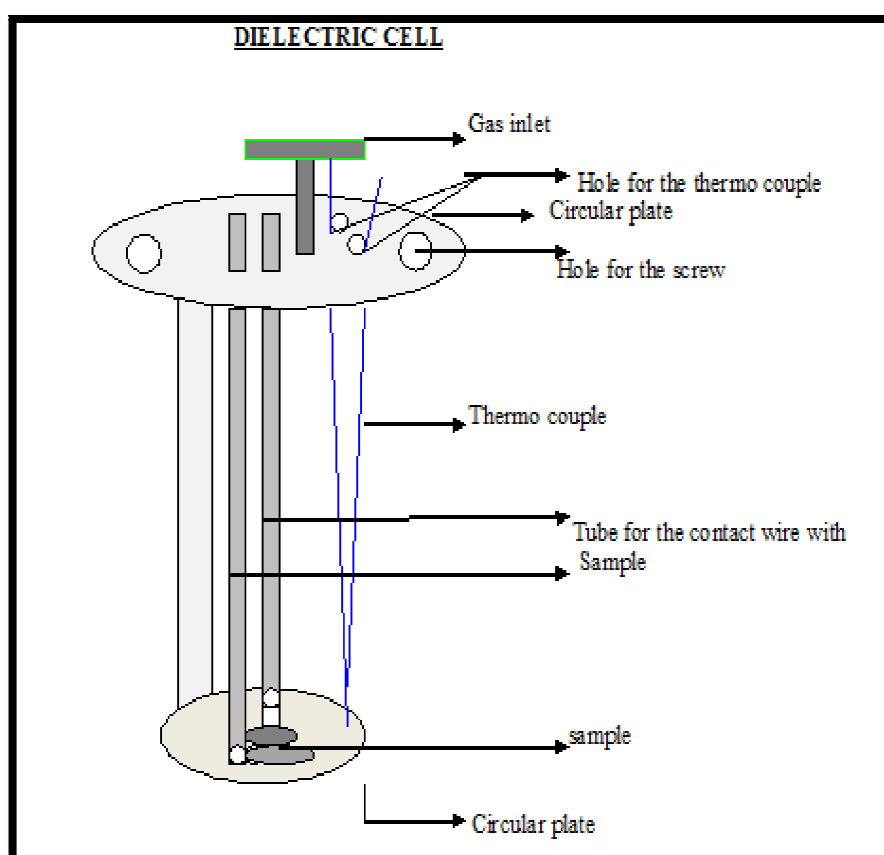
As shown in **Figure 2.9**, the electrical response of a polycrystalline material can be described by simple equivalent circuits consisting of resistors, capacitors [9, 25-26]. The bulk, the grain boundaries in the electrolyte and the interfaces to the electrodes are described each by a simple RC circuit. As depicted in the **Fig. 2.9**,  $R_e$  represents the effective resistance for the electrode reaction and  $C_e$  is the double layer capacitance of the electrode. The terms  $R_{gb}$ ,  $C_{gb}$  and  $R_g$ ,  $C_g$ , correspond to the resistances of conduction and capacitance between the grains and within the grains [9]. Each RC component corresponds to a characteristic semicircle where the frequency as implicit parameter increases from right to left. The intercepts with the real axis give the resistivities and the apex frequencies yield the capacities of the different components of the equivalent circuit [26].



**Fig. 2.9:** Equivalent circuit with contributions from the grains, the grain boundaries and the electrodes [25-26].

### Experimental set up for the electrical characterization

The complex impedance spectroscopic measurements were carried out by applying a constant voltage at varying frequencies. The measurements were carried out using the HIOKI-LCR tester 3532-50 (made in Japan) in the frequency range from 42Hz to 5MHz which is interfaced to a computer. The software controls the measurements and computes the impedance ( $Z$ ), phase angle ( $\theta$ ), Capacitance ( $C_p$ ) and dielectric loss ( $D$ ) at a time for a given frequency. A block diagram of the impedance measurement set-up is shown in **Fig. 2.10**.



**Fig. 2.10:** Sample holder for IS measurements.

The temperature controlled heating arrangement and the sample holder is indigenously developed in our laboratory. The specimen placed inside the furnace (operating upto  $1000^{\circ}\text{C}$ ) with the help of the sample holder. A chromel-alumel thermocouple is attached very close to the sample so as to measure exact temperature of the specimen. Thermotech 4000E temperature controller was used to control and /or read the temperature. Electrical measurements on the specimen were performed in the temperature from  $\text{RT}-600^{\circ}\text{C}$  in air.

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