CHAPTER-III

EXPERIMENTAL PROCEDURES
For the convenience this chapter has been divided into following sections:

3.1 Preparation of the amorphous material.
3.2 Structure determination.
3.3 Electrode formation.
3.4 Methods for d.c. measurements.

3.1 Preparation of the Amorphous Materials

There are number of ways with the help of which amorphous materials can be prepared e.g. condensation from vapours, cathodic sputtering, electrodeposition and quenching from the melt. The bulk form of the amorphous material can be prepared by the quenching technique, while the other techniques are used for preparation of their films.

3.11 Quenching Technique

Bulk samples of \([\text{Se}_{0.7}\text{Te}_{0.3}]_{100-x}Y_x\) \((x = 0, 0.2, 0.5, 1, 5, 10)\) \((Y = \text{Zn, Cd, Pb, Bi})\) were prepared by quenching of a melt in ice cold water. Appropriate materials (99.999% pure, supplied by Loba Industrials Co, Bombay 400 005, India) were weighed as per composition \([\text{Se}_{0.7}\text{Te}_{0.3}]_{100-x}Y_x\), sealed in evacuated \((10^{-6}\text{Torr})\) quartz tubes (inner diameter \(\approx 8\) mm, length \(\approx 6\) cm). The sealed ampules were heated in a rocking furnace. The temperature of the furnace was raised to 217°C i.e. the melting point of Se. It was kept fixed for three hours. A continuous rocking was given to the samples so that Se can be mixed with the rest of materials. Then again
temperature was raised to the temperature of the second component of the composition either Te or Y \([Y = Cd, Zn, Bi, Pb]\) depending upon the melting points which ever is lower, again it was fixed for three hours. Finally the temperature was raised to about 800°C, and maintained for 24 hours. The sealed tubes were continuously rocked to ensure a homogeneous composition. The quenching was done in ice cold water.

3.2 Structure Determination

The prepared bulk materials were tested for the structure using a X-ray Diffractometer (Jeol powder X-ray Diffractometer fitted with a scintillation counter as a detector). The schematic diagram and set-up is discussed in next section.

3.21 X-Ray Diffractometer

X-ray diffraction pattern provides a mean for identifying the structure of a substance. Since when an X-ray beam is made to fall on a substance, it gets diffracted and scattered in all directions. The intensity of these diffracted X-rays depends upon the arrangement of atoms and molecules in the substances. These diffracted X-rays are detected with the help of detector and recorded in a pattern which gives the structural information regarding the substance. The whole arrangement consists of X-ray generation unit, detection unit and recording unit. The general components of the set-up are as follows:
Fig. 3-1 Principle of operation diagram
3.2.1a Operational Principle

The schematic diagram of the X-ray diffraction is shown in Fig. 3.1. A divergent beam emanating from the X-ray source falls on the sample. X-rays diffracted from the sample are focussed at the receiving slit and detected by the scintillation counter. The detected X-rays are fed to the pulse height analyser of the counting and measuring unit, and recorded on the recorder with the help of a rate meter. The criterion for a material to be amorphous in nature is the absence of the structural peaks in the X-ray pattern.

3.3 Electrode Formation

Amorphous materials so prepared with the quenching technique were collected, cut into pieces using a diamond cutter. The specimens were lapped to proper dimensions using emery paper and lapping tools. Aluminium and molybdenum
electrodes on the opposite faces of the samples were fabricated using vacuum evaporation technique.

3.3.1 Vacuum Evaporation Technique

Electrodes were fabricated using a vacuum coating unit (Hind Hivac Model No.124). The major parts of this unit are

(a) Glass bell jar or chamber
(b) Rotary pump
(c) Diffusion pump

The chamber unit comprises of a work holder supported on three pillars fitted with base plate. The ring has a diameter of the order of about 8". This ring is used for uniform coating on the small plain area from a central evaporation source. A d.c. high tension discharge cleaning system consisting of a pure aluminium angular ring shields the work from electron contamination. A shutter swinging over the source position is operated by the external lever provided in front of the cabinet. A standard filament holder is fitted with L.T.line electrode an earth electrode. The filaments are positioned vertically below the center of the work holder to give the uniform distribution of the evaporation. A baffle plate is provided with a tripod just above the base plate aperture. To avoid foreign bodies falling into the baffle valve, a stainless steel wire mesh is fitted over the base plate opening.
FIG. 3.2 A typical oil diffusion-pump evaporation station used in the author's laboratory. The notations stand for
A, quartz iodine lamp heater; B, substrate; C, quartz-crystal rate controller and deposition monitor; D, sub-
strate mask; E, shutter (mechanical or electromagnetic); F, vapors from evaporation source; G, adapter collar
between the bell jar and the pump baseplate flange; H, air-inlet valve; I, baseplate flange; J, Pirani or thermo-
couple gauge; K, roughing valve; L, liquid air trap; M, cooled chevron baffles; N, diffusion pump; O, cooling
coils; P and Q, backing valves; R, Pirani gauge; S, fore-
pump with air-inlet valve T; U, diffusion pump heater;
V, filament holders; W, multiple feedthrough; X, ioniza-
tion gauge; Y, Meissner trap; Z, baffle valve.
The rotary pump is connected to the chamber to produce vacuum inside the chamber. Diffusion pump is fitted to the chamber through the baffle valve. Water is circulated on the outer wall of the pump to maintain its temperature. A heater is housed at the bottom of the main body of the pump. The whole arrangement of the coating unit is shown in Figure 3.2.

To form electrodes firstly the glass bell jar is cleaned with chromic acid and rinsed with acetone, so that it becomes dust free. The samples are cleaned, dried and then placed on the work holder. A pure aluminium element is fixed on the tungsten filament for evaporation. The assembly is covered with the bell jar. The arrangement is cleaned using a high tension electric discharge for five minutes. During this discharge the pressure inside the bell jar is maintained in between 0.05 Torr to 0.1 Torr. The electrodes are fabricated at a pressure about 10⁻⁶ Torr, so that the system remain free from electrode contamination and absorption of other gases.

3.4 Methods for d.c. Measurements

Many techniques of d.c. measurements are available [67,68,69]. In general method for conductivity measurement, one can calculate conductivity using the following relation

\[ \sigma = \frac{I \ell}{VA} \]

Here \( \sigma \) is the conductivity measured in ohm⁻¹ cm⁻¹, \( I \) the current flowing through the material, \( V \) the voltage drop, \( \ell \)
Fig 3.3 Simple method for Conductivity measurements.
is the length and \( A \) is the area of cross-section of the sample. Here in this case the nature of the sample electrodes and other factors which can effect conductivity has been neglected. The conductivity can be measured with accuracy if there is sufficient number of charge carriers and thermal variations in the sample are negligible. These problems are there in case of semiconductors and insulators because of the fact that the number of charge carriers in these materials are very small.

Secondly above definition is true only when the sample chosen is uniform in properties. Thus, studies of stability and uniformity form an important part of the field of d.c. conductivity. To avoid these discrepancies the standard 'Two Probe Method' has been used.

3.41 Two Probe or Potential Probe Method

To eliminate the error of temperature fluctuation, interelectrode effects for metal semiconductor two extra electrodes are used to measure the potential and the method is called potential probe method (Fig.3.4). In this method, the electronic field is applied on the opposite faces of the sample. The potential drop is measured across the probes and the distance between the probes replaces the length of the sample. Here the potential drop used is the average value obtained for both directions of current flow and eliminate the possible errors due to thermoelectric effects or rectifications that may occur due to the inhomogeneities and rectifying boundaries, or other defects.
Potential Probe method for conductivity measurement

Fig 3.4 SAMPLE
The effect due to rectification can further be minimised at the probes by using a potentiometer, or other devices which draw a little or no current. Since under these conditions, probe contact resistance will have little effect, beyond reducing the sensitivity of the potentiometer. Even if the contact resistance is high, use of an electrometer or high impedance device will eliminate this problem, provided that the impedance of the device is of the order of magnitude greater than the largest contact resistance.

Thus, the conductivity with this method can be given by

$$\sigma = \frac{dI}{V_d A}$$  \hspace{1cm} \text{(3.4.1(b))}

Where d is the distance between the probes, A the area of cross-section, $V_d$ the potential measured, and I the current flowing through the material. Here the current is measured with the help of a digital picoammeter (EA 5600 accuracy ±0.25% for current range and ±0.3% for voltage range), the potential drop across the probes is measured using Kaithley Electrometer. The temperature of the sample has been controlled using electric oven (9935) and PID temperature controller SDTC 002 (Accuracy ±0.5%). The temperature has been measured with a Cu-Ni thermocouple and read with digital meter. To ensure the electrical shielding of the sample, it was placed in metallic cell.

The samples of selenium, tellurium, were prepared in accordance with the composition $[\text{Se}_{1-x}\text{Te}_{0.3}]_{100-x}Y_x \ [(x = 0,$
0.2, 0.5, 1.5, 10) (Y = Zn, Cd, Pb, Bi)]. The d.c. conductivity measurements has been done with the two-Probe method. In case of each composition five samples were studied and five readings were recorded for each value of electric field and temperature so as to minimise the errors. The readings were repeated using molybdenum and aluminium electrodes. The experimental data is found to be independent of the electrode material.