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Composition Dependence of Effective Thermal Conductivity and Effective Thermal Diffusivity of Se_{98-X} Cd_2In_x (X=0, 2, 6, 10) Glassy Alloys

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ABSTRACT

Effective thermal conductivity and effective thermal diffusivity of Se_{98-x} Cd_2In_x (x=0, 2, 6, 10) chalcogenide glasses were carried out at room temperature using transient plane source (TPS) technique. The measured values of effective thermal conductivity and effective thermal diffusivity were used to determine the specific heat per unit volume (ρC_p) of these glasses in the composition range of investigation. The values of λ_e and χ_e were found to increase initially with the increase of In concentration in Se-Cd alloy. Results indicated that λe and χ_e are maximum at 6 at.wt% of indium and ρC_p almost constant for all glassy alloys. This is suggestive of fact that $Se_{92}Cd_2In_6$ can be considered as a critical composition of this series, at which the alloy becomes, chemically ordered and better thermally stable than other composition. Further addition of indium in Se-Cd decreases the values of λ_e and χ_e. The behavior is explained on the basis of decrease of localized states and increase in disorderness for higher composition indium.

INTRODUCTION

The chalcogenide glasses have recently attracted the attention because of their use in various solid state devices. The structural studies of these materials are very important for better understanding of the transport mechanisms in them. The studies of chalcogenide glasses are also attractive due to their importance in preparing corrosion resistive and electronic memories materials [1-3]. The selenium has wide commercial applications and its device applications like switching memory, xerography, X-ray imaging, photonic and non-linear applications etc. made it attractive.

It also exhibits unique properties of reversible transformation [4]. The structure of amorphous Se [5–8] and the effect of alloying In into Se have been carried out by workers and reported [9,10] in the literature. These studies indicate that when In is incorporated to amorphous Se it is dissolved in the Se chains to satisfy its coordination requirements and to form a cross-link structure, which retarded the crystallization probability and enhanced thermal stability. Besides, it is also found that the optical band gap of Se–In is of the order of 1.3 eV at 300 K, which is close to the theoretical optimum for solar energy conversion. It is well known that thermal relaxation occurs in these glasses [11], when a glassy substance suffers instantaneous changes in temperature (during the quenching process) relaxes from the state of higher enthalpy towards an equilibrium state of lower enthalpy. This type of thermal relaxation depends on the annealing temperature and time and may be quite fast near the glass transition temperature. The transient plane source (TPS) technique, which was developed by Gustafson [12] as an improved version over the transient hot strips (THS) method was employed to measure simultaneously the effective thermal conductivity and effective thermal diffusivity of these samples. We have studied variation of thermal conductivity and themal diffusivity of Se-Te-Sn-In glassy system [13]. From this point of view in the present paper an effort has been made to study the variation of effective thermal conductivity (λe) and effective thermal diffusivity (χ_e) of Se_{98-x} Cd_2In_x (x=0, 2, 6, and 10) samples with composition of In at room temperature.

MATERIAL PREPARATION

High purity (99.999%) Se, Cd, and In elements were weighed in appropriate atomic weight percent proportions using an electronic balance. The materials were evacuated in quartz ampoules (length 8 cm and internal diameter 12 mm). The ampoules were sealed under a vacuum of 10^{-5} Torr to remove possibility of any reaction of alloys with oxygen at high temperature. The ampoules were heated in an electronic furnace at the rate of 3–4 K/min up to 1098 K for 12 h. They were frequently rocked to ensure homogeneity of the samples. The molten samples were then rapidly quenched in ice-cooled water to obtain the alloys in their glassy state. Amorphous nature of the samples was confirmed through X-ray diffraction pattern. . The X-ray diffraction pattern of as-prepared samples were recorded using Philips PW-1700 powder diffractometer (operating at 20 keV) with Cu-K_α (λ = 1.54056 A°) radiation to confirm the glassy nature of alloys. The XRD pattern of $Se_{92}Cd_2In_6$ glass is shown in **Figure 1.** The samples in the form of pellets of 12 mm diameter and 2 mm thickness have been prepared under a load of 4 ton.

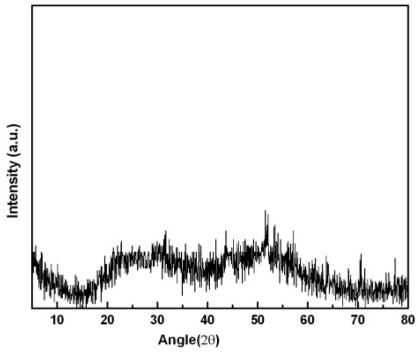

Figure 1. XRD pattern of $Se_{92}Cd_2In_6$ chalcogenide glass.

EXPERIMENTAL DETAILS

The measurements reported in this paper have been made with a TPS element. The power output to the sample was adjusted according to the nature of the sample material and was, in most cases, in the range 0.01– 0.02 W/cm^2. The measurements reported in this paper were performed with a TPS element. It was made of a 10 μm-thick nickel foil (having a resistance of about 3.69 Ω and a temperature coefficient of resistance (TCR) around (4.6×10^{-3} K^{-1}) with an insulating layer made of 50 μm-thick kapton, on each side of the metal pattern. Analysis of the data obtained through these measurements was done in a way that was outlined by Gustafsson [12]. In experiments with insulating layers of such thickness, it is necessary to ignore the voltage recorded during the first few seconds because of the influence of the insulating layers. TPS element, which is source of heat as well as sensor of temperature increase in the sample, was sandwiched between the two pallets of sample material in the sample holder and the surfaces of these pellets were made smooth so as to ensure good thermal contact between the samples and the heating elements. An important aspect of the design of any TPS element is that the pattern should be such that the largest part of the "hot" area should be covered by the electrically conducting pattern. This is due to the fact that there is insulation between the different parts of the pattern. This becomes more important because insulating layers are covering the conduction pattern and also the surface(s) of the sample. It should be noted that the temperature difference across the insulating layer could, after a short initial transient, be considered constant.

RESULT AND DISCUSSION

Simultaneous measurement of effective thermal conductivity and effective thermal diffusivity of twin pallets of $Se_{98-x}Cd_2In_x$ (x=0, 2, 6, and 10) chalcogenide glasses, prepared under a load of 5 tons, were carried out at room temperature using the Transient Plane Source (TPS) technique. The measured values of λ_e and χ_e have been used to obtain the specific heat per unit volume (ρC_p) as a function of the content x of indium (In), and the results are shown in **Figures 2-4,** respectively. It is observed from **Figures 2 and 3** that both effective thermal conductivity and effective thermal diffusivity increase up to 6 at.wt% of In in the Se-Cd system and both are maximum at 6 at.wt% of indium. For further addition of In content, the effective thermal conductivity and effective thermal diffusivity slightly decreases. It has been indicated [14] that in glassy Se about 40 at.wt% of the atoms have a ring structure and 60 at.wt% are bounded as polymeric chain. With the increase of In concentration in Se, a slight increase of polymeric chains of Se is observed. The addition of In at the cost of Se concentration increases the chain length. The effective thermal conductivity and effective thermal diffusivity are found to increase with increase of chain length and decrease with increase in ring concentration [15]. Therefore, the effect of addition of In is opposite on both λ_e and χ_e. Indium atoms also make bond with Se and are dissolved in the Se chains. Therefore, the addition of In breaks the Se chain into mixed rings to satisfy its coordination requirements and to form cross linking structure [16]. The behavior of λ_e and χ_e with In concentration in selenium as shown in **Figures 2 and 3** respectively, can be explained on the basis of concentration of ring. At lower concentration of In, Selenium chains and rings are less effective, while increase in In concentration, increases the length of chains and at 6 at.wt% of In length of chains is maximum and heavily cross linked with ring concentration. This gives the maximum values of λ_e and χ_e. Further addition of in in Se, brings an increase in ring concentration and decrease in chain length which is responsible for the decrease of λ_e and χ_e. It is also found that with increasing the indium content in the glasses some of the original Se–Se structural units are replaced by Se–In structure units. There is no large difference between the bond strength of Se–Se (79.5 Kcal/mole) and Se–In (54.0 Kcal/mole). Therefore, drastic changes in effective thermal conductivity and effective thermal diffusivity can be expected by increasing the indium content. Further addition of indium content favors the formation of In–In bond reducing the Se–In bond concentration and resulting a slight decrease of effective thermal conductivity and effective thermal diffusivity. Same trend found by Kumar and Singh for multi-component chalcogenide glasses [17]. It has been noticed that the bond formation energies in the case of Se-Cd and Cd-In are also small so that the overall structure does not show any change.

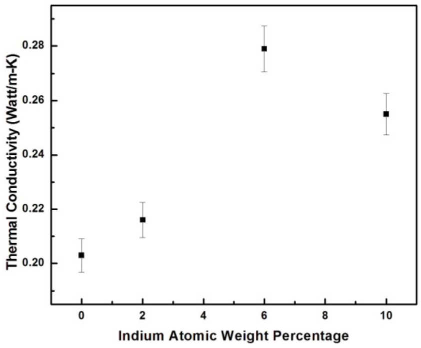

Figure 2. Thermal conductivity vs indium percentage.

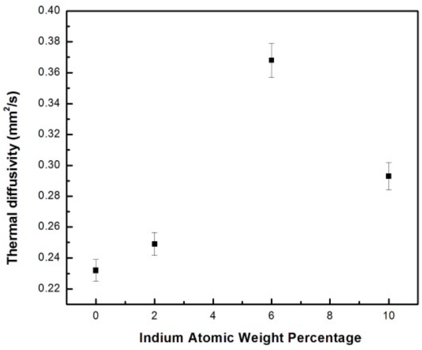

Figure 3. Thermal diffusivity vs indium percentage.

Specific heat per unit volume *(ρC_p)* is experimentally measured from TPS technique. **Figure 4** shows the variation of specific heat per unit volume with the composition of indium in glassy Se-Cd alloys. It can be observed that the variation in specific heat is almost constant. Slightly high values of specific heat at higher composition of indium are due to the availability of the large number of degrees of freedom in the alloy, which could release heat energy.

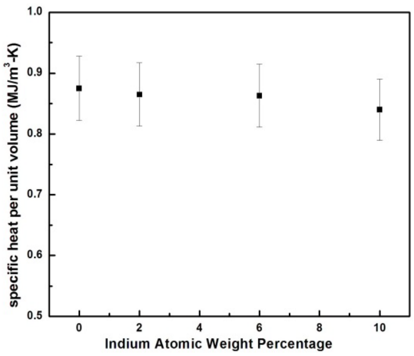

Figure 4. Specific heat per unit volume vs. indium percentage.

CONCLUSION

The effect of Indium on thermal transport properties such as effective thermal conductivity, effective thermal diffusivity, specific heat per unit volume, of Se-Cd glassy alloys has been studied. The results indicate that the simultaneous measurement of effective thermal conductivity and effective thermal diffusivity of Se–Cd glassy alloys varies with addition In content suggests that 6 at. % of In glass is more thermally stable.

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