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CHAPTER - III

EXPERIMENTAL TECHNIQUES

This chapter describes the methods of preparation of glasses and brief details of various experimental techniques employed in the present investigation.

3.1 PREPARATION OF GLASSES

Glass is a result of phase transformation, in which the nucleation and growth of crystallinity has been suppressed. Glassy materials are prepared by fast cooling of the molten liquid so as to bypass the nucleation and crystallization. The common methods for the preparation of glasses are illustrated in Figure 3.1 [1,2].

Low cooling rate is enough for materials with high glass forming ability (e.g., SiO2). These glasses can be prepared by simply turning off the furnace (or) by reducing temperature of the furnace at the required rate. Typical cooling rates, in this case, are in the range \(10^{-4}\) to \(10^{-2}\) K/sec. Some materials require somewhat faster cooling rates and these materials are prepared by quenching the melt in air or water [3]. For still better cooling rates, one can quench the melt in liquid nitrogen. In the present
Different methods of preparing glass. (a) Slow cooling of the melt, (b) Quenching of the melt in liquid nitrogen, (c) Twin roller quenching and (d) Thermal evaporation.
investigation, glasses are prepared by quenching the melt in liquid nitrogen. In this method, the cooling rate is of the order of $10^3$ K/sec. Very fast quenching rates are achieved by pouring the melt between the pre-cooled rotating rollers as shown in Figure-3.1(c), this method is known as twin roller quenching [4]. Glassy materials in thin film form are obtained by thermal (or) flash evaporation or other techniques [5].

The materials studied in the present investigations are quaternary glassy systems with two formers (Hexavalent + Pentavalent)

(1) AgI - AgZnO - (MoOs+VzOs) - Silver Molybdovanadate (SMV)

(2) AgI - AgZnO - (MoOs+AszOs) - Silver Molybdoarsenate (SMA)

Glasses differing in concentrations of the constituents are obtained by directly quenching the melt in liquid nitrogen. This method of preparation is found to be the best for the following aspects

(i) Speedy preparation of inumerable compositions of the glasses with ease in handling.

(ii) Both polycrystalline and amorphous materials can be obtained from the same melt simultaneously and a comparison can be undertaken.
Preparation of the bulk glasses from the melt, by pouring the melt in moulds, and a comparison with pulverised glasses can be undertaken.

Required amount of analar grade chemicals AgI, AgzO3, MoO3, V2O5 (or) As2O3, are mixed in molecular weight percents. The mixtures are heated in an open silica crucible for about 20 minutes at 600°C for SMV system and at 500°C for SMA system. The molten liquid is stirred frequently to ensure the homogeneous mixing of the constituents of the compound. The melt is then quenched in a petri dish / aluminium plate immersed in liquid nitrogen. The compound so formed is finely grounded using agate mortar and stored in a desiccator painted with black paint to avoid atmospheric and light effects on the prepared glasses.

3.2 CHARACTERISATION

The prepared samples are characterised by the following two experimental probes

(1) X-ray diffraction (X.R.D)

(2) Differential Scanning Calorimetry (D.S.C.)

3.2.1 X-Ray Diffraction

The glassy nature of the compounds is confirmed by
X-diffraction studies [1,6]. The diffraction pattern of the powdered samples are obtained by using Philips X-ray generator model no. 1140 using Cu-K$_\alpha$ radiation of wavelength $\lambda = 1.5418$ Å at scanning rate of 2 deg./min. The diffractogram spectra are recorded for 2θ values between 10-70 deg.

3.2.2 Differential Scanning Calorimetry

Change in temperature of the samples is due to either endothermic (or) exothermic reactions. The change in temperature occurring during chemical (or) physical changes is detected by differential methods such as Differential Thermal Analysis (D.T.A.) or Differential Scanning Calorimetry (D.S.C.) [7]. In D.T.A. method, the temperature of the sample is compared with that of the thermally inert reference material during a programmed heating. In D.S.C. method, sample and reference material are maintained at the same temperature during the heating programme. The required extra heat input to the sample (or to the reference), in order to maintain this balance, is measured. Enthalpy changes are therefore measured directly.

Glass is prepared by bypassing the crystallization and the liquid to glass transition occurs in a narrow temperature interval near the 'glass transition' temperature
In the present work, the glass transition temperature $T_g$ is measured by Differential Scanning Calorimeter of Perkin-Elmer make (model DSC-7). Powdered glass samples of 15-20 mg are used and the sample is heated at the rate of 10°C min$^{-1}$.

3.3 INFRARED STUDIES

The infrared (IR) spectra of the samples in the region 400 cm$^{-1}$ – 4000 cm$^{-1}$ are recorded using SHIMADZU - B101 FTIR spectrometer. The transmittance $T\%$ spectra are recorded with a resolution of 4 cm$^{-1}$ and with a data accumulation of 40 cycles. The measurements are carried out with KBr pellet and Nujol mull. The principles of the spectrometer and other details are described in standard texts [8,9].

3.3.1 KBr Pellet

Spectral grade potassium bromide (KBr) is used for the preparation of pellets. Sample and KBr are mixed in 1:20 weight ratio and is grounded into a fine powder in a clean agate mortar. The powders are pressed to form thin pellets of diameter 15mm using a KBr press. Reasonably good transparent pellets are obtained and the pellets are dried in an oven to reduce moisture content. The IR spectra for all the samples are recorded at room temperature.
3.3.2 Nujol Mull

Very finely grounded sample is suspended in (1-2 drops of) Nujol oil (liquid paraffin), and grounded until a smooth paste is obtained. The prepared mulls are used to record IR spectrum at room temperature.

3.4 TRANSPORT STUDIES

The transport studies are performed on pressed pellets of the ground compounds. The pellet preparation is described as follows:

Very finely grinded samples are used for the preparation of pellets in the form, "conducting electrode/sample/conducting electrode". The conducting electrode is a mixture of silver powder and 15% - 20% of the sample under study [10]. The sample (15%-20%) is added to the electrode material to have better electrode/sample interfacial contacts. The pellets are prepared by compressing the sample and electrode materials using a KBr press (Spectralab make) at a pressure of 5000 kg/cm². This pressure is fixed by studying pressure dependence of total conductivity of the sample [11]. The dimensions of the pellets (thickness of electrolyte & electrode, radius, and weight) are measured 4 hours after preparation. The density of the pellet is calculated using the pellet dimensions.
3.4.1 Total Conductivity

The total conductivity is due to two parts ionic and non-ionic (generally non-ionic part is electronic conductivity). The total resistance of the sample pellet is measured, if \( R \) is the resistance, the total conductivity \( \sigma_t \) is given by

\[
\sigma_t = \frac{t}{A} \frac{1}{R}
\]

(3.1)

where, \( t \) is the pellet thickness and \( A \) is the area of cross section of the pellet.

Figure 3.2 shows the experimental setup used for the conductivity and thermoelectric power measurements. The sample pellet under study is fixed between the two silver discs (D1 & D2). The connecting leads (L1 & L2) from the discs to measuring meter are made of pure silver wires to minimize contact resistance. The temperature of both the faces of pellet is measured by using Cr-Al thermocouples (Ti & Tz). The whole arrangement is kept inside a evacuable glass tube. The temperature dependence of conductivity the sample is studied by heating the cell. The sub-heater arrangement in the cell is used only for the thermoelectric power measurement. The electrical conductivity measurements are carried out on the pellets, at a pressure of \( 10^{-4} \) to
Fig. 3.2 Sketch of the cell used for the measurement of conductivity and thermoelectric power. In figure, D1 & D2 - Silver discs, L1 & L2 - Silver leads, T1 & T2 - Thermocouples, G - Sample, H - Sub heater, W - Sub heater leads, S - Spring, O - O ring, C - Vacuum stop cork, R - Supporting rod, J - outer jacket and F - Furnace.
$10^{-2}$ torr, using General Radio Impedance Bridge (1650-B) / Elico Conductivity bridge (CM82T) at a fixed frequency of 1 kHz.

3.4.2 Electronic Conductivity

The electronic contribution to the total conductivity, for the highest conductivity composition of the glass, is measured by Wagner's d.c. polarisation technique [12,13]. The sample pellet is sandwiched between the blocking electrode (graphite) and non-blocking electrode (silver) and is polarised by applying a d.c. potential as shown in Figure 3.3. Sufficient time was given to the sample to attain steady state current, after the application of the potential. The steady state current was measured as a function of applied voltage using Digital Multimeter (Philips make, model 2525), at room temperature. In the present investigation, the applied voltage is in the range of 10-150 mV. Relevant theory of the analysis of the electronic conductivity will be discussed in next chapter.

3.4.3 Transport Number

The total conductivity of the sample is given by

$$\sigma_t = \sigma_e + \sigma_i$$  \hspace{1cm} (3.2)
Fig. 3.3 Setup for electronic conductivity measurement by Wagner's dc polarisation method. In figure, NBE - Non blocking electrode (silver) and BE - Blocking electrode (graphite.)

Fig. 3.4 Experimental arrangement for the transport number measurement by e.m.f. method.
where, \( \sigma_t, \sigma_i \) & \( \sigma_e \) are respectively total, ionic and electronic conductivity of the sample. The transport number for ionic and electronic parts are given by

\[
t_i = \frac{\sigma_i}{\sigma_t} \\
t_e = \frac{\sigma_e}{\sigma_t}
\]

(3.3) (3.4)

By measuring the total and electronic conductivity using the above mentioned methods, the transport number of ionic (or) electronic component can be calculated.

E.M.F. Method

The sample is sandwiched between the two electrodes of chemical potential \( \mu_1 \) & \( \mu_2 \), as shown in Figure 3.4. The cell of configuration Ag/electrolyte(sample)/I is used for the present study. The e.m.f. developed in the cell is noted by measuring the open circuit voltage of the cell. The transport number is found out by comparing the e.m.f. with the thermodynamically calculated voltage of the cell.

3.4.4 Thermoelectric Power

The cell used for the conductivity measurements, shown in Figure 3.2, is also used for thermoelectric power measurements. The sample is held between the two silver
discs (D₁ & D₂). Differential method is chosen for thermoelectric power measurements [9,11]. Using a sub-heater (H), one face of the pellet is heated to maintain a temperature gradient across the sample. The temperature difference, ΔT, between the two end faces of the sample is measured by using the thermocouples (T₁ & T₂). Different ΔT values are obtained by adjusting the voltage supply to the sub-heater. The assembly is enclosed by glass jacket and heated externally by a furnace. The thermo e.m.f. generated is measured, for difference ΔT at different temperatures. The thermo e.m.f. measurements are carried out at 10⁻² torr at various temperatures. The temperature of the furnace is controlled by a temperature controller (± 1°C).

3.4.5 Impedance / Admittance Analysis

The electrochemical processes cannot always be represented by a simple combination of ideal resistances. Hence, d.c. measurements cannot yield the exact resistances of the samples owing to the choice of the electrode and the polarisation at the electrode-electrolyte interfaces. The electrochemical processes represent a complex combinations of various individual circuit elements (R,C,L); the contributions of any given component being dependent on the frequency of measurement. Complex plane analysis is a mathematical technique, in which the individual component
values are determined from the data obtained over a wide range of frequencies [14-18]. It involves the plotting of the real and imaginary part of the complex electrical quantities such as

(1) $Z^*$ - Complex Impedance  
(2) $Y^*$ - Complex Admittance  
(3) $\varepsilon^*$ - Complex Permittivity  
(4) $M^*$ - Complex Modulus

The subsequent plots are characteristics of particular equivalent circuits and consist of a combinations of semicircles and straight lines. Intercepts with real axis and frequency values at maximum or minimum positions lead to simple component values. This technique has been frequently used for liquid electrolytes since 1947, as suggested by Randles [19]. Bauerle, in 1969 [20], first applied this technique to solid electrolytes. Since then, the complex plane analysis technique has become a basic tool in the study of solid electrolytes. The impedance and admittance plane representations are commonly used for analysing the response of solid electrolytes. Alternatively, the modulus and permittivity plane plots are used for representing the response of the dielectric systems.

General A.C. Theory

The applied a.c. signal and the measured currents in an electrical network is given by
\[ V(t) = V_0 \exp(j \omega t) \]  
\[ I(t) = I_0 \exp(j \omega t + \phi) \]

where, \( \phi \) is the phase angle.

The impedance \( Z(\omega) \) of the circuit is given by

\[ Z(\omega) = |Z| \exp(-j \phi) \]
\[ = |Z| \cos \phi - j |Z| \sin \phi \]
\[ = Z_r - j Z_i \]

where \( Z_r \) and \( Z_i \) are real and imaginary parts of the complex impedance. The relationship between various quantities are

\[ |Z| = [ Z_r^2 - Z_i^2 ]^{1/2} \]  
\[ \tan \phi = (Z_r/Z_i) \]  
\[ Y = 1/Z(\omega) = G + j B \]

Conductance

\[ G = \frac{Z_r}{Z_r^2 + Z_i^2} = 1/R \]  
\[ \text{Susceptance, } B = \frac{Z_i}{Z_r^2 + Z_i^2} = \omega C \]

Complex Impedance and Admittance Analysis

The real and imaginary parts of the impedance/admittance of the sample are plotted in a complex plane and their frequency dispersion curves possess information about the effects of electrolyte-electrode interface, bulk
resistance, grain boundary resistance, etc. The idealised plot for the certain lumped circuit elements are shown in Figure 3.5. For a parallel RC combination, we have

\[ Z_r = \frac{R}{1 + \omega^2 R^2 C^2} \quad \text{and} \quad Z_i = \frac{\omega R^2 C}{1 + \omega^2 R^2 C^2} \quad (3.12) \]

Elimination of \( \omega \) from equation 3.12 leads to

\[ (Z_r - R/2)^2 + Z_i^2 = R^2/4 \quad (3.13) \]

which is an equation of a circle of radius \( R/2 \) with centre at \((R/2,0)\) (refer Figure 3.5).

Consider a solid electrolyte having a non-blocking electrodes and its equivalent circuit consists of a geometrical capacitance \( C_b \) in parallel with the bulk resistance \( R_b \). The corresponding impedance and admittance plots are as shown in Figure 3.6. The intercept of the dispersion curve to the real axis gives the bulk resistance / conductance.

Many real systems exhibit impedance behavior which is not consistent with any of the standard results mentioned above and such results are shown in Figure 3.6. For example, as shown in Figure 3.6(a), in addition to a semicircle, a straight line at low frequencies is observed. This is a characteristic of a double layer capacitance. In polycrystalline samples, there may be a contribution to the
Fig. 3.5 Impedance & Admittance plots for some R-C circuits. 
$Z'$ - Real part and $Z''$ - Imaginary part.
Fig. 3.6 Different impedance and admittance behaviours observed in solid electrolytes.
impedance due to the presence of grain boundaries. The grain boundaries may act as a hindrance to the ion transport or they might also provide a high conductivity path (since the defect density may be larger in the interface region). In the first case, one can detect a second semicircle in the impedance plot representing grain boundary resistance [17]. The bulk resistance in such a case is obtained from the intersection of the high frequency impedance circle with real axis (refer Figure 3.6(b)). If we have an increased conductivity at the grain boundary, it will give an apparent bulk resistance that is lower than the real bulk resistance. A study of the conductivity dependence on grain size may help to identify the conduction mechanism, if single crystals are not available. Another common impedance behaviour is the depression of the high frequency semicircle, so that the center of the circle is situated below the real axis (Refer Figure 3.6). It has been shown that, in this case, a Constant Phase Element (CPE) connected in parallel with the bulk resistance will result in the depression of the semicircle [17].

In the present investigation, the impedance admittance analysis of the glasses of varying composition in SMV and SMA glasses have been studied. The studies have been carried out on the pressed pellets of the glasses with silver electrodes. Solatron’s Frequency Response Analyser
(model-1250) aided with Electrochemical Interface (model-1286) and Hawlett Packard Computer (model-9122) is used for the frequency dependant study. For studying the temperature dependence, the sample is kept in a furnace with resistive heating. The temperature is controlled by a temperature controller / indicator (Century Inst. model-806) with an accuracy of ±1°C. The measurements are made in the frequency range 6.5Hz to 65.0KHz. External effects due to lead connections, sample support, etc., are carefully minimised.
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