CHAPTER 3

Experimental Details

CHAPTER -3

EXPERIMENTAL DETAILS

3.1 INTRODUCTION:

This chapter contains the detailed description of methods used for preparing samples and characterization of glass samples. The various measurement techniques used for studying glasses have been described. The procedure used for analysis of the observed Mössbauer spectra is also presented in this chapter.

3.2 GLASS PREPARATION:

The samples have been prepared by mixing appropriate amount of analytical grade chemicals V_2O_5, H_3BO_3, K_2CO_3 and Fe_2O_3 in a porcelain crucible. The mixture was kept in a muffle furnace whose temperature was controlled by using a temperature controller of Toshniwal Indust. Pvt. Ltd., range 0-1200 °C($\pm 1^{\circ}C$ accuracy). The temperature of the mixture was kept initially at 400 °C for half an hours for removing CO_2 and H_2O contents from the mixture and then the temperature was raised to 900 °C and is kept for four hours. These melts are then quenched onto a cleaned copper plate at room temperature and subsequently pressed by another Cu plate to provide a faster quenching rate. The method produced beaded glasses. A portion of the bead is crushed into fine powder by using agate mortar and is used for Mössbauer spectroscopic, FTIR and DSC studies, while for DC conductivity, electrical switching, thermoelectric power measurements, the beads are cut in the rectangular pellet of about 2-3 mm in thickness. All the samples are kept in a vacuum descicator to protect them from atmosphere.

3.3 MÖSSBAUER SPECTROSCOPY:

3.31 Mössbauer Spectroscopic Measurement:

The fine powder of beaded glass samples are obtained by crushing the samples in an agate mortar. Weighed quantities of these samples are taken such that 5 mg/cm^2 of natural iron is present in each disc of 2 cm^2 size and 2 mm thickness. These powder samples are brought into disc form by applying a pressure of about 2 tons in a hydraulic press. Then this disc is kept in an aluminium sheet cavity of the same size as that of a pellet sample which is placed in a absorber holder for taking a Mössbauer spectra at room temperature. The spectra are recorded by using **Wissvl Mössbauer Spectrometer (Germany)** operating in the multiscaling mode (256 channels) in conjunction with an electromechanical drive operating in constant acceleration mode. The detecting system consisted of a proportional counter filled with argon and 10 % CO_2. The pulse from the detector are amplified by the pre-amplifier followed by amplifier and pulse height analyzer in order to select 14.4 KeV gamma rays. The function generator operating in a triangular mode, along with driving unit, provides constant accelerating source in Rhodium (Rh) matrix is used which, when coupled to the transducer, vibrates with a constant Doppler acceleration. The multichannel analyzer and the function generator are precisely synchronized. The readout of MCA was printed. The system is frequently checked and the velocity scale is calibrated by using the observed lines of standard iron foil. The spectrum of this is shown in Figure 3.1.

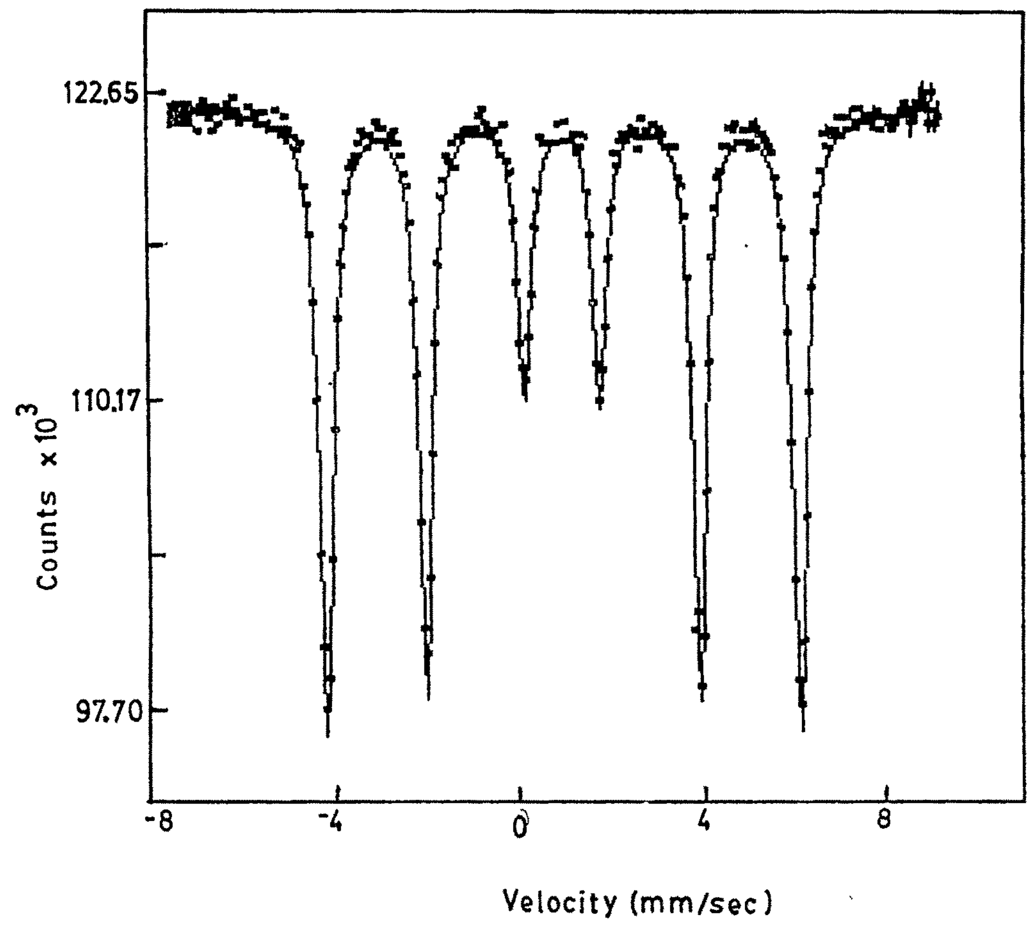

Figure 3.1 : Fe-57 Mössbauer spectrum of Natural Iron foil.

3.32 Mössbauer Data Analysis:

The analysis of the spectra has been done by using a computer programme developed by E. Von Meerwal[1]. The fitting procedure used in this programme is selected to yield a maximum region of convergence in the presence of strong overlapping lines. A non-linear variable matrix minimization technique is used iteratively to optimize the parameters of the theoretical function by minimizing χ^2 for the spectral data. The least square fitting method is applied by assuming Lorentzian profiles. Intensities and widths are constrained to be unequal for components of each doublet in a paramagnetic region and to be different for a pair of corresponding lines of Zeeman sextet.

The analysis results the isomershift and quadrupole splitting with an accuracy better than 0.01 and 0.02 mm/sec respectively.

The mathematical function used to fit the data has the form

$$F(x,p) = P_{L+1} + \sum_{L=3m-2}^{L} (p_j, p_{j+1}, p_{j+2}, x) \tag{3.31}$$

Where, P_{L+1} represents a background and p_j, p_{j+1}, p_{j+2} are the centroid, full height and full width at half maxima (FWHM) respectively of the m^th^ line. The function f has the Lorentzian form

$$F((p_j, p_{j+1}, p_{j+2}, x) = p_{j+1}\left[\frac{4(x-p_j)^2}{p_{j+2}} + 1\right]^{-1} \tag{3.32}$$

The computer analysis of the Mössbauer data yielded peak position, intensity, line width and total area of the spectrum.

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[1] E. Von Meerwal, Computer Physics Communications, 9(1975)117.

3.33 Fe-57 Mössbauer Spectrometer:

Figure 3.2 shows a block diagram of the Fe-57 Mössbauer spectrometer. This spectrometer comprises of a Mössbauer drive capable of operating at high velocities and fast data acquisition electronic and velocity calibrator. The important units of this spectrometer are

(a) Mössbauer source and absorber
(b) Gamma rays detector system
(c) Doppler velocity drive system
(d) Data aquisition system.

(a) Mössbauer source and absorber:

Radioactive isotope is an essential thing to all Mössbauer experiments which acts as a source of radiation in Mössbauer experiment. A 15mCi ^{57}Co(Rh) source is used in the present experiment. ^{57}Fe is formed by electron capture in ^{57}Co. ^{57}Fe is formed in excited state and three gamma rays, 14.4 KeV, 123 Kev and 137 KeV are emitted on decay to stable ground state (Figure 3.3). In addition to this, gamma rays of 6 KeV are also emitted as a consequence of the electron vacancy created after electron capture.

Mössbauer absorber are prepared from finely grounded powder of the glass sample. The distance between source and absorber was kept 10 cm as a compromise between counting rate and parabolic effect.

(b) Gamma-Ray Detection Unit:

Gamma ray detection unit consists of Argon filled proportional counter and charge sensitive pre-amplifier. The pre-amplifier is a low noise FET charge sensitive preamplifier with noise level less than 600 μV peak to peak.

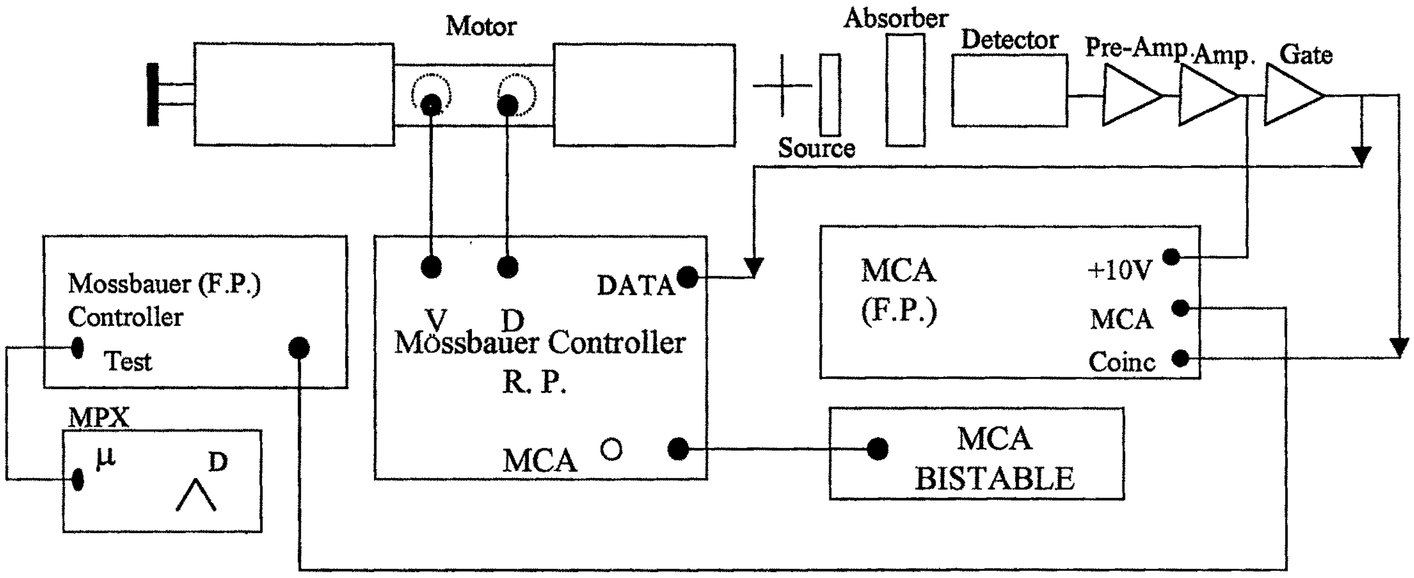
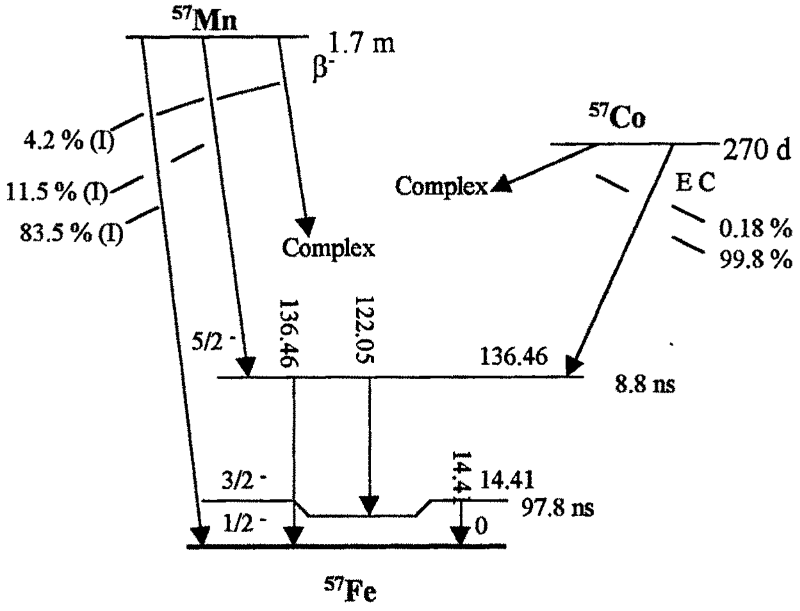


Fig. 3.2 : **Block Diagram of Fe-57 Môssbauer Spectrometer.**

$^{57}_{26}$Fe(14.4keV,136.5keV)



Measurement Properties (E_γ= 14.4 keV)	**Measurement Properties (E_γ= 136.5 keV**
E_γ= 14.4125 ± 0.0006 keV	E_γ= 136.46 ± 0. 05 keV
$t_{1/2}(\gamma M)$ =97.81 ± 0.14 ns)	$t_{1/2}(\gamma M)$ =8.7 ± 0.4 ns)
$\alpha_T(\gamma M)$ =8.18 ± 0.16	$\alpha_T(\gamma M)$ =0.1
IA = 2.19 %	$\rho(\gamma M)$ =12 %
MG = + 0.0904206 ± 0.0000012 nm	MM = +0.88 ± 0.05 nm
MM = - 0.15491± 0.00023 nm	
QM = +0.187 ± 0.005 b	

Figure 3.3 : Decay Scheme of ^{57}Co Mōssbauer Source

(c) Doppler Velocity Drive:

The emitted 14.4 KeV γ -rays from the Mössbauer source are modulated using a velocity transducer in conjuction with the spectrometer controller. The velocity transducer consists of a electromechanical device of a moving coil in a fixed magnetic field. A second coil is included on the armature to produce a velocity related signal which is fed back into the Mössbauer spectrometer controller and error correction. This velocity transducer is capable of sweeping a Mössbauer source through a velocity range of upto ± 6 cm/sec with high linearity.

A velocity transducer is a drive with a constant acceleration using a constant acceleration fly-back mode. In the fly-back mode the spectrometer controller generates an asymmetrical triangular wave at a frequency of 6 Hz. The long linear portion of the asymmetrical triangular pulse drives the Mössbauer drive through the desired Doppler velocity spectrum. The short linear portion of the signal provides an optimum retrace wave form and further stops the address advance of MCA until the retrace has been completed. The retrace time of the signal is 0.005 seconds. The advantage of using fly-back signal for driving the Mössbauer drive is that one can utilize the full number of the channels of the MCA for accumulation of one spectrum rather than the mirror image spectra as in the case of normal constant acceleration mode.

(d) Data Aquisition System:

A Wissvl Series MCA was used to record the Mössbauer spectrum. The spectra were recorded in 256 channels of the MCA. The recorded spectra were then brought into the form of data from the MCA to print form by using the dot matrix printer.

3.4 FTIR SPECTROSCOPY:

About 5 mg of powdered glass sample was mixed and ground with a relatively large quantity of KBr which is transparent to IR radiation. Disc for measurement of IR absorption spectra were formed by pressing the mixture at a pressure of 10-15 tons for few minutes under vacuum. The resultant pellet known as KBr pellet of the sample is kept in the sample holder of Bomem Michalsons Series FTIR spectrometer (Picture 1) having resolution 4 cm^{-1}. The FTIR spectra of the glass sample are taken from range 510-4000 cm^{-1} with a scanning rate of 2.7 sec/scan in a 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.

3.5 DIFFERENTIAL SCANNING CALORIMETRY:

The finely crushed powders of samples were used for DSC measurement. About 20 mg of powdered sample was taken in a non-hermetic aluminium pan and was creeped by a Creeper in each case. The creeped aluminium pan is kept in a DSC sample holder of DSC instrument DSC-2910 TA Instrument (USA) and the sample was heated at the rate of 20 °C /min. upto 600 °C. TA-2910 instrument is a microprocessor based controlled which is operated by inbuilt programme. The DSC spectra of these glasses contain endothermic and exothermic peaks. Figure 3.4 shows a schematic diagram with components of a DSC system. TA-2910 has a facilities to store or recall thermograms, perform peak temperature and energy analysis, compare the curves and determine peak areas. Figure 3.5 shows a DSC curve taken using a TA-2910 instrument at the heating rate of 20 °C/min. The endothermic and

Picture 1: Photograph of Bomem Michalsons Series FTIR Spectrometer.

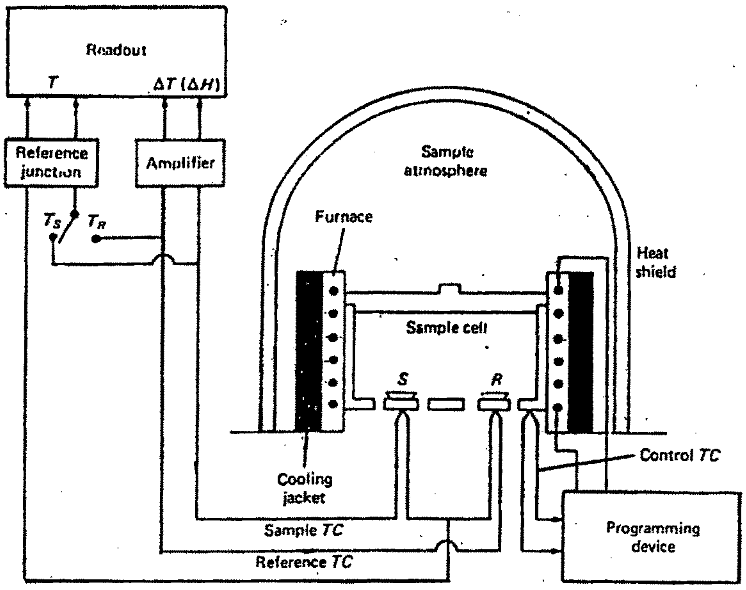


Figure 3.4 : **Schematic Diagram of DSC apparatus.**

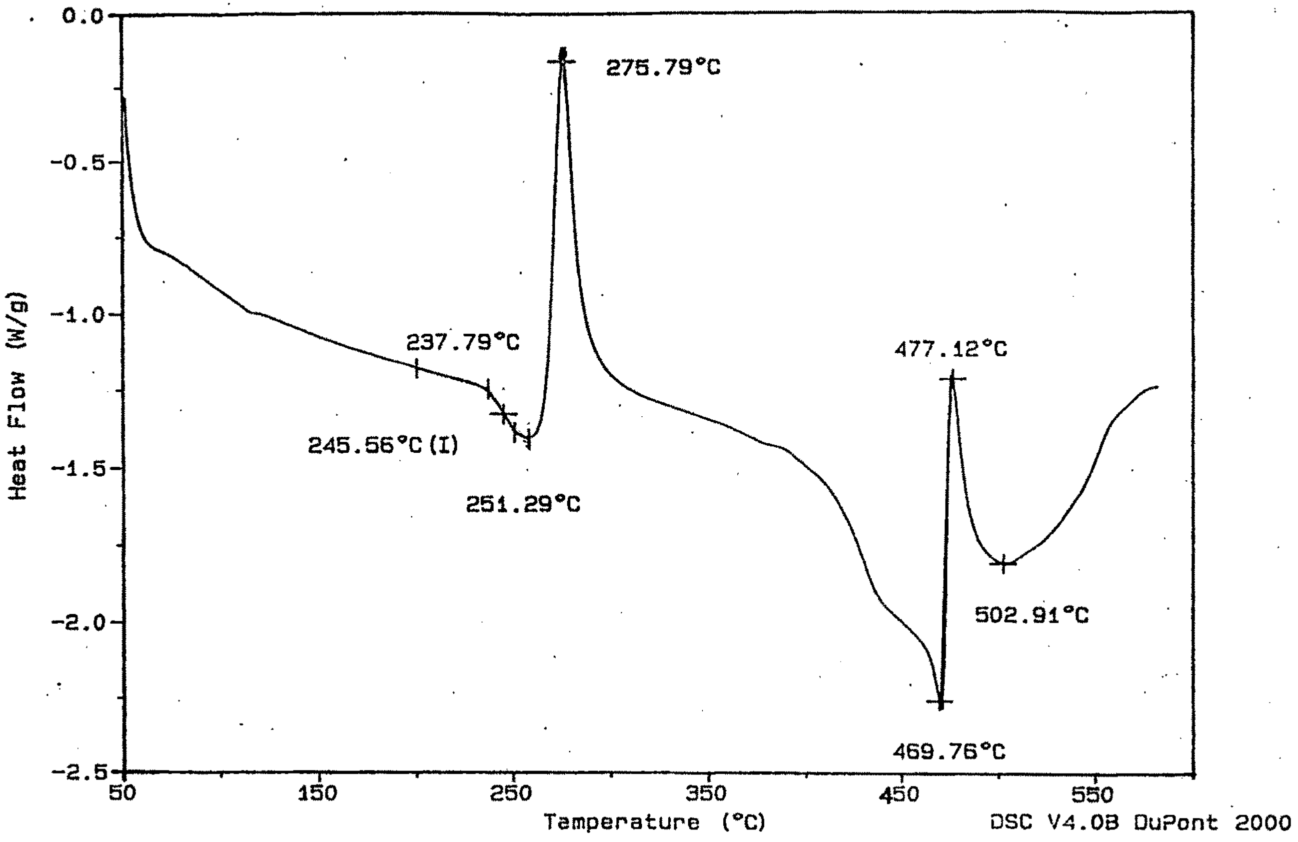


Figure 3.5 : DSC curve of TA-2910 instrument.

crystallization peak are marked using peak finder. All the spectra are taken by keeping the same heating rate of 20 °C/min.

3.6 CHEMICAL ANALYSIS:

In all the glass samples, vanadium ions are assumed to be present as V^{+4} and V^{+5} and not in lower valences states. The amount of V^{+4} and V_{total} are determined from the photometric titration of the glass solution.

A method for preparing a glass solution is given as follows.

(A) PREPARATION OF GLASS SOLUTION:

Finely ground powdered glass samples are used for preparation of glass solution for photometric titration. The amount of V^{+4} ions was determined by photometric titration of solution of the glass in 2N perchloric acid ($HClO_4$) with 0.01N potassium permanganate ($KMnO_4$) as indicator.

A 2N ($HClO_4$) and 0.01N $KMnO_4$ were prepared in the following way.

(i) Preparation of 2N $HClO_4$:

56.25 ml of $HClO_4$ is added in a 250 ml volumetric flask and distilled water is added upto the mark of a volumetric flask. A resulting solution is 2N $HClO_4$.

(ii) Preparation of 0.01N $KMnO_4$:

0.01N $KMnO_4$ solution is obtained by dissolving 0.079 gm of $KMnO_4$ in 250 ml volumetric flask containing distilled water and shaken it well.

A known amount of powdered glass sample was dissolved fully in a 2N $HClO_4$ (perchloric acid) such as to make a 100 ml solution. A part of solution (a known amount) from this is added to H_3PO_4, 0.01N $KMnO_4$ and distilled water such as to give a 10 ml of solution.

H_3PO_4 (0.5 ml) + Glass solution (5 ml) + 0.01 N $KMnO_4$ + H_2O = 10 ml

Amount of $KMnO_4$ is chosen as per requirement and corresponding amount of water is added to make a 10 ml of solution and $\cong$ 5 ml H_3PO_4 is added for making a glass solution clear.

(B) EXPERIMENTAL METHOD:

The glass sample solution is titrated for different amount of $KMnO_4$ solution (0.2 to 2.4 ml) and a titration point for $KMnO_4$ are measured from knowing percentage of absorption by using a **Spectrophotometer-106-Systronics,** in a wavelength of 540 nm for $KMnO_4$. A plot between absorption versus $KMnO_4$ gives the exact titration point for $KMnO_4$ which is used to calculate the amount of V^{+4} ions present in a given glass sample.

After titration, the total vanadium content of the solution was determined with 0.1N ammonium ferrous sulphate using diphenylamine sulphonic acid as the indicator.

The amount of potassium permanganate solution added beyound the end point in the V^{+4} titration is corrected in calculating the total vanadium from the result of titration. The V^{+4}/V_{total} ratio of the glass are calculated. Also, the amount of V^{+5} ions are also calculated by knowing V^{+4} and V_{total} amount.

3.7 ELECTRICAL SWITCHING MEASUREMENTS:

The electrical switching measurements are studied by usual technique of two probe method. Figure 3.6 shows a schematic diagram for electrical switching measurement. The samples of convenient shape and size were cut and polished first with coarse and then with fine lapping paper. The samples were in the form of rectangular pellets of about 2 mm thickness. Silver paste was painted on the polished rectangular surface of the sample. Then these samples are kept in a furnace at about 80 to 90 °C for one an half hour for removing moisture and stress produced during polishing. With painted silver paste good ohmic contacts are found. The sample is pressed between two electrodes of a sample holder and the cell was kept in a heating furnace whose temperature was controlled by using Jumo Mercury Contact Thermometer (±1 °C accuracy) and Relay (Germany). For I-V characteristics measurements, a regulated voltage source of range 0 to 20 volt of Scientific (Model No. HM 8040, Tripple Power Supply) make was connected in series with the sample and a fixed resistance of 100 ohm, 10 watt. A current through the sample was measured by digital pico-ammeter. I-V characteristics were taken for different ambient temperatures. The temperature difference between the sample and the ambient was measured by thin Al-Cr-Al thermocouple wires which were attached to the sample. The electro-motive-force (e.m.f.) across the thermocouple was measured by digital microvoltmeter. The voltage at which switching occurs was measured at different ambient temperatures. As the voltage across the sample (electrical field) is increased gradually, a ohmic behaviour is observed for low applied voltage and when a sufficient high voltage (not more than 30 volt) is applied gradually, the current suddenly increases and the voltage starts decreasing across the sample. Thus the I-V characteristics were measured for different glass samples at different ambient temperature.

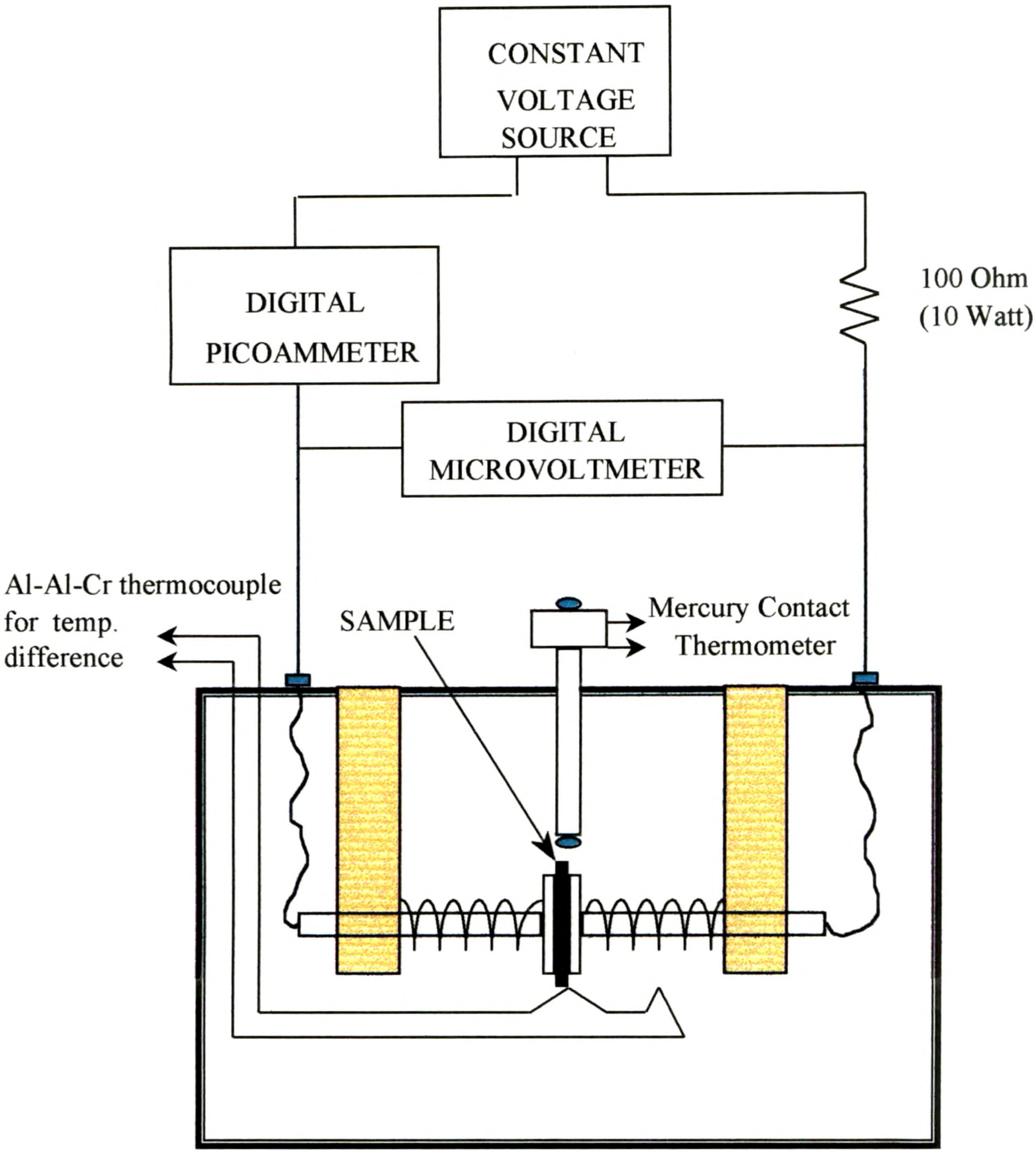
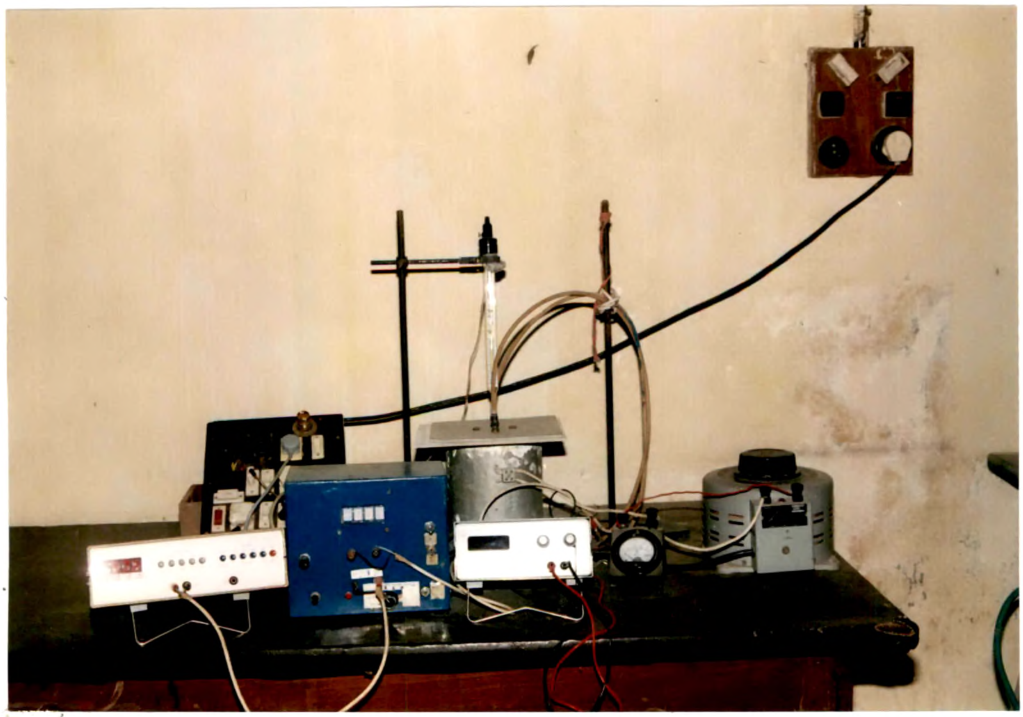


Figure 3.6 : Schematic Diagram of electrical switching measurement.

3.8 ELECTRICAL CONDUCTIVITY:

The samples were cut in the form of rectangular pellets of about 2 mm thickness. The pellets were lapped and polished first with coarse and then with fine lapping paper. Silver paste was painted on the polished rectangular surface of the sample. This sample is kept in a furnace at about 90 °C for one an half hour for removing a moisture and stress from the sample. With painted silver paste a good ohmic contact is found. This sample is kept in between two electrodes of a cell and the cell was kept in a furnace controlled by mercury contact thermometer (Jumo, Germany) and relay. For the I-V characteristics, a constant current source of range 10 nA to 1000 μA was connected in a series with the sample and digital microvoltmeter (Systronics 412) was connected parallel to the sample. Schematic diagram and experimental setup for electrical conductivity measurement are shown in Figure 3.7 and Picture 2.

A current through a sample was kept constant and value was selected in such a way that the voltage drop across the sample should not exceed 12 volt. For a given constant current source, voltage drops across the given glass sample are measured at different ambient temperature starting from room temperature to 150 °C. The sample was heated at the interval of 10 °C. The conductivity of the sample was calculated by knowing the dimension of a given glass sample. The data were plotted on a graph. The slope of a line was calculated by least square fit method.



Picture 2: Experimental setup of Electrical Conductivity measurement.

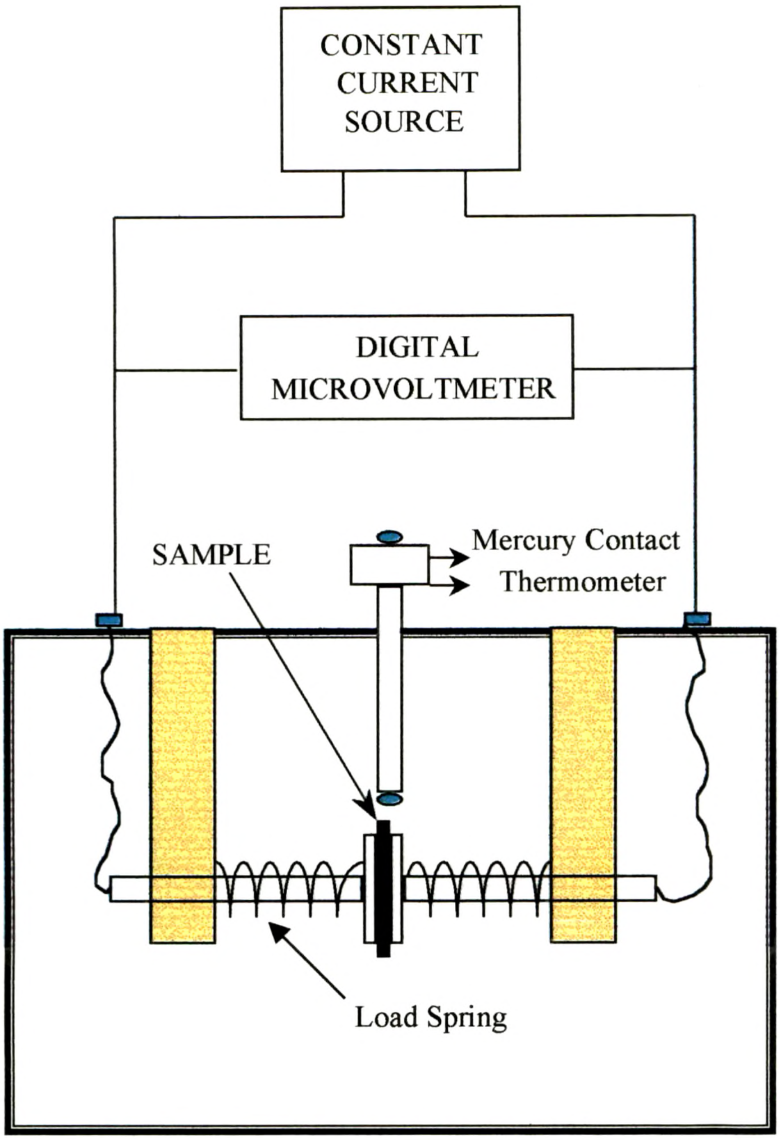


Fig. 3.7 : Schematic Diagram of Electrical Conductivity Measurements

3.9 CONSTANT CURRENT SOURCE:

A constant current source (10nA-1mA) was designed and fabricated indigenously in the laboratory for conductivity and switching measurements to be carried out on the present glass samples. Figure 3.8 (a) & (b) shows a circuit diagram of a constant current source of range 10 nA to 1mA which consist of a power supply, constant current unit, A/D convertor and Seven Segment LED display unit. The heart of the circuit is op-amp MOSFET IC 3140 [Figure 3.8 (b) (ii)] which has two input pin 2 & pin 3 inverting and non-inverting respectively, pin 6 is output and supply Vcc at. Pin 4 and pin 7 are -5 V and +15 V dc respectively. A 10 kΩ of 10 turns potentiometer is used for adjusting the current very accurately. A load is connected across 2 & 6 pin in IC1. Output of IC1 is given to non-inverting pin 3 in IC2 and output of IC2 is given to to pin 3 of IC4. Here IC2 acts as a buffer for a given IC1 and IC4.. Output voltage is taken from pin 6 at point B. Similarly, pin2 of IC1 is connected to input of IC3 at pin 2 and output of which is taken as current at point A which gives a constant current irrespective of value of load connected between pin 2 and pin 6 of IC1. Point A and B are connected to the A/D converter for conversion of analog signal to digital signal with the help of A/D IC ICL-7107 [Figure 3.8 (b) (i)]. Output of A/D converter is given to the 3 ½ seven segment LED Display for displaying the desired value of current/voltage.

A range selector switch is used for selecting a particular range of current made up of a resistance whose values are set according to 100 mV A/D converter [Figure 3.8 (b) (iii)]. All resistors used for the circuit are of ± 1 % tolerance.

A power supply [Figure 3.8 (a) (ii)] for 3140 is designed using TTL ICS 7815 ,7805 and step down transformer of 0-15 Volt, 500 mA, which gives output of +15 and –5 and +5 Volt.

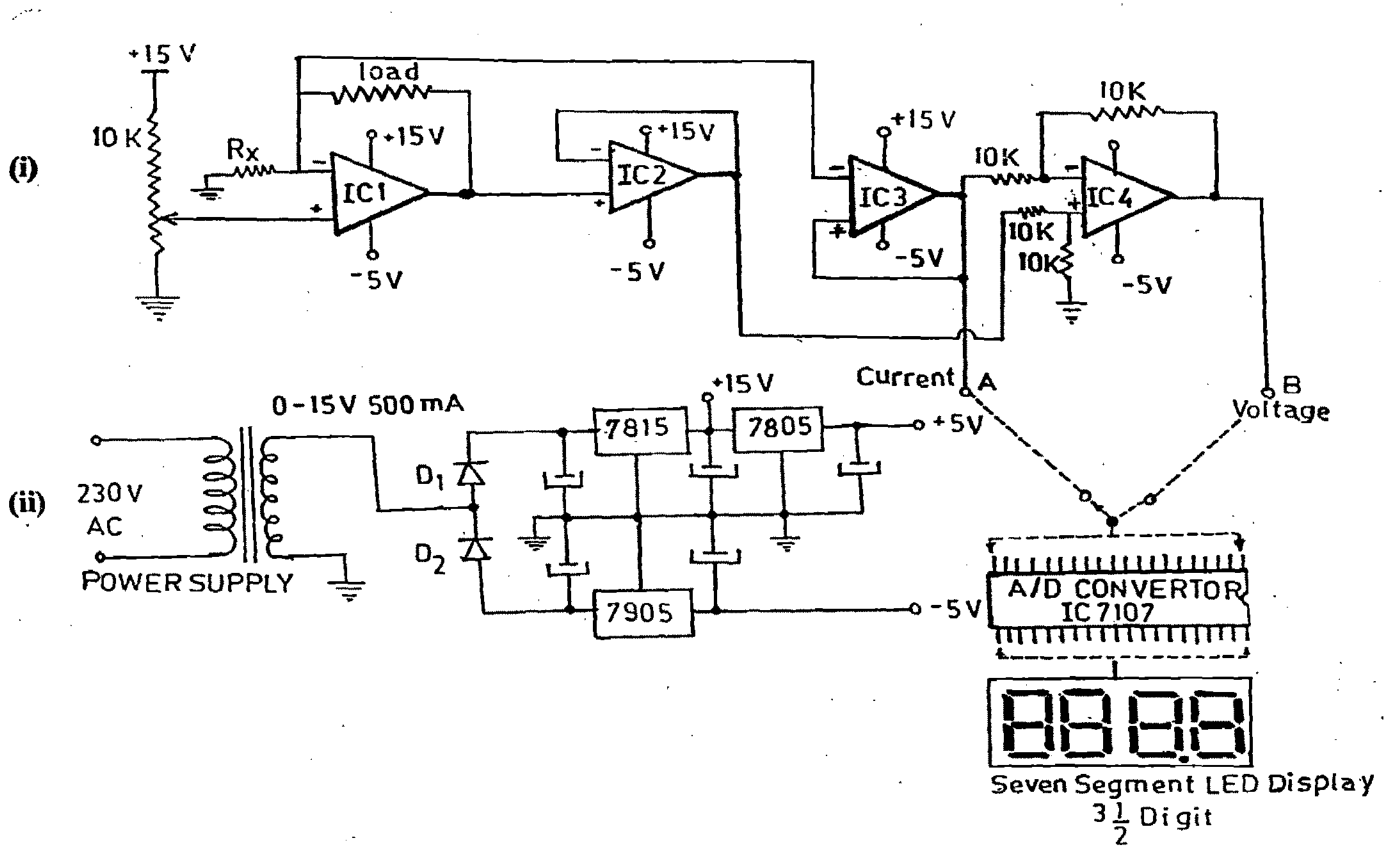


Figure 3.8 (a) (i) Circuit diagram of Constant Current Source.
(ii) Power Supply, +5 V, -5 V and +15 V.

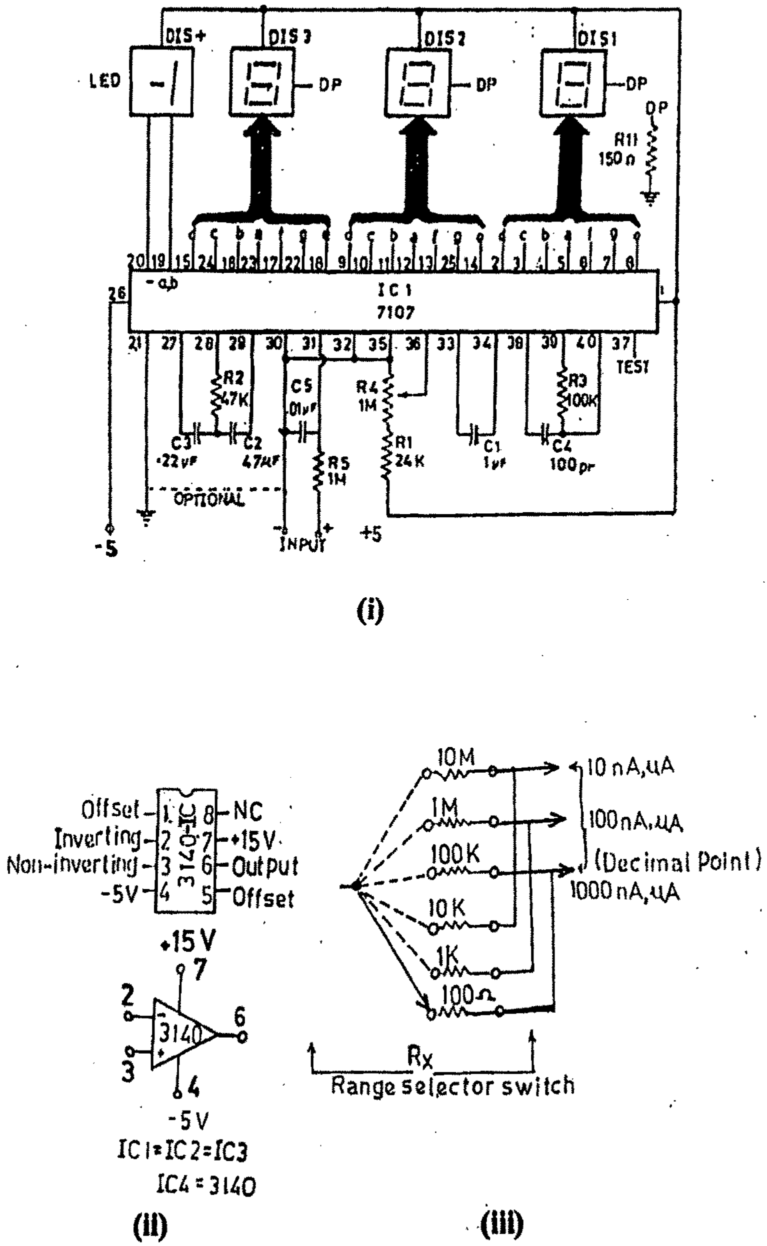


Figure 3.8 (b) (i) Circuit diagram of digital panel meter.
(ii) Pin configuration of IC 3140.
(iii) Range Selector Switch.

A current through the sample is adjusted in such a way that the voltage drop across a given load should not exceeds 12 volt due to the saturation of IC 3140. The circuit was designed using general purpose PCB (printed circuit board) and was mounted in a box. For connection purpose RG-8 coaxial wire were used. The constant current has following accuracy in different range of current.

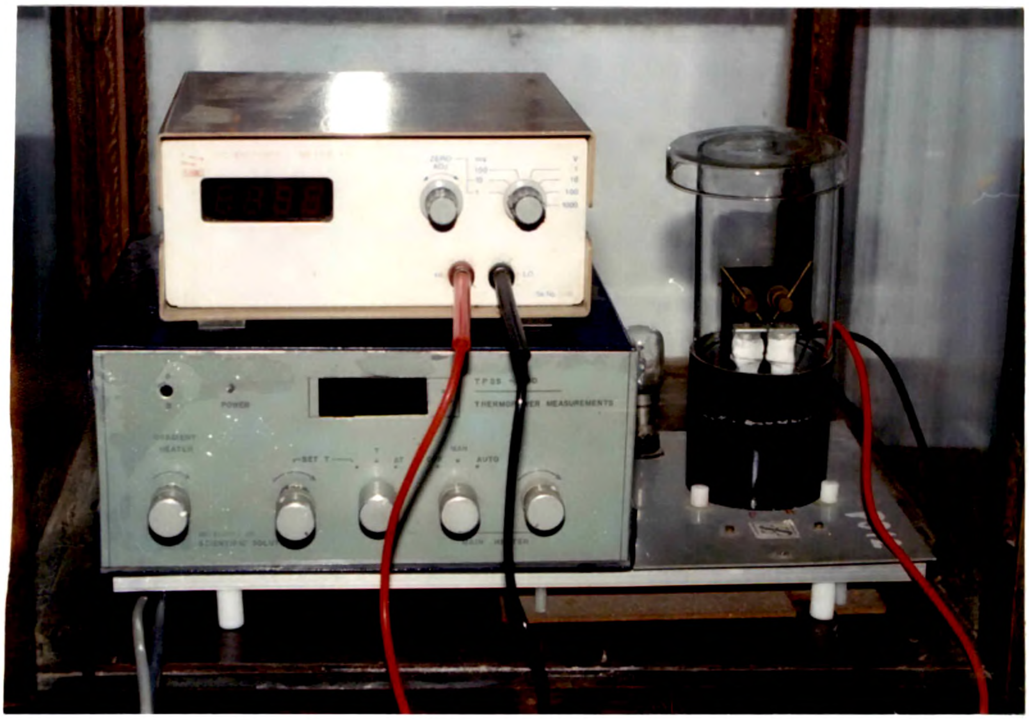
Max. Current	**Accuracy**
10 nA	0.1 nA
100 nA	1 nA
1000 nA	10 nA
10 μA	0.1 μA
100 μA	1 μA
1 mA	10 μA

3.10 THERMOELECTRIC POWER MEASUREMENT:

The beaded samples were cut and polished with a coarse and then fine lapping papers and pellet of 2 mm thickness were obtained. The pellet is kept in a sample holder of thermoelectric power measuring apparatus. A thermoelectric power of the present glass system is measured using a differential method, where the thermo e.m.f. across the two points of the glass sample is being measured keeping at different ambient temperatures. The thermoelectric power is measured in the temperature range 313°K to 423°K.

The apparatus designed, block diagram and experimental setup for the measurement of Thermoelectric power are shown in Figures 3.9, 3.10 and Picture 3. Thermoelectric power, Q, of all the glasses 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 auxilliarly heaters wounded on each of the sample holders shafts. The thermo e.m.f. across the points of the sample is measured for different temperatures from 25 °C to 150 °C. The temperatures of two main heaters are measured using Cr-Al thermocouple with high impedance digital microvoltmeter.

The operation of the system is based on the principle of ac power control using controlled rectifiers. Using triac as the power control device the power to the heater and hence the temperature can be controlled. An error signal proportional to the difference of the measured and the set temperature along with external bias is used to decide the firing angle of the triac hence controlling the temperature. The output of the sensor (thermocouple) mounted on the main heater is amplified by the preamplifier U_1 to get the voltage proportional to the temperature reading which is displayed as T. The same signal is also fed to the error amplifier U_2 which compares this signal with the set temperature signal obtained from a stable reference sources. The gain of



Picture 3: Experimental setup of Thermoelectric power measurement.

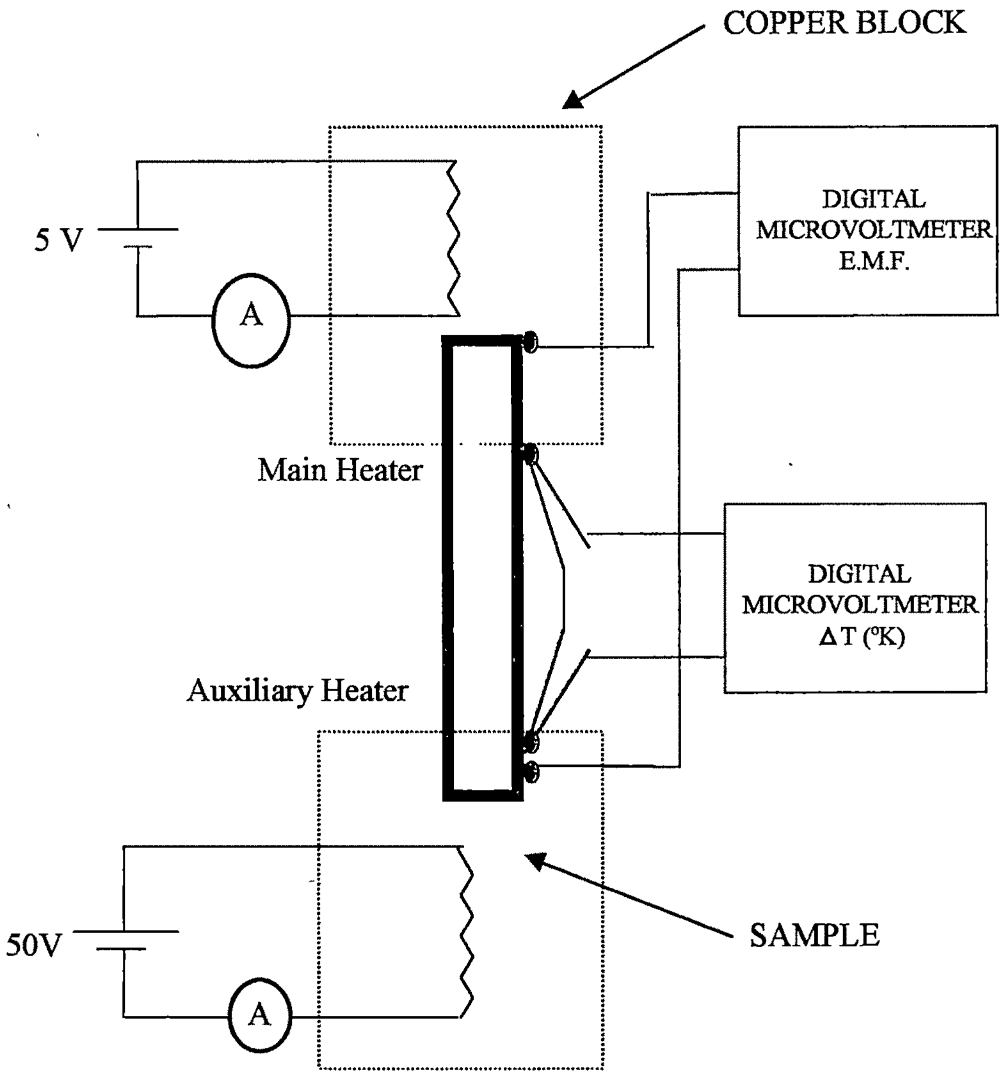


Figure : 3.9 Experimental Setup for Thermoelectric Power Measurement.

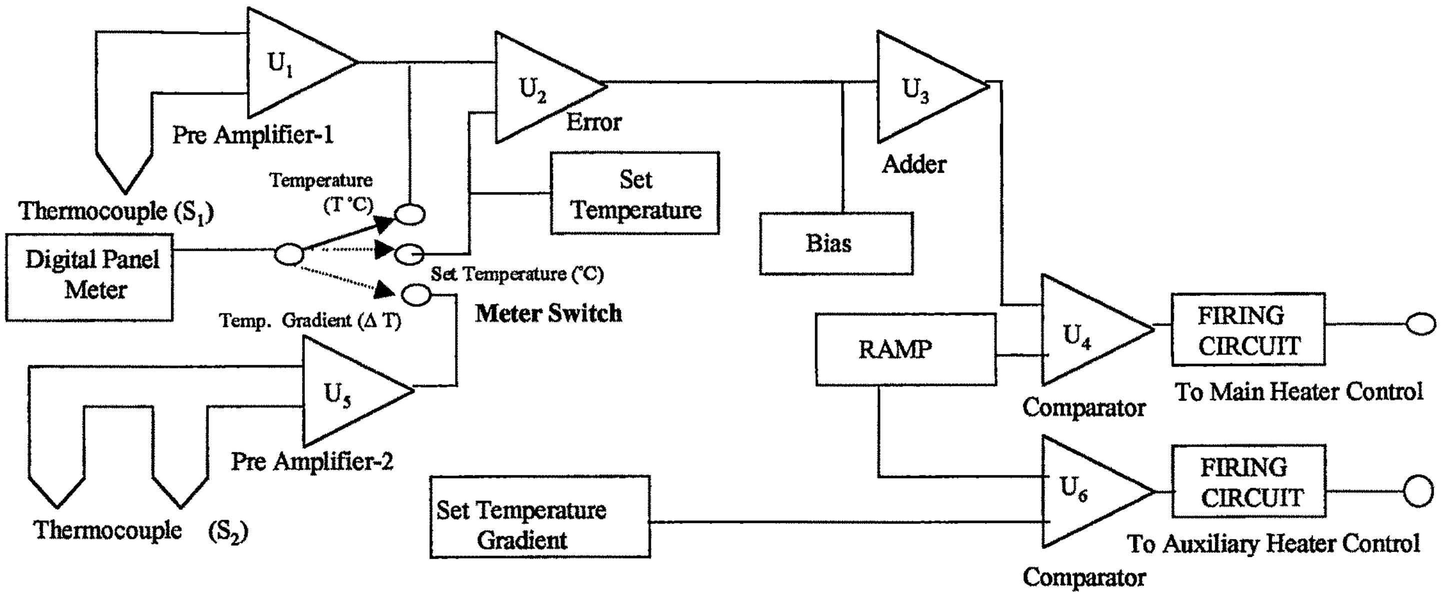


Figure 3.10 : Block Diagram For Measurement of Thermoelectric Power.

the error amplifier controls the proportional band of control and is presetted to about 30 % of the full scale. The error amplifier output is then summed with a bias signal from the bias control in the summing amplifier U_3 the output of which is the voltage proportional to the temperature difference. The dc control signal is then compared to a linear Ramp of 0-3V (0 to full power) in the comparator U_4. The output of the comparator which control the firing angle of the triac is then given to the firing circuit. A similar low power control circuit is used to control the power to auxiliary heater. Preamplifier U_5 amplifies the output of the differential thermocouple for the indication of ΔT which is the temperature gradient. This thermopower measurement system has following specifications.

Temperature Range : 25 °C – 200 °C
Temperature Control : ± 1 °C
ΔT : 2 °C to 10 °C
Sensors : Thermocouple Cr/Al
Power Dissipation : 60 W.

3.11 DENSITY MEASUREMENT:

Density of the present glass system is measured by using Archemedies principle. A glass sample of any shape and size was tied to a weight less nylone strand thinner than human hair and was hanged to the hook of electromechanical weighing machine in air and the weight of the sample in air was taken and then the same sample was weighed immersed in liquid (methanol) whose density is known (0.7914 gm/cc). Using Archemedies principle the density of the glass sample was calculated.

3.12 X-RAY DIFFRACTION ANALYSIS:

Among various characterization techniques, X-ray diffractometer techniques plays a very important role in structural characterization. A fine powdered glass samples were taken in a sample holder and X-ray diffraction study were made on these glasses. In the present study the X-ray diffractometer Philip PM 8203 with PW 1390 channel control and PW 1373 goniometer have been used for characterization of glass samples. It was operated at 35 to 40 KeV and 20 mA with Cu target (λ=1.5418 Å).