Chapter-III

Experimental Techniques

In this chapter, a detailed description of method used for preparing samples and the experimental technique used for characterization like XRD, DSC, FTIR, Transport number measurement by EMF method and conductivity measurements of silver based quaternary glass system is explained.

3.1 Preparation of glasses:

Present quaternary glasses are prepared using high purity chemicals, Ag_2O, $BaCO_3$, V_2O_5, and TeO_2. Commercially available analytical reagent (AR) grade materials have been used in all the preparations. Using these chemicals, the following series of samples were prepared.

1) x (BaO : 1.5 Ag_2O) - (95-x) V_2O_5 – 5 TeO_2;

where x = 25, 30, 35, 40, 45 mol%.

2) 10 BaO-y Ag_2O-(85-y) V_2O_5-5 TeO_2;

where y = 20, 25, 30, 35, 40, 45, 50, 55 mol%.

3) 5 BaO-z Ag_2O-35 V_2O_5- (60-z) TeO_2;

where z = 25, 30, 35, 40, 45, 50, 55, 60 mol%.

The starting materials were weighed in the desired proportions using micro analytical balance. The weighed materials were thoroughly mixed in an agate mortar-pestle nearly for an hour by wet grinding method. Initially 5 gm batch of the mixture was kept in an alumina crucible in a controlled electric furnace at 400^0C for half an hour in order to remove CO_2 and prevent foaming on melting. The temperature of the furnace was then raised gradually up to 810^0C and kept for four hours at that temperature for melting the mixture. The melt was then poured on to a Cu plate block kept at room temperature and immediately pressed the melt by another Cu plate block. The obtained solid materials were crushed to fine powder by using agate mortar and were used for other studies like XRD, FTIR, DSC, transport number measurement while for dc and ac conductivity measurements, samples were cut into pieces of about 1 mm in thickness and were

coated with silver paint to serve as electrodes. All the samples were kept in desiccators to protect them from atmosphere.

3.2 Characterization Techniques

The various characterization studies performed on glass samples are described below.

3.2.1 X-ray Diffraction:

In the present investigation, room temperature x-ray diffraction patterns of the finely powdered samples have been recorded for the prepared systems using a Shimadzu X-ray diffractometer employing a monochromatic Cu-Kα radiation (λ=1.5418). The measurements were recorded for 2θ values from 10^0-80^0 at a scanning rate of 2^0 per minute. Fig.3.1 shows the diagram of the XRD sample holder.

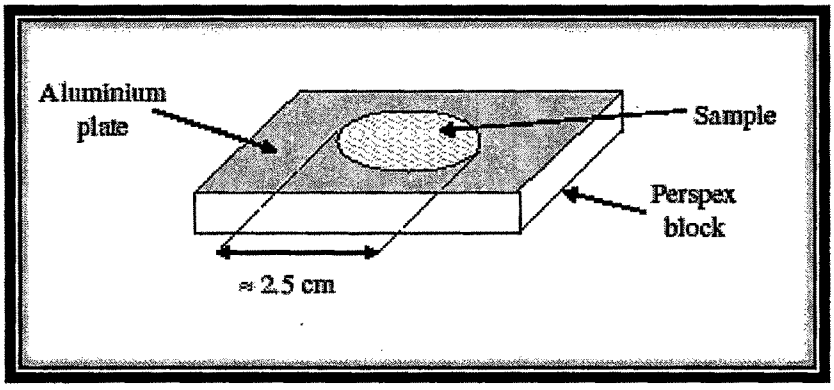

Fig.3.1. XRD sample Holder.

3.2.2 Differential Scanning Calorimetry:

DSC is the most widely used thermal analysis technique, which is applicable to glasses, polymers, various organic materials as well as inorganic materials. This technique has many advantages which contribute to its widespread usage, including fast analysis time (usually less than 30 minutes), easy sample preparation, applicability in both solids and liquids, wide temperature range and excellent quantitative capability.

In the present work, DSC measurements have been carried out using Modulated DSC-2910 TA Instruments. Fig.3.2 shows the schematic diagram of DSC apparatus. Prior to the measurements, the base line has been obtained in order to

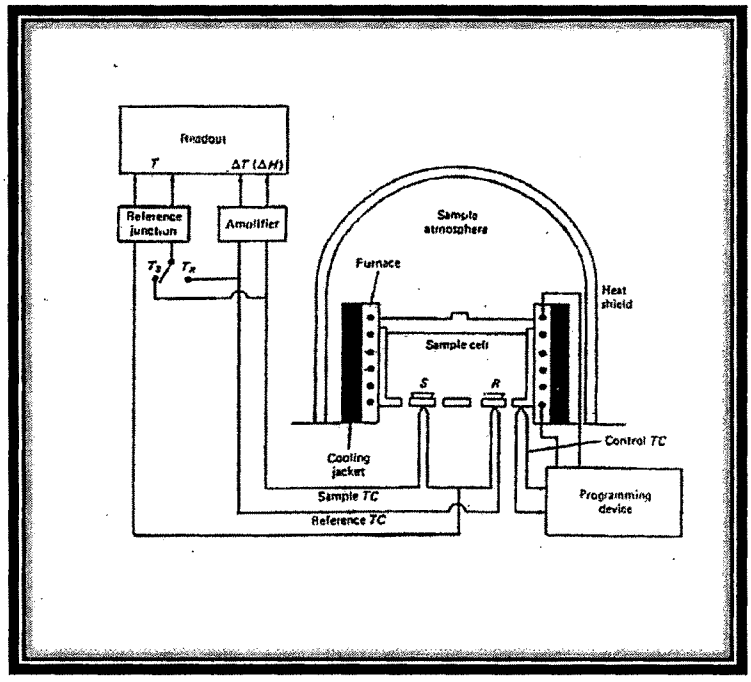

Fig. 3.2: Schematic diagram of DSC apparatus.

compensate the difference in the signal, which may account for the possible non identical nature of pans or heating elements. The baselines are obtained under the experimental conditions required for the system under study. The investigation on glassy electrolytes has been aimed at determining (i) the glass transition temperature (T_g) at which the glass transforms from super cooled liquid state into crystalline phase and (ii) crystallization temperature at which the glass devitrifies (T_c). In this technique, the powdered samples of about 10-15 mg were encapsulated in aluminium pans of DSC instrument for measurements over the temperature range from room temperature to below glass transition temperature. The heating rate for first series is 20^0C/min while for second and third series heating rate is 10^0C/min. The result of the DSC experiment is a curve in which there is an endothermic and exothermic peak corresponding to glass transition temperature (T_g) and crystallization temperature (T_c) (Fig.2.4).

3.2.3 Fourier Transform Infrared Spectroscopy:

FTIR spectroscopy is used for the structural investigation of glasses. It is the advanced technique of conventional IR spectroscopy. Here the optical pathway to detect radiations coming from sample and reference source is designed to produce an interferogram, a plot of intensity versus time. This signal is converted into frequency domain, using Fourier transformation. The IR covers a range of wavelength in electromagnetic spectrum from 7.8×10^{-5} to 1×10^{-1} cm. In IR spectroscopy, the absorption is expressed in wavenumber ν, whose unit is cm^{-1}. It is divided into three regions (1) near infrared spread over from (7.8×10^{-5} to 2.5×10^{-4}) cm (2) middle infrared region lies in the range (2.5×10^{-4} to 5×10^{-3}) cm and (3) far infrared region lies in between (5×10^{-3} to 1×10^{-1}) cm. The most useful IR

region is 2.5×10^{-4} to 5×10^{-3} cm (wavelength range) or 4000 cm^{-1} to 200 cm^{-1} (wavenumber range) because it gives the important information about the vibration of the molecules and hence its change in structure [1, 2].

Samples for IR studies- KBr Pellets:

For observing the IR spectra, a very small amount (less than 2 mg) of the powdered glass sample was ground and mixed with a relatively large quantity of KBr (approximately 100 mg) which is transparent to IR radiation. The mixture was pressed in a 'die' under a pressure of 5000 kg/cm^{-2}. The resultant transparent pellet known as KBr pellet of the sample was put in the sample holder of the Bruker model vertex 70 spectrophotometer and the FTIR spectra of the glass samples are taken in the range of 400-2400 cm^{-1} with the scanning rate of 2.7 sec/scan in a transmittance mode.

3.2.4 Transport number measurements:

The EMF method was employed for the evaluation of the contribution of silver ions in the present silver based barium vanado-tellurite glass system. For this method the cell of the type $Ag|sample|I_2+TMAI+C$ were fabricated, where in the anode was made of silver powder while the cathode was a mixture of iodine, tetramethyle ammonium iodide (TMAI) and graphite respectively in the ratio of 81:2:17. 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 6514.

The ionic transport number is calculated by the following relation

$$t_i = \frac{E_{obs}}{E_{theo}} \qquad \text{..... (3.1)}$$

where E_{obs} is the observed value of open circuit voltage at room temperature and E_{theo} is the theoretical value of emf corresponding to the cell reaction obtained from thermo dynamical calculations for Ag/I_2 couple, which is 0.687 V [3].

3.2.5 Density Measurements:

Densities of all glass samples of three different series were measured separately at room temperature using the suspended weight method based on the Archimedes principle. Methanol was used as the immersion liquid whose density is known (0.7814 gm/cc at room temperature). For measuring density, a small piece of sample was taken in a single pan of weighing machine and the weight of the sample was measured in the air. Let the weight in air is represented by '*a*' gm. Then the same piece of sample was weighed immersed in methanol represented by '*b*' gm. Then the density was calculated according to the equation

$$\text{Density} = \left(\frac{a}{a-b} * 0.7814 \right) \qquad \text{..... (3.2)}$$

By calculating the density and chemical compositions of the glass samples, the molar volume, ion concentration per unit volume, ion-ion spacing have been calculated. The change in density with composition, in oxide glass system, can be expressed in terms of apparent volume occupied by 1 g atom of oxygen which can be calculated from the density and composition using the formula [4] given as

$$V_m = \frac{\Sigma(n_i M_W)}{d} \qquad \text{..... (3.3)}$$

where M_w is the molecular weight of oxide, n_i the molar fraction and d is the density of the substance.

3.3 Conductivity Measurement:

The evaluation of electrical conductivity essentially means the measurement of sample resistance in terms of ratio of the electric potential applied across the sample to the electric current passing through the sample. A most conventional dc potential method can be employed for the resistance measurement. However, there are several limitations and complications which are introduced during dc measurement, especially when the system is an ionic, super ionic or mixed electronic-ionic. Many undesirable factors of resistance viz. electrode-glass polarization, grain boundary, electrode contact etc. contribute to the true bulk resistance (R) and it becomes practically difficult to determine the actual resistance of the sample. Thus for this reason, ac method is generally preferred over the dc method for such type of systems. Impedance spectroscopy is a powerful ac technique, which has received the wide spread acceptance today for the determination of true bulk conductivity of ionic/super ionic/mixed electronic-ionic systems [5-11]. This technique involves the measurement of complex impedance or true bulk resistance (R) of the material.

For the impedance measurements, all the glass samples were cut into small pieces of about 1mm thickness and were coated with silver paint to serve as electrodes. With painted silver paste a good ohmic contact is found. The measurements were made with two probe method. The sample inside the sample holder (as shown in Fig.3.3) is kept in contact with two polished, cleaned and spring loaded copper electrodes of a cell and the cell was kept in a furnace controlled by mercury contact thermometer and relay. Fig.3.4 shows the conductivity measurement setup for impedance analysis. The impedance measurements were made using Solartron

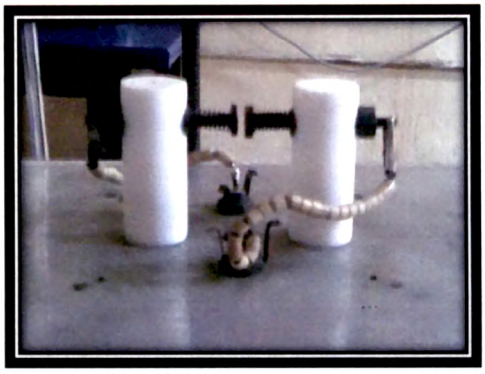

Fig.3.3. Sample holder for the conductivity measurement.

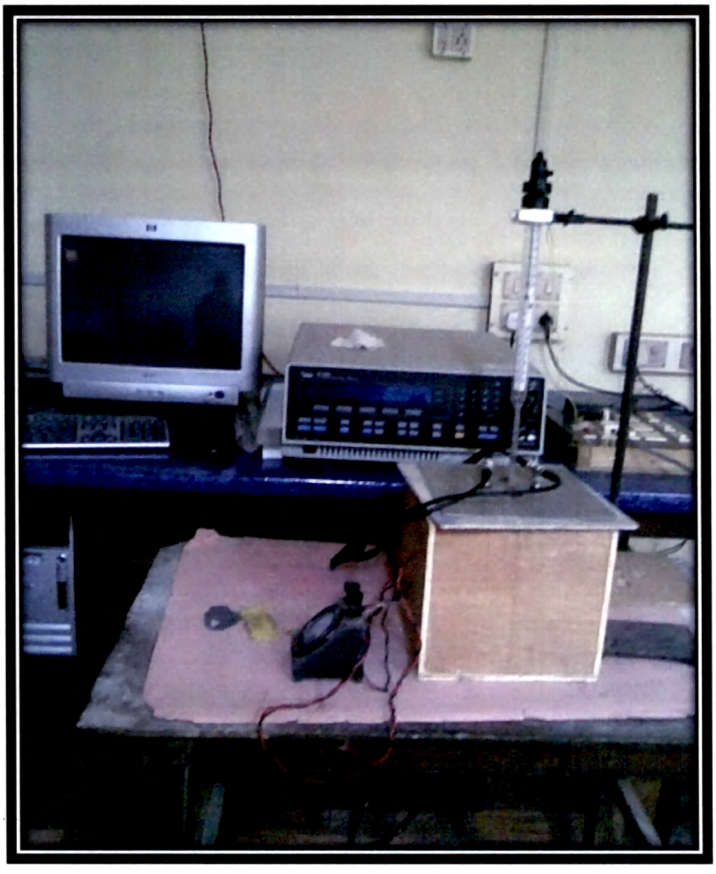

Fig.3.4. AC Conductivity measurement setup.

1260 in the frequency range from 1 Hz to 32 MHz at different temperatures and the sample was heated at the interval of 10^0 C.

Impedance Spectroscopy (IS) refers to the semicircular plots. Generally, a small portion of the semicircle appears on the *Z'-Z"* complex plot and the extrapolation of the plot intercepting the real *Z'* axis gives the bulk resistance (*R*), by which dc conductivity of the samples is calculated using Eqn.3.4

$$\sigma = \frac{1}{R}\left(\frac{t}{A}\right) \qquad \text{.....(3.4)}$$

where t and A are the thickness and cross section area of the specimen, which were found out using micrometer screw gauge.

The dc conductivity for first series samples was also measured by Keithley constant current source 220. Current source was connected in series and Keithley

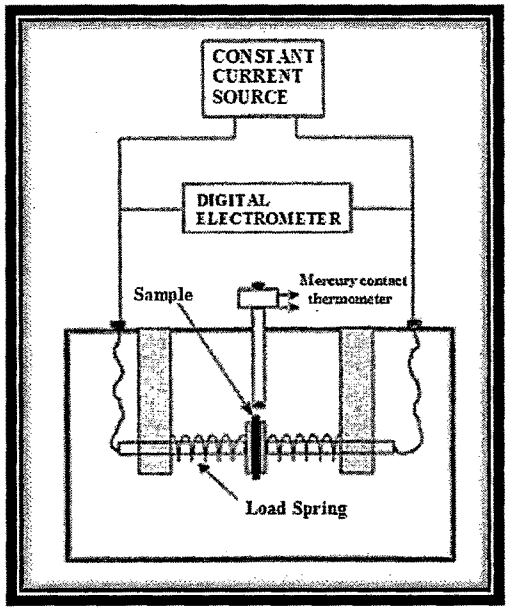

Fig.3.5. DC Conductivity measurement setup for first series.

Electrometer model 6514 was connected parallel to the sample for voltage measurement. Experimental setup for this is shown in Fig.3.5. A current through the sample was kept constant and the voltage drops across the given sample was measured at different temperatures starting from room temperature to below glass transition temperature. The resistance was then calculated using the relation $V=IR$, using this R values, conductivity is calculated by the Eq. 3.4.

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