Role of cadmium incorporation on the specific heat in glassy $Se_{80}Te_{20}$ alloy

S. SARASWAT*, S. D. SHARMA
Department of Chemistry, IFTM University, Moradabad, India

In this work, we have reported the specific heat measurements in glassy $Se_{80-x}Te_{20}Cd_x$ ($0 \leq x \leq 15$) alloys using differential scanning calorimetry (DSC) technique. A tremendously huge raise in the specific heat (C_p) has been observed at the glass transition temperature. We have also observed that the values of C_p below glass transition temperature and after glass transition are highly composition dependent. This is the sign of that fact that the incorporation of Cd in binary $Se_{80}Te_{20}$ alloy influences its glassy structure drastically. The observed changes in the specific heat of the ternary alloys as compared to binary alloy are explained in terms of atomic weight of the additive element Cd.

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1. Introduction

Chalcogenide semiconducting glasses are principally well-known and promising materials, due to their low phonon energy, wide infrared transparency, high refractive index, high photosensitivity and reversible phase change optical recording etc [1]. Chalcogenide glasses (ChGs) are used as core materials in optical fibers for light transmission, especially when short wave lengths and flexibility are required. They exhibit a unique property of reversible transformation. This property makes them very useful in optical memory devices. [2-5].

Specific heat is an imperative thermal property of chalcogenide glasses, which is useful to understand the thermal relaxation process in these glasses. Specific heat is very sensitive to the way in which atoms or molecules are dynamically bounded in a solid [6]. Thus, the measurement and analysis of this parameter lead to an effective test for characterizing a material as a glassy substance. An abrupt change in specific heat at the glass transition is characteristic of all chalcogenide glasses.

The specific heat in chalcogenide glasses shows a sudden change at the glass transition. This jump of the specific heat is very close to the Dulong and the Petit value $C_p = 3R$. In old [7-12] and recent past [13-16], some endeavor are reported regarding the variation of the specific heat in chalcogenide glasses. However, the explanations for the change in specific heat before and after glass transition are of diversified in nature. More experimental work is required in this direction. These days our laboratory is engaged in this direction [13, 14].

Literature survey shows that the electrical, photo-electrical, and calorimetric studies have been studied by various workers [17-24] in cadmium containing chalcogenide glasses of Se-Te system. However, very less attempts have been made to report specific heat studies in these materials. This motivated us to start work on this problem. The present paper reports the effect of Cd additive on the specific heat in binary $Se_{80}Te_{20}$ alloy.

Isothermal and non-isothermal crystallization of some Se-Te-Cd chalcogenide glasses has been reported by Predeep et al [17, 18]. The relaxation effects and heat capacity measurements on Cd doped Se-Te glasses have also been studied by the same workers [19]. Photo-crystallization in amorphous thin films of $Se_{70}Te_{30-x}Cd_x$ has been investigated by Dwivedi et al [20]. The results indicate that photo-crystallization is suppressed on addition of Cd in binary $Se_{70}Te_{30}$ alloy. Effect of Cd impurity on the electrical properties of thin films of $Se_{80}Te_{20}$ has been studied by Tripathi et al [21]. The results show that at low concentration of Cd (0.5 at %), the photosensitivity remains unchanged but decreases quite significantly at higher concentration of Cd (10 at %). Calorimetric studies in glassy $Se_{80-x}Te_{20}Cd_x$ have been reported by Singh et al [22]. The kinetic parameters of glass transition and crystallization have been evaluated by these workers. A discontinuity in various kinetic parameters is observed at 10 at % of Cd, which is explained in terms of a mechanically stabilized structure at a particular average coordination.

Current-voltage characteristics have been studied in amorphous thin films of $Se_{70}Te_{30-x}Cd_x$ (x = 2, 4, 6) in dark as well as in presence of light by Kushwaha et al [23]. A detailed analysis shows that conduction is Poole-Frenkel type in the present thin films in dark as well as in presence of light. The Meyer-Neldel rule is also observed by these workers in $Se_{70}Te_{30-x}Cd_x$ (x = 2, 4, 6) system for high field conduction [24].

The present paper reports the calorimetric studies of specific heat in glass transition region for glassy $Se_{80-x}Te_{20}Cd_x$ ($0 \leq x \leq 15$) alloys using DSC technique.

2. Experimental

Glassy alloys of $Se_{80-x}Te_{20}Cd_x$ ($0 \leq x \leq 15$) were prepared by quenching technique. High purity materials (5N pure) were weighed according to their atomic percentages and were sealed in quartz ampoules under the vacuum of 10^{-5} Torr. Each ampoule was kept inside a furnace at high temperature. The ampoules were rocked frequently for 10 hrs at the maximum temperature to make the melt homogeneous. Quenching was done in ice water and the glassy nature of alloys was checked by XRD technique.

Differential scanning calorimetry (DSC) is used to measure the caloric manifestation of the phase transformation. Standard aluminum pans containing 10 mg of each sample in powder form were used for thermal analysis in the DSC Unit. The accuracy of the heat flow was ± 0.01 mW and the temperature precision as determined by the microprocessor of the thermal analyzer was ± 0.1 K.

3. Results and discussion

Fig. 1 shows the typical DSC thermogram for ternary alloy $Se_{70}Te_{20}Cd_{10}$ at different heating rates. Similar thermo-grams were obtained for other glassy alloys. When a material is subjected to a linear temperature program, the heat flow rate into the sample is proportional to its instantaneous specific heat. Since the scanning rate of the DSC analyzer is linear and the instrument measures heat flow directly, the specific heat of a sample material is easily calculated.

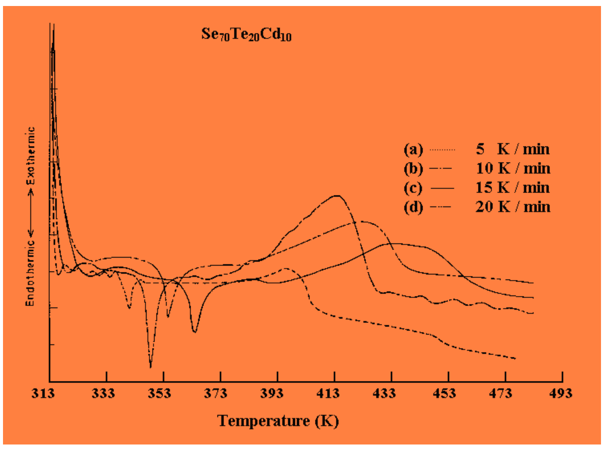

Fig. 1. DSC thermogram for ternary alloy $Se_{70}Te_{20}Cd_{10}$ at different heating rates.

The variation of C_p as a function of temperature at the heating rate of 10 K/min for each glassy alloy is shown in Fig. 2. It is clear from this figure that below glass transition temperature, C_p is weakly temperature dependent. However, near glass transition temperature, C_p increases drastically with the increase of temperature and shows maxima at glass transition temperature. After glass transition temperature, C_p attains a stable value which is slightly higher as compared to C_p below glass transition temperature. The observed peak in C_p at glass transition temperature T_g may be due to the fact that the structural relaxation times at this temperature becomes of the same order as the time scale of the experiment.

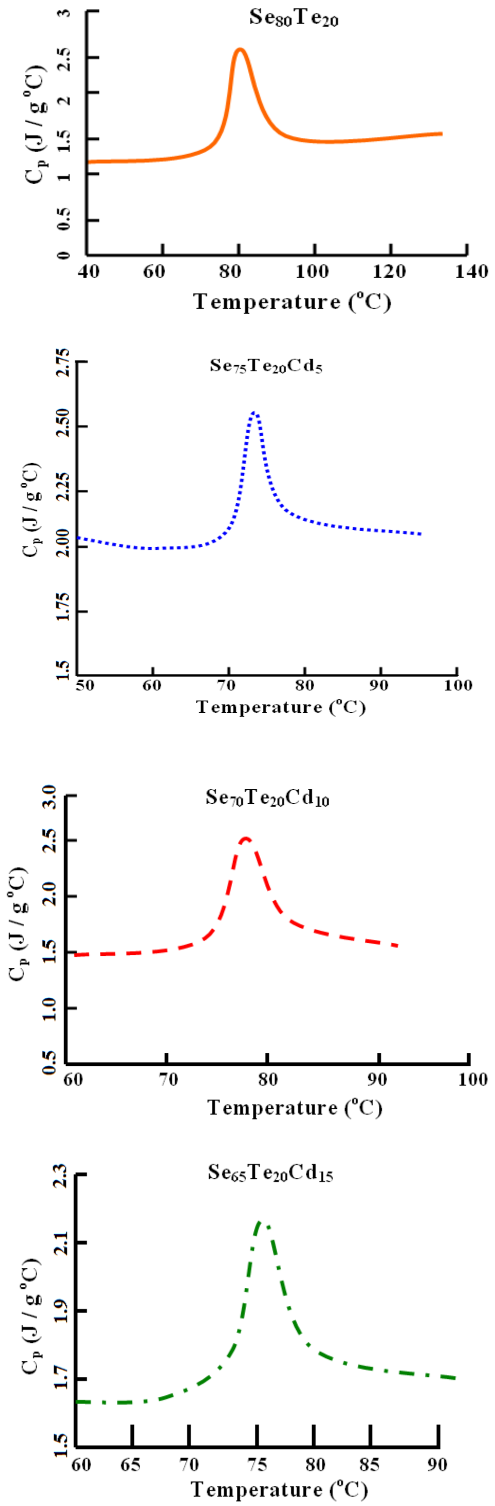

Fig. 2. Temperature dependence of specific heat in glassy $Se_{80-x}Te_{20}Cd_x$ ($0 \leq x \leq 15$) alloys.

The difference of specific heat values (ΔC_p) after glass transition (i.e., equilibrium liquid specific heat C_{pe}) and before glass transition (i.e., glass specific heat C_{pg}) has been calculated for each glassy alloy and the values of C_{pe}, C_{pg} and ΔC_p are given in Table 1. From this table, it is observed that the value of glass specific heat C_{pg} and equilibrium liquid specific heat C_{pe} are higher for ternary alloys as compared to binary alloy $Se_{80}Te_{20}$.

Table 1. Values of various specific heat parameters for glassy $Se_{80-x}Te_{20}Cd_x$ ($0 \le x \le 15$) alloys.

Sample	C_{pe} (J / g ^oC)	C_{pg} (J / g ^oC)	ΔC_p (J / g ^oC)
$Se_{80}Te_{20}$	1.40	1.20	0.20
$Se_{75}Te_{20}Cd_5$	2.07	2.12	0.05
$Se_{70}Te_{20}Cd_{10}$	1.59	1.67	0.08
$Se_{66}Te_{20}Cd_{15}$	1.68	1.75	0.07

This increase in C_{pe} and C_{pg} of ternary Se-Te-Cd alloys can be explained in terms of atomic weights of Se and Cd. The additive element (Cd) is added in Se-Te system at the cost of Se in the present glassy system. The atomic weight of Cd (112.4 gm / mol) is more than that of Se (78.96 gm / mol). It is well-known that during the glass transition phenomenon in chalcogenide glasses, some thermally-induced structural relaxation takes place in the glassy network. The atomic weight of Se (78.96 gm / mol) is less than that of Cd (112.4 gm / mol). Thus more specific heat is required for structural rearrangements with the increase in the mean atomic weights in ternary alloys. This is probably the reason for increase in C_p values after incorporation of Cd. Similar behavior was observed by our group in another glassy system [14].

4. Conclusions

Calorimetric measurements have been performed in glassy $Se_{80-x}Te_{20}Cd_x$ ($0 \le x \le 15$) alloys to study the effect of Cd additive on the specific heat in glassy $Se_{80}Te_{20}$ alloy. The values of C_p and T_g have been found to be increased in ternary alloys due to incorporation of third element (Cd) in Se-Te system. This indicates that the Cd additive drastically changes the structure of the binary $Se_{80}Te_{20}$ alloy. The composition dependence of the specific heat, C_{pe}, of equilibrium liquid and glass specific heat, C_{pg}, in glassy $Se_{80-x}Te_{20}Cd_x$ ($0 \le x \le 15$) system is explained in terms of mean atomic masses of ternary alloys.

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*Corresponding author: dr_shipra_saraswat@yahoo.com