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Specific heat studies in a-Se and a-$Se_{90}M_{10}$ (M = In, Sb, Te) alloys

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Abstract Specific heat measurements have been made in a-Se and a-$Se_{90}M_{10}$ (M = In, Sb, Te) alloys using differential scanning calorimetry (DSC) technique to see the effect of additives In, Sb and Te on the specific heat in a-Se. An extremely large increase in the specific heat values has been observed at the glass transition temperature. It has also been found that the values of C_p below glass transition temperature (C_{pg}) and after glass transition (C_{pe}) are highly composition dependent. This indicates that the additives used in the present study influences the structure of the a-Se. Specific heat and atomic mass values of the additive elements are found to be significant for the explanation of present results.

Keywords Chalcogenide glasses · Differential scanning calorimetry · Phase transition

Introduction

Recently, numerous potential applications of chalcogenide glasses are proposed in the civil, medical and military areas [1–9]. It is possible to produce industrially many devices such as electrical switches, xerographic and thermoplastic media and holographic media, optical filters, optical sensors, thin films waveguides, nonlinear elements, etc. on the base of chalcogenide glasses [1–9]. Among these glasses, Se–Te, Se–Sb and Se–In alloys have recently gained much importance as these alloys are found to be more photosensitive and harder than a-Se. They have higher glass transition and crystallization temperatures and smaller ageing effect as compared to a-Se. Due to these technical advantages of chalcogenide glasses, these materials are being studied all over the world by scientists as well as engineers.

One of the most important problems in the research field of glasses is the understanding of glass transition temperature and structural relaxation [10–14]. The glass transition is revealed as an endothermic peak or a shift in the base line in the scan of Differential Scanning Calorimetry (DSC) due to change in specific heat.

Specific heat is very sensitive to the way in which atoms or molecules are dynamically bound in a solid [15]. Thus measurement of such parameter like heat capacity will lead to an effective test for characterizing material as glassy substance. An abrupt change in specific heat at the glass transition is characteristic of the all chalcogenide glasses. The parameter detects sensitively the change in the microstructure of the glass which can be seen by the jump of the specific heat close to the Dulong and the Petit value $C_p = 3R$. Some attempts [16–24] have been made to measure the specific heat of 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.

In case of chalcogenide glasses, the variation in specific heat on changing the composition of Sb and Te in $Se_{100-x}Sb_x$ and $Se_{100-x}Te_x$ systems is studied by some workers [19, 24]. It is interesting to study the specific heat variations in a particular glassy system by changing the additive element. The present paper reports the effect of some additives (In, Sb, Te), on the specific heat measurements in a-Se.

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Experimental

a-Se and a-$Se_{90}M_{10}$ (M = In, Sb, Te) alloys were prepared by quenching technique. High purity Se, Te, In and Sb element (5N pure) were weighed according to their atomic percentages and were sealed in quartz ampoules under the vacuum of 10^{-5} Torr. Ampoules were kept inside the furnace at 1,000 °C (where the temperature was raised at a rate of 3–4 °C min^{-1}). The ampoules were rocked frequently for 10 h at the maximum temperature to make the melt homogeneous. Quenching was done in ice water and the glassy nature of alloys was checked by X-ray diffraction technique. For this, X-ray diffraction (XRD) patterns of all the four samples were taken at room temperature by using a X-ray diffractometer (Philips, PW 1140/09). The copper target was used as a source of X-rays with $\lambda = 1.54$ Å (Cu $K_{\alpha 1}$). The XRD pattern of a-$Se_{90}Sb_{10}$ alloy is shown in Fig. 1. Absence of any sharp peak in XRD pattern in Fig. 1 confirms the glassy nature of a-$Se_{90}Sb_{10}$ alloy. Similar XRD patterns were obtained for the other three glassy alloys.

The glasses, thus prepared, were ground to make fine powder for DSC studies. Constant heating rate of 10 °C min^{-1} was used for DSC scans. Before DSC experiment, the Thermogravimetric Analysis has been made on each glassy sample. Perkin Elmer TGA7 Thermogravimetric is used for this purpose. In Thermogravimetric Analysis, the percent mass loss of a test sample is recorded while the sample is being heated at a uniform rate in an appropriate environment (inert-nitrogen gas). The loss in mass over specific temperature ranges provides an indication of the composition of the sample, including volatiles and inert filler, as well as indications of thermal stability. The TG curve for a-$Se_{90}Sb_{10}$ alloy is shown in Fig. 2, which is a plot of percent mass loss versus temperature. From this figure, it is clear that there is no drastic loss in the mass of the sample over the entire temperature range. Similar TG curves are obtained for the other three glassy alloys.

The thermal behaviour was investigated using differential scanning calorimeter (Model-DSC plus, Rheometric Scientific Company, UK). The temperature precision of this equipment is ±0.1 °C with an average standard error

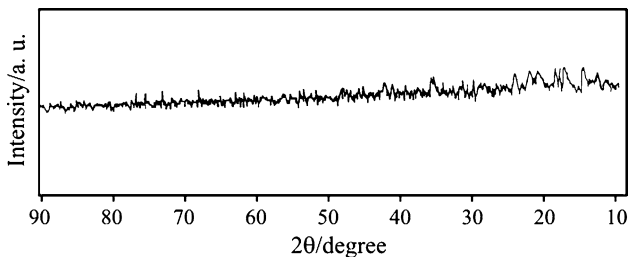

Fig. 1 XRD pattern of glassy $Se_{90}Sb_{10}$ alloy

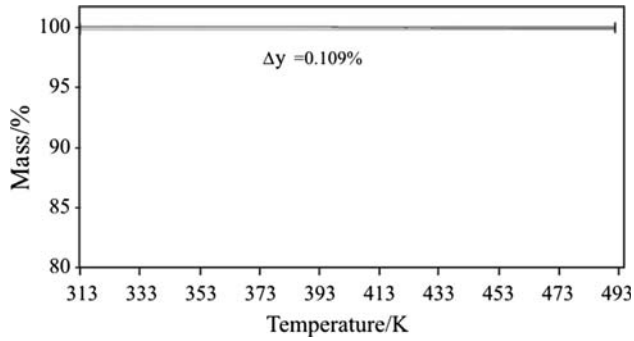

Fig. 2 TG curve for glassy $Se_{90}Sb_{10}$ alloy

of about ±1 °C in the measured values (glass transition and crystallization temperatures).

10 to 20 mg of each sample was heated at a constant heating rate of 10 °C min^{-1} and the changes in heat flow with respect to an empty pan were measured. Measurements were made under almost identical conditions.

Results and discussions

Figure 3 shows the typical DSC curves for a-Se and a-$Se_{90}M_{10}$ (M = In, Sb, Te) alloys at the heating rate of 10 °C min^{-1}. Figures 4, 5, 6, 7 show the variation of C_p as a function of temperature at the heating rate of 10 °C min^{-1} for each glassy alloy. It is clear from Figs. 4, 5, 6, 7 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 sudden jump in C_p value for each alloy at glass transition can be attributed [25] to anharmonic contribution to the specific heat. The overshoot in the value of C_p at the upper end of the "C_p jump" at glass transition is due to the relaxation effects. The time scale [15] for structural relaxation is highly dependent both on temperature and on the instantaneous structure itself. The observed peak in C_p at 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.

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_{pg}, C_{pe} and ΔC_p are given in Table 1. From this table, it is observed that the values of C_{pg} and C_{pe} falls when additive (In, Sb, Te) is added to a-Se alloy. The additive elements (In, Sb, Te) are added in a-Se alloy at the cost of 10 at % of Se concentration. The room temperature values of C_p of additive elements In,

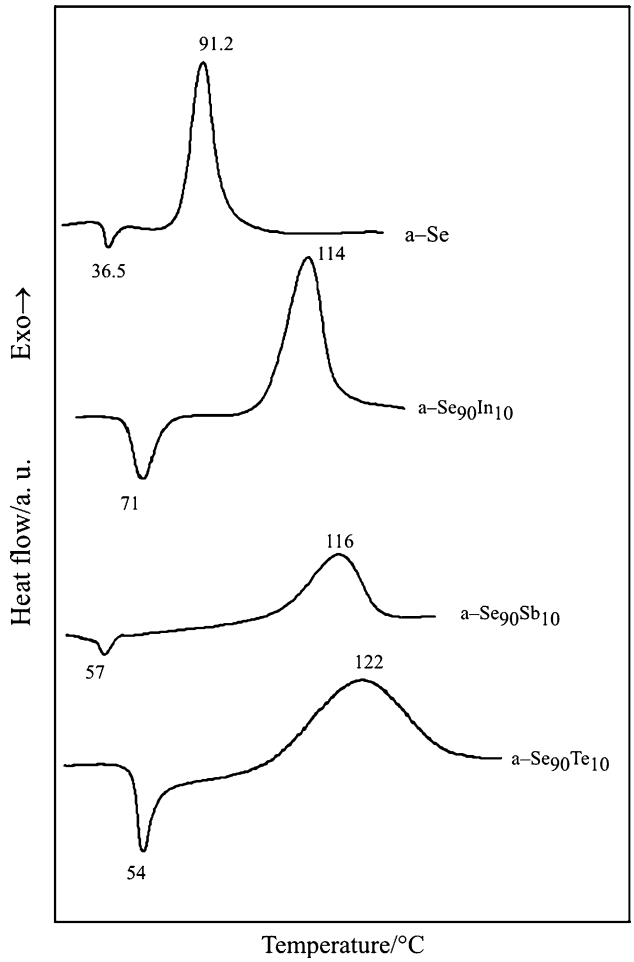

Fig. 3 DSC curves for a-Se and $Se_{90}M_{10}$ (M = In, Sb, Te) alloys at heating rate of 10 °C min^{-1}

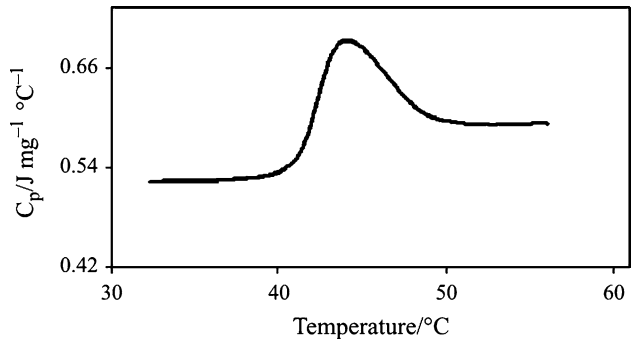

Fig. 4 Temperature dependence of C_p in a-Se at heating rate of 10 °C min^{-1}

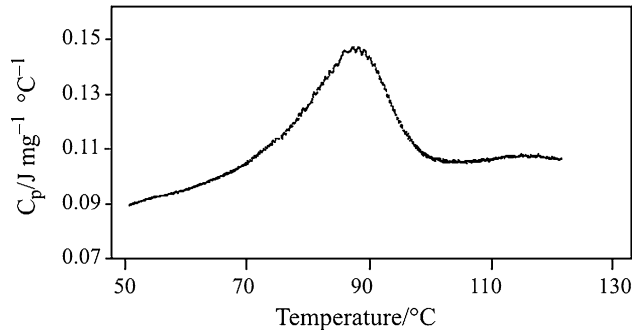

Fig. 5 Temperature dependence of C_p in a-$Se_{90}In_{10}$ alloy at heating rate of 10 °C min^{-1}

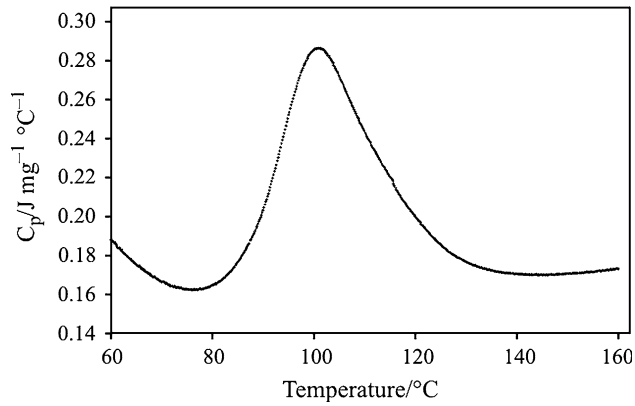

Fig. 6 Temperature dependence of C_p in a-$Se_{90}Sb_{10}$ alloy at heating rate of 10 °C min^{-1}

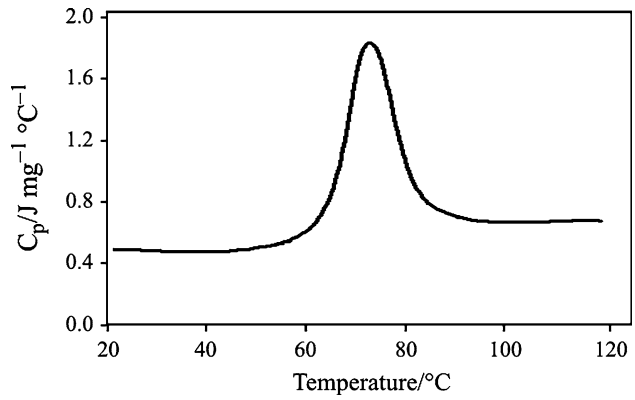

Fig. 7 Temperature dependence of C_p in a-$Se_{90}Te_{10}$ alloy at heating rate of 10 °C min^{-1}

Sb, Te are smaller than C_p of Se (See Table 2). This is probably the reason of lower C_{pg} and C_{pe} values of a-$Se_{90}M_{10}$ (M = In, Sb, Te) alloys. The decreasing order of ΔC_p in binary alloys is (a-$Se_{90}Te_{10}$) > (a-$Se_{90}Sb_{10}$) > (a-$Se_{90}In_{10}$), which can be explained in terms of mean atomic masses of additive elements (In, Sb, Te). It is well-known that during glass transition phenomenon in chalcogenide glasses, some thermally induced structural relaxation takes place in the glassy network. The decreasing sequence of atomic masses M of additive elements is Te > Sb > In (See Table 3). Thus more specific heat is required for structural rearrangements with the increase in the mean atomic masses of binary alloys. This may be the reason of observed

Table 1 The values of C_{pe}, C_{pg} and ΔC_p (J gm^{-1} $°C^{-1}$) for a-Se and a-$Se_{90}M_{10}$ (M = In, Sb, Te) alloys

Sample	C_{pg}	C_{pe}	ΔC_p
Se	0.522	0.602	0.08
$Se_{90}In_{10}$	0.089	0.102	0.013
$Se_{90}Sb_{10}$	0.193	0.209	0.016
$Se_{90}Te_{10}$	0.410	0.590	0.18

Table 2 The room temperature values of specific heat of elements Se, In, Sb and Te

Element	Specific heat (J gm^{-1} $°C^{-1}$)
Se	0.32
In	0.23
Sb	0.21
Te	0.20

Table 3 Atomic masses of elements In, Sb and Te

Element	Atomic masses (gm mol^{-1})
In	114.8
Sb	121.7
Te	127.6

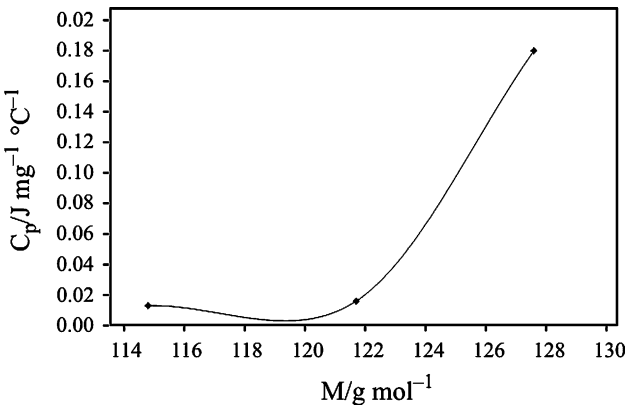

Fig. 8 Plot of ΔC_p against M

decreasing sequence of ΔC_p values in binary alloys. The plot of ΔC_p vs M is shown in Fig. 8.

Conclusions

Calorimetric measurements have been performed in a-Se and $Se_{90}M_{10}$ (M = In, Sb, Te) alloys. The values of C_{pg} and C_{pe} have been found to be decreased in binary alloys due to incorporation of third element (In, Sb, Te) in a-Se. This is explained interms of higher value of specific heat of Se as compared to additive elements. The decreasing sequence of ΔC_p values in binary alloys is explained in terms of their mean atomic masses.

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