CHAPTER 2

EXPERIMENTAL TECHNIQUES

In this chapter a detailed description of method used for preparing samples and the experimental techniques used for characterization and conductivity measurements.

2.1. Sample preparation

The samples were prepared by melting the analytical grade reagents chemicals CdI_2, Ag_2O, V_2O_5 and H_3BO_3. The following series of samples were prepared.

(1) $xCdI_2$-(100-x) [$2Ag_2O$-($0.7V_2O_5$-$0.3B_2O_3$)] where $5 \leq x \leq 30$ in steps of 5 and modifier to former ratio 2:1.

(2) $20CdI_2$-80[xAg_2O-y($0.7V_2O_5$-$0.3B_2O_3$)] where $1 \leq x/y \leq 3$ in step of 0.25.

(3) $20CdI_2$-$53.4Ag_2O$-26.6[xB_2O_3-(1-x)V_2O_5] where x=0, 0.2, 0.4, 0.6, 0.8 and 1.

The starting materials were weighed in the desired proportion using micro analytical balance. The weighed materials were thoroughly mixed with an agate pestle-mortar. The mixture was taken in a quartz ampoule and kept in a muffle furnace whose temperature is controlled by using a temperature controller of Toshniwal Industries Pvt. Ltd., in the range of 0-1200°C (±1°C accuracy). The temperature of the mixture was kept initially at 400°C for half an hour for removing CO_2 and H_2O contents from the mixture and then the temperature was raised to the temperature range 600°C-800°C for 4 hours. Continuous stirring was adopted to get the homogenous melt. The homogeneous melt obtained was then quenched in a beaker containing liquid nitrogen to form the glass. The obtained solid materials were crushed to fine powder by using agate mortar and are used for other studies. The samples are kept in a desiccator to protect them from atmosphere.

2.2. Characterization studies

The obtained glass compounds were ground into fine powders and were characterized by X-ray diffraction (XRD), infra red (IR), and Differential Scanning Calorimetric (DSC) techniques etc.

2.2.1. X-ray diffraction

All the prepared samples were examined for their amorphousity by X-ray diffraction studies. The finely powdered samples were taken in a sample holder and X-ray diffraction study was made by using Rigaku miniflex X-ray diffractometer employing a monochromatic CuK_{α} radiation of wavelength λ =1.5418Å. X-ray diffraction spectra which were recorded for 2θ values between 0-90° at a rate of 2°/minute.

2.2.2. Differential Scanning Calorimetry

Differential Scanning Calorimetry is considered as a sensitive recorder to examine the thermal stability of the prepared samples. The finely crushed powders of the samples were used for DSC measurements over the temperature range 293 K- 493 K using Modulated DSC 2910 model Differential Scanning Calorimeter (TA Instrument). For this, the sample powders were encapsulated in aluminum pans and were scanned at a heating rate of 10°C/minute. A cross sectional diagram of the DSC cell is shown in Fig.2.1 (a) and the typical DSC plot is shown in Fig.2.1 (b). The cell is based on a 'heat flux' design which uses a constantan disk as a primary means of transferring heat to the sample and reference positions. The sample contained in a metal pan and the reference (on empty pan) sits on raised platforms formed in the constantan disk. As heat is transferred through the disk, the differential heat flows to the sample and reference is measured by thermocouples formed by the junction of the constantan disk and chromel wafers which

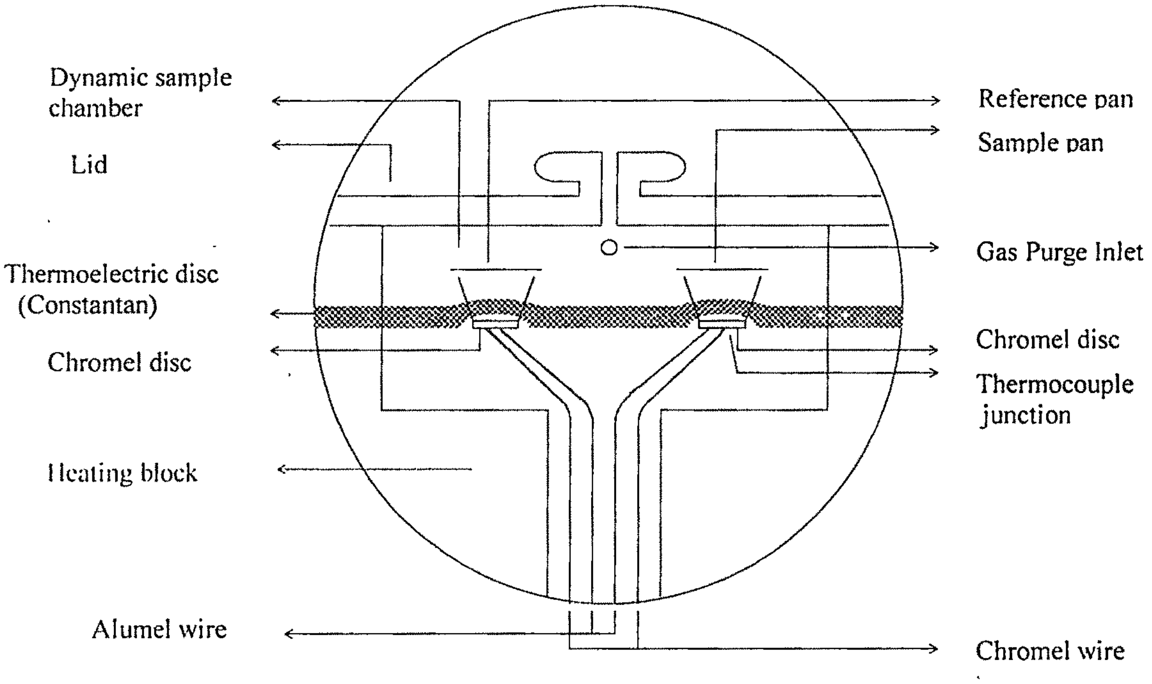

Fig.2.1 (a). Schematic representation of DSC Heat Flux

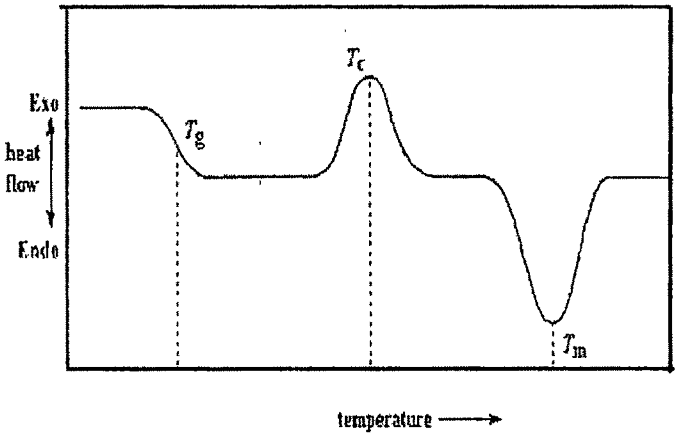

Fig.2.1 (b). Typical DSC plot

cover the underside of the platforms. Chromel and alumel wires attached to the chromel wafers form thermocouple which directly measures the sample temperature.

2.2.3. Fourier Transform Infra red Spectroscopy

Fourier transform infra red spectra were recorded for the samples using Bomem Michelson's series FTIR spectrometer. About 5 mg of the powdered glass sample was ground and mixed with a relatively large quantity of KBr which is transparent to IR radiation. The thin pellets for the measurement of IR absorption spectra were made by pressing the mixture at a pressure of 10 tons for few minutes under vacuum. The resultant pellet known as KBr pellet and is kept in the sample holder of the FTIR spectrometer having a resolution of 4 cm^{-1}. The IR transmittance spectra were recorded on thin pellets in the wave number range 400-2500 cm^{-1} at room temperature with a scanning rate of 2.7 sec/scan in the transmittance mode and the spectra are taken on a paper by using a dot matrix printer TVSE NOVO-130. The spectra are analyzed by plotting each spectra on a single paper for the purpose of comparison. An FTIR instrument uses Felgett's advantage or not reducing light intensity with a monochromator to make the most of the IR source. From the IR source light travels to the beam splitter, 50% of the light is reflected to the fixed mirror and 50% is transmitted to the movable mirror. Light travels to each of the mirrors and recombines at the beam splitter before passing through the sample and to the detector. As the light intensity of the recombined beam is recorded at the detector, the moveable mirror travels towards the beam splitter, producing an inteferogram. As the movable mirror travels, different frequencies are reflected in different ways. The summation of constructive and destructive interference over time makes an interferogram,

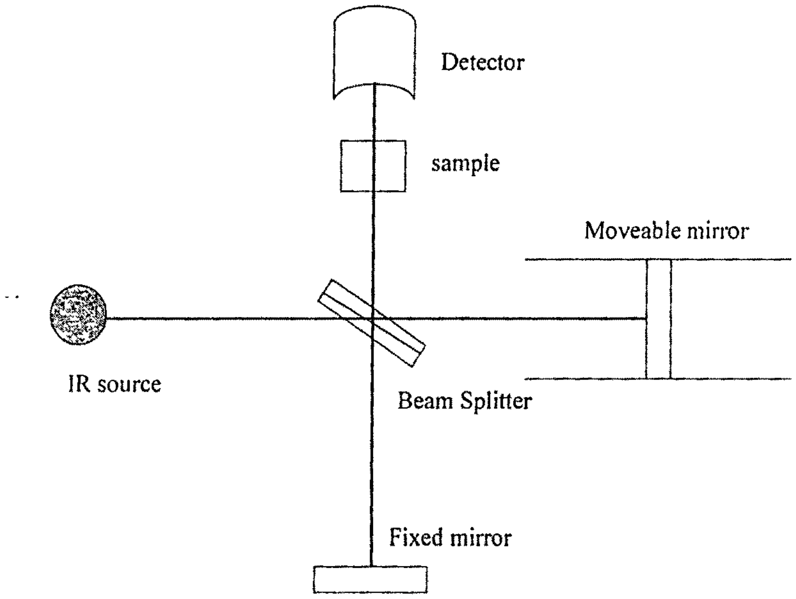

Fig.2.2. The optical diagram of a Fourier transform Infrared Spectrometer.

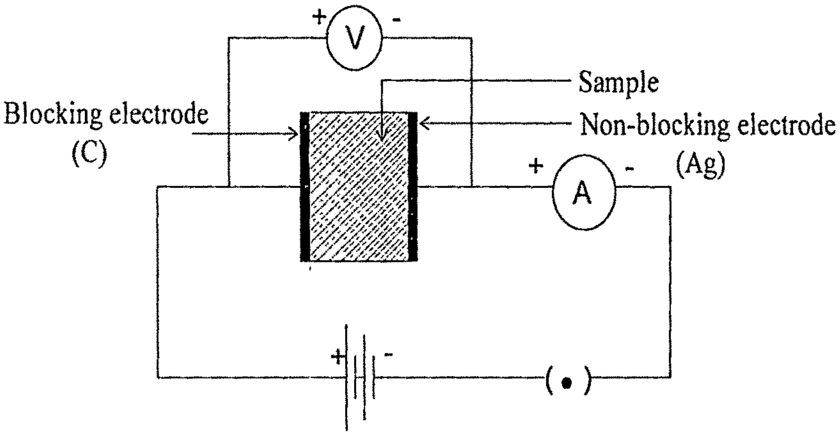

Fig.2.3. Schematic diagram for measuring the electronic conductivity by Wagner's dc polarization method

from which a Fourier transform is used to calculate a spectrum. Fig.2 shows the optical diagram of the Fourier transform Infrared spectrometer.

2.2.4 Density measurement

The density of the present glass system was determined at room temperature using Archimedes principle with xylene as the immersion fluid. The density of the xylene is 0.86 at room temperature. The glass sample of any shape and size was tied to a weight less nylon strand thinner than human hair and was hanged to the hook of the single pan electromechanical weighing machine in air and the weight of the sample in air was taken as '*a*' gm and then the same sample was weighed immersed in xylene as '*b*' gm respectively. The density was calculated according to the equation

$$Density = \frac{a}{a-b} \times 0.86$$

2.3. Transport number measurements

Transport number measurements have been done to understand the ionic and electronic contribution of the total mobile species. Transport number measurements were done by Wagner's polarization method and to find out the silver ion contribution among the mobile charges emf method was adopted.

2.3.1. Wagner's polarization method

The transport number of the mobile species is defined as the ratio of the current due to mobile ions to the total current. There are many methods to measure the transport number. We have adopted the Wagner's polarization technique for measuring the ionic transport number. The experimental arrangement for measuring the transport number is shown in Fig.2.3. For this, a polarization cell was made in the form of a pellet with a non- blocking electrode consisting of a mixture of silver metal powder and electrolyte and a blocking electrode, carbon on either side of the pellet. This pellet is placed between two silver plates and a constant dc potential of 50 mV is applied across the cell with polarity (-) (Ag + electrolyte) /electrolyte/ carbon (+). The current was measured using a Keithley Electrometer Model 614 till the current becomes constant indicating the fully depleted condition of the blocking electrode.

2.3.2. emf method

The emf method was employed for the evaluation of the contribution of silver ions in the present CdI_2 doped system. A cell of the type (Ag + electrolyte)/ electrolyte /(I_2+C+ electrolyte) was used. The anode consisted of a mixture of silver powder and the electrolyte material in the weight ratio 2:1 and the cathode was made from resublimed I_2, C and electrolyte in the ratio 1:5:1. The cell was made in the form of a pellet by pressing the cell components under a pressure of 5000 kg cm^{-2}. The open circuit voltage of the cell is measured using Keithley Electrometer Model 614. The transport number of the silver ions t_{Ag+} can be found by the relation $t_{Ag+}= E/E_0$. where E the emf measured is the open circuit voltage at room temperature and E_0 is the standard emf corresponding to the cell reaction obtained from thermo dynamical calculations for Ag/I_2 couple.

2.4. Thermoelectric power

Thermo electric power (TEP) measurements were carried out by measuring the potential difference developed between two faces of the sample across which a known temperature gradient is maintained of the cell configuration Ag (T)/ electrolyte / Ag (T+ΔT). For this purpose, all the solid samples were made into circular pellets of 1cm diameter at a palletizing pressure of 5000 kg/cm^2. Silver paste was applied on both the faces of the pellet in order to make the face electrodes. The pellet was mounted in a sample holder of the thermoelectric power apparatus. The thermoelectric power of the present system is measured using a differential method, where the thermo emf across the glass sample is being measured at different temperatures. The thermoelectric power is measured in the temperature range 303 K- 373 K. Thermoelectric power of all the samples is measured by the two main matched heaters mounted along the axis of the two sample holder shafts. The two heaters provide a controlled temperature gradient of ±5°C which is maintained between two sample holders by using the auxiliary heaters wounded on each of the sample holder shafts. The thermo emf across the points of the sample is measured at different temperatures from room temperature to below the glass transition temperatures. The average of the sample temperature was taken as $(T_1+T_2)/2$. The temperatures of the two main heaters are measured using Cr-Al thermocouple with high impedance digital micro voltmeter. TEP (θ) values were thus calculated using the relation

$$\theta = \frac{\Delta V}{\Delta T}$$

where ΔV is the thermo emf developed across the sample and ΔT is the temperature difference across the two faces of the sample.

2.5. Impedance measurements

The electrical conductivity measurements were carried out by complex impedance method. For this purpose, all the fine powdered samples were pressed into pellets in the form of conducting electrode (Ag) /sample/conducting electrode (Ag) at an optimum pressure of

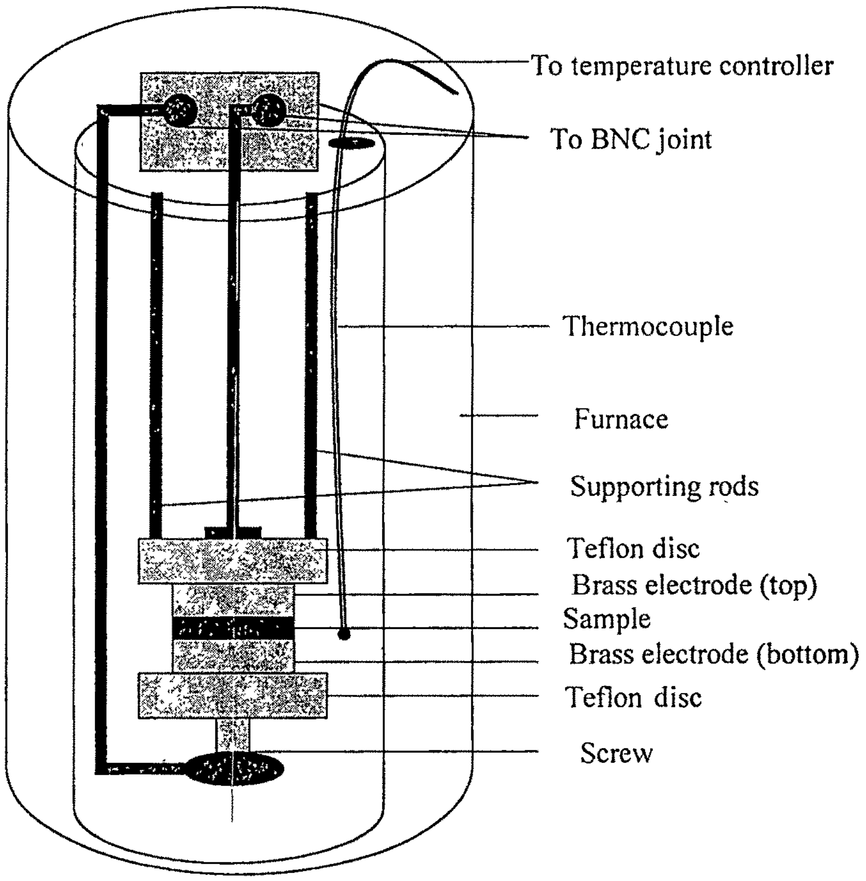

Fig.2.4 Conductivity set up for the ac measurements

5000 $kgcm^{-2}$. The impedance measurements were carried out using Alpha Dielectric Analyzer in the frequency range 100Hz-10MHz at different temperatures below the glass transition temperature. From the complex impedance plots obtained, the value of the bulk resistance of the materials was estimated and hence their conductivity values calculated. Fig.2.4 shows the experimental set up used for the conductivity measurements.

2.6. Solid State Battery: Fabrication

In order to understand the practicality of the electrolytes studied, they were used to fabricate the solid state battery, in which all the electrode and electrolyte materials are solids. Anode layer consists of a mixture of silver and electrolyte and cathode layer consists of iodine, carbon and electrolyte. The anode, electrolyte and cathode layer spread over a die and pressed together to form a cell of diameter around 1 cm. The cells prepared were used to study the discharge and polarization characteristics and is described briefly in chapter 5.