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DIFFERENTIAL SCANNING CALORIMETRY STUDY OF $Ge_{1-x}Sn_xSe_{2.5}$ GLASSES

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Abstract

The glass-forming tendency and specific heat in ice cold water-quenched $Ge_{1-x}Sn_xSe_{2.5}$ glassy alloys with $0<x<0.6$ were investigated by means of differential scanning calorimetry. The heat of fusion ΔH_f, the heat ΔH_c associated with the crystallization of an amorphous phase and the glass transition temperature T_g were deduced from the DSC curves. The composition dependence of glass forming ability, T_g and crystallization behavior has been discussed.

Keywords: DSC, $Ge_{1-x}Sn_xSe_{2.5}$ glasses, glassy alloys

Introduction

The system Ge–Se provides a wide range of concentration where it is possible to prepare bulk glasses. The photoelectric [1, 2], IR and Raman spectra [3, 4] and other properties like photoinduced absorption [5], photoluminescence [6] and phase transition [7] have been studied in this system. Evidence for layer-like clusters as the dominant feature in the structure of melt-quenched $GeSe_2$ glass has been well established [4, 8–14]. The effect of the addition of Sb, Bi, Te, In, etc. in the Ge–Se system has also been reported in relation to its structure [15, 16] and photoluminescence [17]. Substitution of tin into the $GeSe_2$ makes the system of interest. The system $Ge_{1-x}Sn_xSe_2$ ($0<x<0.7$) has been studied with emphasis on the effect of tin on the tendency for the system to phase separate into the constituents $GeSe_2$ and $SnSe_2$ binary components [14, 18, 19]. Related to the phase-separation of the glasses during quenching of the melt is the difficulty in preparing completely homogeneous samples. By setting the composition on the selenium rich side of the stoichiometric compound $GeSe_2$, the tendency to crystallize is strongly reduced [20, 21]. In the present

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study, therefore, the sample composition of interest, $Ge_{1-x}Sn_xSe_{2.5}$ $(0<x<0.6)$, were chosen as the composition of these alloys is slightly Se rich (related to $GeSe_2$) in order to avoid crystallization of any significant fraction of the sample which might lead to phase-separation and an unknown composition of the glassy residue. This pseudo-binary system has not been studied in detail. However, Raman scattering [22] and optical absorption [23] in $Ge_{1-x}Sn_xSe_{2.5}$ glassy compositions have been studied. Differential thermal analysis and crystallization kinetics in glassy compositions in this system assure the homogeneity for melt-quenched samples [22, 23]. The present paper reports the glass-forming tendency and the thermal behaviour in one of the important glassy chalcogenide system $Ge_{1-x}Sn_xSe_{2.5}$ $(0<x<0.6)$ using differential scanning calorimetry technique.

Experimental

The glassy alloys of $Ge_{1-x}Sn_xSe_{2.5}$ ($x=0$ to 0.6) were prepared using the conventional melt-quench technique. The high purity (99.999%) elemental constituents were weighed and mixed in quartz ampoules which were then sealed under vacuum ($\sim 10^{-4}$ torr). This was followed by heat treatment in steps upto 950°C for about 24 h. In each case, the reacting elements were first allowed to heat in a high temperature electric furnace at 210°C for 2–3 h so that the element Se melts completely. The ampoules were kept rotating with a motor at about 5 r.p.m. The temperature of the furnace was then increased to 400°C and kept constant for 3–4 h. The temperature was then raised slowly and gradually to 950°C, and the ampoule kept at this temperature for 15–16 h, rotating it as mentioned earlier. The ampoule was then quenched in ice-cold water. The X-ray diffraction patterns of the resulting alloy compositions showed only a broad peak as indicative of the non-crystalline nature of the material. Calorimetric studies were carried out on about 15 mg of these materials by Du-Pont 2000 differential scanning calorimeter. For measuring the various thermal parameters, glassy samples were prepared in pellet form and kept in a DSC pan. The instrument was calibrated using Alumina powder as standard material. All the DSC measurements were performed with the heating rate of 10 deg·min^{-1}.

Results and discussion

Figures 1 and 2 show the typical differential scanning calorimetry curves of the various compositions in the system $Ge_{1-x}Sn_xSe_{2.5}$ ($x=0.1$ to $x=0.6$). It is evident from the figures that well defined endothermic peaks are observed at the glass transition temperature (T_g) and melting temperature (T_m) and, exothermic peaks at the crystallization temperature (T_r). The values of these three characteristic features T_g,T_m and T_r for different glassy alloys are summarized in Table 1. The values of T_r-T_g, T_m-T_r and T_g/T_m are also shown in the table. When the crystallized samples were heated again, no endothermic or exothermic peaks were observed in the above temperature range except for melting peaks which ensured complete crystallization in first cycle. The analysis of DSC curves was done using a method of tangents according to rules given in reference [24].

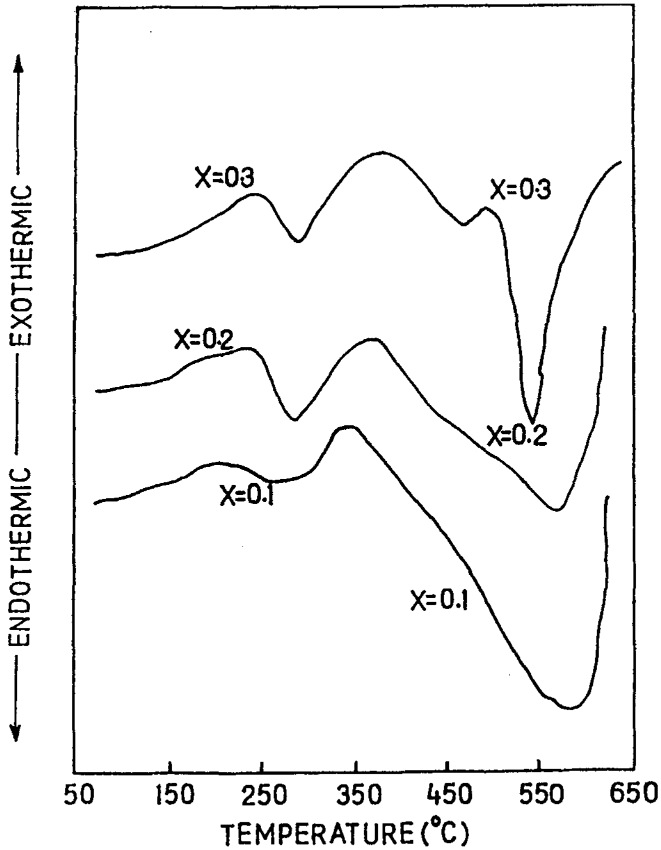

Fig. 1 DSC plots of amorphous $Ge_{1-x}Sn_xSe_{2.5}$ alloys ($x=0.1$, 0.2 and 0.3). Ordinate scale is shifted for clarification

The DSC curves for the glassy alloys $x=0.1$ and $x=0.2$ show very broad crystallization and melting peaks whereas $x=0.3$ composition shows a broad crystallization peak and sharp melting peak. The other compositions, $x=0.4$ to 0.6, show very sharp melting and crystallization peaks. The DSC plots for various glassy alloys $x=0.1$ to $x=0.6$ show that the glass transition temperature at first increases with x in the interval $0.1<x<0.4$ and then decreases upto $x=0.6$. Several DSC scans were taken on all the compositions to reconfirm the increasing trend of T_g in the interval $0.1<x<0.4$. This behavior of T_g is qualitatively similar to As_xSe_{1-x} [25], Ge_xSe_{1-x} alloys [20] and $(PbSe)_x(GeSe)_{65-x}(GeSe_2)_{35}$ [26] but is in contradiction to results reported earlier [23] where in glass transition temperature was found to decrease with increasing x in the interval $0<x<0.4$. Further, the glass transition temperature ranges from 254 to 293°C over the composition range studied.

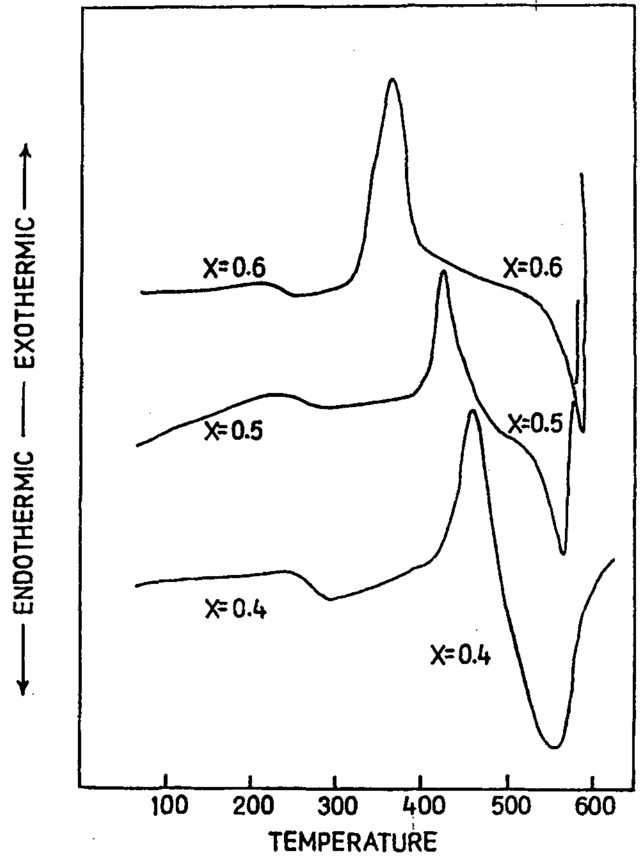

Fig. 2 DSC plots of amorphous $Ge_{1-x}Sn_xSe_{2.5}$ alloys (x=0.4, 0.5 and 0.6). Ordinate scale is shifted for clarification

The heating rate of the sample during DSC measurements greatly influence the glass transition temperature. The variation of the glasstransition temperature with heating rate is shown in the DSC scans for a typical composition x=0.6 for different heating rates (Fig. 3). The glass transition temperature increases with increase in heating rate of the sample. The crystallization temperature is also found to increase with the increase in heating rate during the DSC scan.

The increase in glass transition temperature in our measurements upto x=0.4 suggests that the entropy of the system $Ge_{1-x}Sn_xSe_{2.5}$ decreases with the

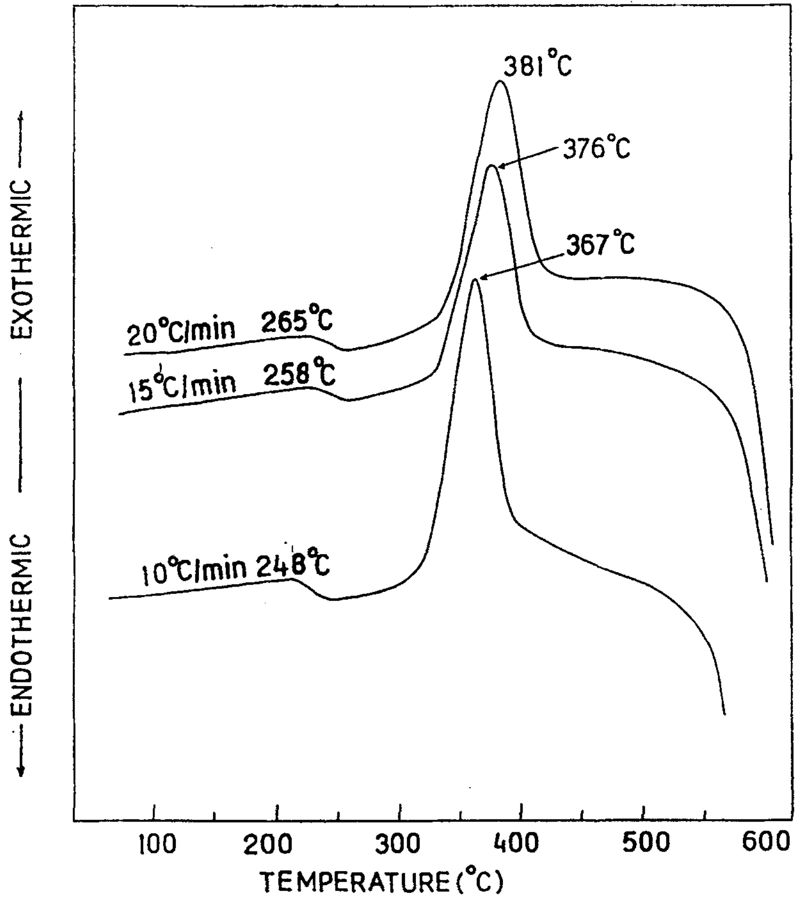

Fig. 3 DSC plots of amorphous $Ge_{1-x}Sn_xSe_{2.5}$ alloy for $x=0.6$ at different heating rates

increase in x [27]. As T_g in our measurements increases with the increase in x values, it is suggested that the replacement of Ge-atoms by Sn-atoms in $Ge_{1-x}Sn_xSe_{2.5}$ glassy alloys would cause a lowering of entropy and hence the reduction in randomness [27]. Our study of electrical properties in these glassy alloys shows that the activation energy of conduction decreases with increasing x in $Ge_{1-x}Sn_xSe_{2.5}$ ($x=0$ to 0.3) compositions (results to be reported in next article). This further confirms the reduction in randomness [28] of the glassy compositions $Ge_{1-x}Sn_xSe_{2.5}$ with increase in Sn-content.

There is no absolute criterion to parameterize the glass formation, but empirical parameters are extensively used for its qualitative characterization. Some parameters are related to the equilibrium phase diagram. One of them is the reduced glass transition temperature, $T_{rg}=T_g/T_m$ which has a value of about 2/3 for a large number of glassy substances [29]. Turnbull [30] analyzed their relation and found its limited applicability when confronted with experimental data. Another parameter introduced by Hruby [31] is K_{gl} defined as $K_{gl}=T_r-T_g/T_m-T_r$, where the interval T_r-T_g is directly proportional to the glass-forming tendency and interval T_m-T_r is indirectly proportional to the glass-forming tendency. The value of glass-forming tendency $K_{gl}\approx 0.1$ reveals that the preparation of glass is very difficult. For $K_{gl}=0.5$, glass is easily prepared merely by free cooling of the melt in air. For values $K_{gl}=1.0$ and more, one has to do with a glass of high molecular polymer type.

The glass-forming tendency, K_{gl}, is 0.38, 0.44, 0.45 and 0.54 for $x=0.1$, 0.2, 0.3 and 0.6 compositions respectively. This value of glass-forming tendency shows that the glasses of these compositions can be prepared very easily merely by free cooling of the melt in the air. The values of K_{gl} equal to 1.59 and 1.03 for the compositions $x=0.4$ and $x=0.5$ reveal the high molecular polymer type character of the glasses. The glass-forming tendency increases with the increase in x upto $x=0.4$ composition. Thereafter, the glass-forming tendency decreases. This composition dependence of the glass-forming tendency, K_{gl}, and glass transition temperature, T_g, for $Ge_{1-x}Sn_xSe_{2.5}$ alloys in the interval $0.1<x<0.4$ suggests that the network in this region is dominated by rigid or overconstrained clusters with softening occurring above $x=0.4$. When Sn-atoms are substituted for Ge-atoms in Ge–Sn–Se system, the mole volume per atom decreases with the increase in tin concentration [26]. Our far-IR transmission studies [32] show that the Sn-atoms substitute for the Ge-atoms at the outtrigger sites upto $x=0.4$ only. Therefore, it is suggested that the mole volume decreases with the increase in x upto $x=0.4$. For $x>0.5$, the glass has an increasing ability to relax and optimize bent Se–Se–Se bonds because the large chemically order clusters become floppy [33, 34] presumely increasing the free volume available. This further confirms that the network in the interval $0.1<x<0.4$ is dominated by rigid or overconstrained clusters with softening occurring above $x=0.4$.

In the DSC curves of all the compositions, a single glass transition and a single crystallization peak was observed indicating that all the alloy compositions are homogeneous. So by setting selenium rich composition at $Ge_{1-x}Sn_xSe_{2.5}$ inhibits the natural tendency for phase separation and crystallization to occur at $GeSe_2$ composition which has been reported earlier also [22].

The heat of fusion (ΔH_f) and heat of crystallization (ΔH_c) were determined for the compositions $x=0.1$ to $x=0.6$ (Table 1) by comparing the peak area of the sample to that of a known weight of the Indium reference using relation

$$\Delta H_f = A\ /\ m\ [\ (60\ B\ E\ \Delta qs)] \tag{1}$$

Table 1 Thermal analysis parameters of various glassy compositions $Ge_{1-x}Sn_xSe_{2.5}$

Composition	T_g	T_r	T_m	T_r–T_g	T_m–T_r	T_g/T_m	K_{gl}	ΔH_c	ΔH_f	C_p
$x = 0.1$	254	345	588	91	240	0.61	0.38	29.07	56.41	–
$x = 0.2$	279	367	567	88	200	0.66	0.44	12.20	4.97	–
$x = 0.3$	290	368	543	78	175	0.69	0.45	17.68	18.19	0.26
$x = 0.4$	293	460	565	167	105	0.67	1.59	35.95	30.38	0.33
$x = 0.5$	282	429	571	147	142	0.66	1.03	53.25	34.61	0.40
$x = 0.6$	248	367	588	119	221	0.61	0.54	56.54	62.41	0.45

T_g: glass transiton temperature in °C, T_r: onset of crystallization in °C, T_m: onset of melting in °C, K_{gl}: glass-forming tendency, ΔH_c: heat of crystallization in $J \cdot g^{-1}$, ΔH_f: heat of fusion in $J \cdot g^{-1}$, C_p: specific heat at a temperature of onset of transformation in $J(g\text{–}at)^{-1}K^{-1}$

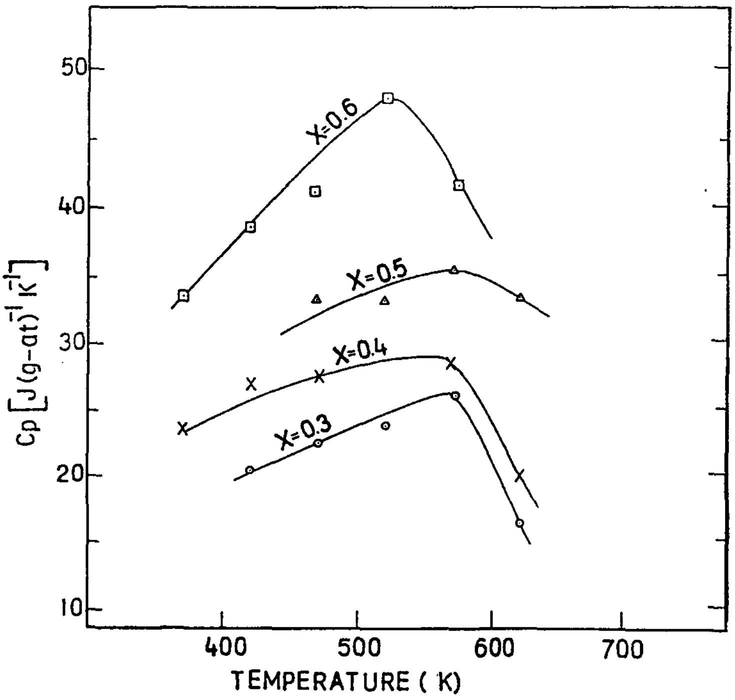

Fig. 4 Variation of specific heat with temperature for compositions x=0.3, 0.4, 0.5 and 0.6

where A=peak area in cm^2, m=mass of the sample in mg, B=time base scaling in min/cm, E=cell calibration coefficient at temperature of the experiment and Δqs=Y-axis scaling in mW/cm.

There is a linear relationship between the degree of crystallinity and ΔH_f values [35]. The materials having higher values of ΔH_f show an increase in the degree of crystallinity. The values of ΔH_f increase with increasing x showing that crystallization becomes more dominant as Sn-contents increase. The higher value of ΔH_c in x=0.5 and 0.6 compared to other compositions further confirms the fast rate of crystallization because the extent of the crystallization (number of bonds formed) is directly proportional to the ΔH_c values.

The heat capacity was calculated from the DSC curves for the glassy compositions x=0.3 to x=0.6 in the system $Ge_{1-x}Sn_xSe_{2.5}$, using the relation

$$C_p = [60E\ \Delta qs\ /\ H_r]\ \Delta Y\ /\ m \qquad (2)$$

where the parameters involved have their conventional meaning used above. H_r is the heating rate and ΔY is the difference in the Y-axis deflection between sample and blank curves at temperature of interest in cm. The heat capacity is also seen to increase with x increasing in the glassy alloys studied (Table 1).

Figure 4 shows the variation of the specific heat with temperature in the temperature region of the glass transformation for the glassy compositions $x=0.3$ to $x=0.6$. All the compositions show an abrupt increase in the specific heat in the glass transition region. As ordering sets in near the glass transition temperature the entropy decreases with temperature and this corresponds to an additional contribution to the specific heat.

Conclusions

The bulk-quenched samples in the alloy system $Ge_{1-x}Sn_xSe_{2.5}$ ($x=0.1$ to 0.6) were prepared for the differential scanning calorimetry studies. The glass transition temperature, glass-forming tendency, the heats of the crystallization and fusion and the specific heat variations were seen in the compositions studied. The glass transition temperature was found to increase with x increasing upto $x=0.4$ composition thereafter decreasing upto $x=0.6$ composition. The increase in T_g with increasing x is expected due to lowering in entropy of the system when more and more Ge-atoms are being replaced by the Sn-atoms [27]. The glass forming tendency was also seen to increase upto $x=0.4$ composition thereafter decreasing upto $x=0.6$ composition. The glass transition and crystallization region contained only a single and sharp peak each indicating that the samples prepared were homogeneous. The increase in T_g and K_{gl} in the interval $0.1<x<0.4$ suggests that the network in this region is dominated by rigid or overconstrained clusters with softening occurring above $x=0.4$. Heats of crystallization and fusion and the specific heat was found to increase with x increasing in the composition range studied indicating that the crystallization becomes dominant in the higher x region.

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Zusammenfassung — Mittels DSC wurde die spezifische Wärme und die Tendenz zur Glasbildung von in eiskaltem Wasser abgeschreckten $Ge_{1-x}Sn_xSe_{2.5}$ Glassubstanzen mit $0<x<0.6$ untersucht. Anhand der DSC-Kurven wurde auf die Schmelzwärme ΔH_f, die Wärme ΔH_c, für die Kristallisation der amorphen Phase sowie auf den Glasumwandlungspunkt T_g geschlossen. Dabei wurde die Abhängigkeit der Glasbildungsfähigkeit, des T_g und der Kristallisation von der Zusammensetzung diskutiert.