Summary

TITLE: STUDY OF TRANSPORT MECHANISM IN CADMIUM AND LEAD SULPHIDE DOPED VANADIUM PHOSPHATE GLASSES.

The twenty years in the recent past have seen a remarkable growth in the subject of structure and properties of condensed disordered systems such as liquid metals and glasses of microscopic levels. Transport properties of semiconducting glasses are very interesting and provide useful information about conduction mechanism. Now-a-days glasses have a prominent role in the field of electronics and have wide applications in industry, space research and computer memories.

Much work on the V₂O₅ – P₂O₅ glass system has been done by various research workers, but less attention seems to has been given when it is doped with CdS and PbS. CdS and PbS are the photosensitive materials used for the preparation of light dependent resistors individually. Similarly the electrical properties of vanadate phosphate system after doping with the CdS and PbS could be interesting, as CdS and PbS are photosensitive. The resistivity range of V₂O₅ – P₂O₅ glass system is of the order of 10³ to 10⁷ (ohm-cm.), which is quite useful for electronic semiconductors.

Thesis comprises the study of transport mechanism in cadmium and lead sulphide doped vanadium phosphate glasses. The conductivity, photoconductivity and optical behavior of these glasses are investigated. The thermoelectric effect is also studied for all the compositions of these glasses.

CHAPTER 1: General Introduction

A glass can be defined as a non-crystalline solid formed by undercooling of liquids. The glasses are characterized by networking oxides (Glass formers), which gives rise to random linked tetrahedral arrangement broken at some places by the network modifier (Glass modifier). The conventional technique of glass preparation involves melting of the thoroughly mixed ingredients and quenching of the homogeneous melt.

The three series of glasses X V₂O₅ – (100-X)P₂O₅, X V₂O₅ – (90-X)CdS- 10P₂O₅ and X V₂O₅ – (90-X)PbS- 10P₂O₅ of various compositions were prepared in the laboratory by mixing appropriate amounts in mol % of different chemicals (AR-grade) in powder form. The constituents were weighed on K-Roy monopan balance having accuracy ± 0.00001 gm. Repeated grinding of the mixtures was done to ensure homogeneity. Homogeneous mixture was transferred to silica crucible which was then subjected to melting in automatically controlled muffle furnace at temperature ranging from 700 °C to 1200 °C ±10 °C. The duration of melting was generally two hours. The homogeneous molten glass was cast on steel plate. All the samples after annealing are subjected to finishing process such as polishing and applying silver paint etc. These samples were then used for electrical characterization.

CHAPTER 2: D C Conductivity

Different models such as polaron hopping model, Schnakenberg’s model, percolation theory are discussed and applied to study the conduction mechanism in the glasses under study. Mott’s formula for variable range hopping and Nagel’s two-channel model are also discussed.
The dc conductivity of the glass sample was measured by using V-I characteristics method in the temperature range 313 to 523 K. A digital microvoltmeter having input impedance 1000 MΩ (model DGM 02, RSI, Roorkee make) was used to measure the voltage across the sample. The current flowing through the sample was measured as a function of temperature at constant voltage. The current is measured using a digital picoammeter (model PM 01, RSI, Roorkee make, having resolution 1 pA). A muffle furnace having automatic temperature regulator (digital) was used for heating the sample. The temperature of the sample was measured using a digital temperature indicator.

Dc- electrical conductivity study of cadmium and lead sulphide doped vanadium phosphate glasses containing 50 – 80 % of V_2O_5 has been presented. The activation energy is found to be in the range of semiconducting glasses and the behavior of log σ versus 1/T is linear as observed in the case of many semiconducting glasses. The nature of hopping conduction is studied from the linearity of the Log σ versus activation energy at fixed temperatures. Adiabatic hopping conduction (small polaron hopping) is observed for series 1 (V_2O_5 –P_2O_5). And nonadiabatic, small polaron hopping conduction is observed for series 2 (V_2O_5 –CdS –P_2O_5) and series 3 (V_2O_5 –PbS –P_2O_5), suggesting that the conductivity is not mainly controlled by activation energy.

CHAPTER 3: Thermoelectric power and glasses.

Thermoelectric effect in crystalline and amorphous solids is important, which is directly connected with the transport of charge carriers. Thermoelectric power mainly depends on the relative carrier concentration, structure parameters, defects and impurity.

The temperature difference between the two ends of the semiconductor gives rise to a e.m.f., known as thermo e.m.f. (V_t). The system for TEP measurement consists of two brass contact probes. The glass sample is fixed between the two probes. Copper wires soldered to the brass plates were connected to the digital microvoltmeter. Two chromel-alumel thermocouple were attached to the two brass plates for measuring the temperature of the two ends. On both the sides of the sample small heaters are installed and were insulated from the sample with an asbestos sheet. The temperature of both the probes is raised in such a way that the temperature gradient of 4 to 5 °C is maintained between them. The temperature of the hotter probe is raised to 200 °C. The thermo-emf developed across the sample was measured with the help of digital microvoltmeter having input impedance of greater than 1000 MΩ.

Conduction mechanisms i.e. band conduction of electrons in extended state and localized states, are discussed and applied to our results. The activation energy, hopping energies are calculated for all the series of glasses.

The thermoelectric power is relatively large and stable over wide range of temperatures. This feature along with its small dependence on temperature suggests the possible use of such semiconducting glasses as good, low cost temperature sensors. The hopping of carriers through localized states near band edge is observed for all the glasses.

CHAPTER 4: Photoconductivity studies on glasses.

Photoconductivity is the increase in the electrical conductivity of an insulating material caused by the light radiation incident up on it. In this chapter the field dependence, temperature dependence, intensity dependence of photoconductivity and spectral studies are discussed. The growth and decay curves are also studied. The parameters such as Rise time, Decay time, Probability (p), Trap depth and Thermal activation energies (E_t), corresponding to different compositions for all the glasses are calculated.
The sample was mounted in a dark chamber with a slit, where from the light was allowed to fall over the sample. The illumination was provided by a halogen lamp. The intensity over the sample was varied by changing the distance. Different excitation wavelengths were obtained by filters. The light intensity was measured with a digital luxmeter. The photocurrent was measured with a digital picammeter. A small furnace is prepared in which sample holder is placed. The furnace is kept in a chamber. The photocurrent is measured at different temperatures ranging from RT to 473 K. The temperature of the sample can be measured by digital temperature indicator.

The field dependence in these glasses is $I \propto V^n$ in nature. The photocurrent increases as the intensity of the illumination is increased. The spectral response in these glasses has also been found sensitive to the composition. The transmission edges are corresponding to the photocurrent peak positions, and these peaks are due to the transition of electron from the valence band to the conduction band. Temperature dependence study shows that the glasses are semiconducting in nature.

**CHAPTER 5: Optical properties**

Transmission and absorbance measurements were made on Systronic UV – VIS spectrophotometer (wavelength range of 200 nm to 900 nm). Measurement reading of % transmittance, absorbance, and concentration factor are displayed digitally, as per the selected mode of operation.

Transmission and absorbance measurements were used to determine the absorption coefficient as a function of incident photon energy. The optical absorption edge for all samples shows two distinct regions of behavior. A high photon energy region in which $I \propto \alpha$ varies linearly with $(\alpha V)^2$, is associated with valence to conduction band transition. A low energy tail is associated with interband transitions involving impurity states within the gap.

Variation of optical energy gap ($E_{opt}$), dielectric constant at infinite high frequency ($\varepsilon_{\infty}$), refractive index ($n_0$), constant (B) and ratio of carrier concentration to effective mass ($N/m^*$) with different glass composition are studied and reported.

The transmittance versus wavelength plot shows the peak at a particular wavelength in $V_2O_5 - P_2O_5$ glasses and this value of peak wavelength changes with $V_2O_5$ composition. In $V_2O_5 - CdS - P_2O_5$ glasses similar type of peak is observed at single wavelength 600 nm only which is independent of $V_2O_5$ as well as CdS composition. In $V_2O_5 - PbS - P_2O_5$ glasses no peak is observed but knee is observed after which the transmittance remains same more or less. The optical energy gap $E_{opt}$ is compositional dependent in all three series of glasses.