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Evaluation of specific heat and related thermodynamic properties of $Ge_{1-x}Sn_xSe_{2.5}$ ($0 \leq x \leq 0.5$) glasses

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Abstract This paper presents the result of thermodynamic studies on $Ge_{1-x}Sn_xSe_{2.5}$ ($0 \leq x \leq 0.5$) glasses using differential scanning calorimetry. The obtained experimental results on phase transformations have been employed to obtain thermodynamic parameters like entropy difference between metastable states in the glassy region, difference of Gibbs free energy, specific heat, entropy between the glassy and the crystalline phase and the enthalpy released during phase transformation (glassy to crystalline). The results yield that, $Ge_{0.7}Sn_{0.3}Se_{2.5}$ sample is least stable among all the samples. The stability increases on addition of Sn beyond 0.3 at. mass% upto 0.5 at. mass%.

Keywords Enthalpy · Entropy · Gibbs free energy · Specific heat · Stability

Introduction

The phenomenon of undercooling a liquid below its melting point into the metastable regime provides a unique opportunity to explore metastable phase selection sequence which can result in "frozen liquid" or commonly called 'glass', when crystallization can be suppressed. In order to predict these transformations, when a system is driven away from equilibrium to a non-equilibrium state, the knowledge of thermodynamic properties of the undercooled liquid is essential. The glass transition of undercooled liquid is considered a kinetic event, at which the structural state of a liquid is frozen-in during cooling on the time scale of the experimental observation. The final frozen in state depends on the cooling rate and has an important influence on the thermodynamical properties of the glass at room temperature. Because of the kinetic nature of the glass transition, a simple heating of the sample at constant heating rate in DSC allows the system to relax. The process is obvious because the major phenomena observed, changes in specific heat, enthalpy, expansion coefficient and so forth, are no more then the consequences of the system under observation falling out of complete thermodynamic equilibrium at some point of the experiment. In view of absence of complete thermodynamic equilibrium, glasses are subjected to the factor of destability, which is proportional to the difference between the thermodynamic potential of the amorphous glasses and the equilibrium (crystalline) states.

In view of this, the present paper reports the specific heat and related thermodynamic properties of $Ge_{1-x}Sn_x Se_{2.5}$ ($0 \leq x \leq 0.5$) glasses. Difference in entropy of glassy and crystalline state and Gibbs free energy difference between the glassy and crystalline state has been studied to see the thermodynamic changes occurring in the system, when the system transforms from glassy to crystalline state. Besides this, entropy difference between metastable states in glassy region is also studied along with specific heat for the deeper understanding of the thermodynamic changes in glass transition region. The difference in enthalpy released during relaxation and crystallization process has also been studied in order to determine the stability of glassy system under consideration. Differential Scanning Calorimetry (DSC) has been employed widely [1, 2] and is used in the present study for the investigation and interpretation of thermal events in these materials.

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Gibbs free energy for the crystallization of undercooled liquid, ΔG, is an important parameter in the study of crystallization kinetics. It is well known that the exact temperature dependence of ΔG can be calculated if the heat capacities of the liquid and crystalline solid are known as a functions of temperature. However, the heat capacity data of undercooled liquid is not available easily due to its metastable nature. Therefore, in case of non-availability of the specific heat data in the undercooled region, the functional dependence of ΔG on undercooling must be estimated theoretically. Various expressions for ΔG are available in the literature [3–8]. These expressions depend on some kind of assumption for the temperature dependence of the heat capacity. Thompson and Spaepan [3] have shown that some knowledge of the crystal and liquid heat capacities of a material is necessary for choosing appropriate approximation for ΔG. Assuming that no specific heat data is available, one has to look for an approximation for ΔG with minimum number of known experimental parameters.

Few efforts have been made by the researchers to study the thermodynamics of glassy systems in the past decade. Li et al. [9] have studied the specific heat and the related thermodynamic properties of an undercooled germanium melt. Thermodynamics of La based La–Al–Cu–Ni–Co alloys has been studied by Lu et al. [10] using temperature modulated DSC. Tiwari et al. [11] have studied the composition dependence of specific heat in SeTeAg glasses while Imran et al. [12] have investigated the theoretical and experimental aspects of thermodynamics of SeTeIn glasses.

Experimental

The glassy alloys of the $Ge_{1-x}Sn_xSe_{2.5}$ system with x values between 0 and 0.5 has been prepared by the conventional melt quenching technique. High purity (99.999%) Ge, Sn and Se in appropriate atomic mass percentage proportions were weighed into a quartz ampoule and sealed at a vacuum of 133.3×10^{-5} Pa. The ampoules were then heated at 900 °C for about 15 h with continuous rotation to facilitate the homogenization of the sample. The molten sample was rapidly quenched in ice-cooled water to get glassy state. The ingot of so produced glassy sample was taken out of the ampoule by breaking the ampoule and then ground gently in mortar and pestle to obtain powder form. Amorphous nature of the samples has been ascertained through XRD.

The thermal behavior of the samples has been investigated using Rigaku DSC 8230. The accuracy of heat flow measurement is ±0.01 mW and the temperature precision as determined by the microprocessor of the thermal analyzer is ±0.1 °C. DSC runs have been taken at five different heating rates, i.e. 2, 4, 6, 8 and 10 °C min^{-1} on accurately weighed samples (10–15 mg) taken in aluminum pans under non-isothermal conditions. The temperature range covered in DSC was from room temperature (27 °C) to 500 °C. The DSC equipment is calibrated prior to measurements, using high purity standards Pb, Sn and In with well-known melting points. The instrument constant of this DSC, as measured is 1.12. For the measurement of specific heat, Alumina (Al_2O_3) was taken as reference material.

Result and discussion

The phase transformations of the samples have been studied through DSC at five different heating rates, i.e. 2, 4, 6, 8 and 10 °C min^{-1} under non-isothermal conditions. Figure 1 shows the DSC thermogram of $Ge_{0.5}Sn_{0.5}Se_{2.5}$ glassy sample at a heating rate of 6 °C min^{-1} with marked characteristic temperatures i.e. glass transition temperature (T_g), onset crystallization temperature (T_c) and peak crystallization temperature (T_p) as a representative case. DSC thermograms of all the other samples with required details have been given elsewhere [13].

Thermodynamic properties

Composition dependence of the enthalpy released during transformation from glass to crystalline state

The enthalpy released during transformation from glass to crystalline state (ΔH_{gc}) is given by :

$$\Delta H_{gc} = \Delta H_g - \Delta H_c \tag{1}$$

where, ΔH_g and ΔH_c represents the enthalpy released during relaxation process and crystallization process respectively.

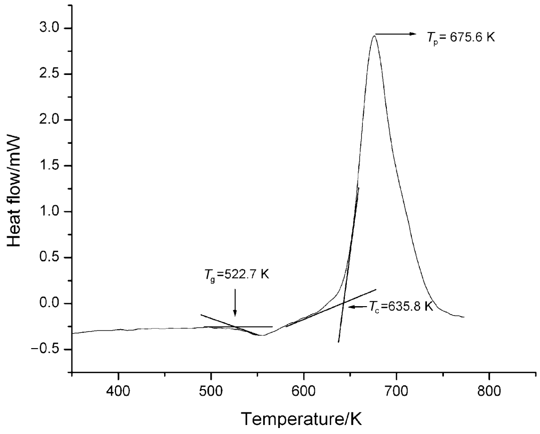

Fig. 1 DSC thermogram of $Ge_{0.5}Sn_{0.5}Se_{2.5}$ glassy sample at a heating rate of 6 °C min^{-1}

The relaxation enthalpy 'ΔH_g' has been evaluated by determining the area under the curve of the specific heat versus temperature i.e.

$$\Delta H_g = \int C_p \mathrm{d}T \tag{2}$$

whereas the crystallization enthalpy, ΔH_c has been calculated by measuring the area under the crystallization peak. The overall enthalpy released during transformation from glassy to crystalline phase is obtained using Eq. 1.

Figure 2 shows the dependence of ΔH_{gc} on Sn composition at a heating rate of 6 °C min^{-1}. It is observed that enthalpy released is highest for $x = 0.3$ at. mass% Sn. The release of energy ΔH_{gc} is associated with the stability of the glasses. The least stable glasses, i.e. the glasses with the lowest value of $(T_c - T_g)$ [14, 15] will have maximum value of ΔH_{gc}. The plot of $(T_c - T_g)$ against Sn composition at a heating rate of 6 °C min^{-1} is shown in Fig. 3. From the plots of $(T_c - T_g)$ and ΔH_{gc} against Sn composition, it is observed that glass with higher $(T_c - T_g)$ corresponds to lower ΔH_{gc}. Hence, it can be inferred that the glass with 0.3 at. mass% of Sn is found to be least stable among all other samples of the series.

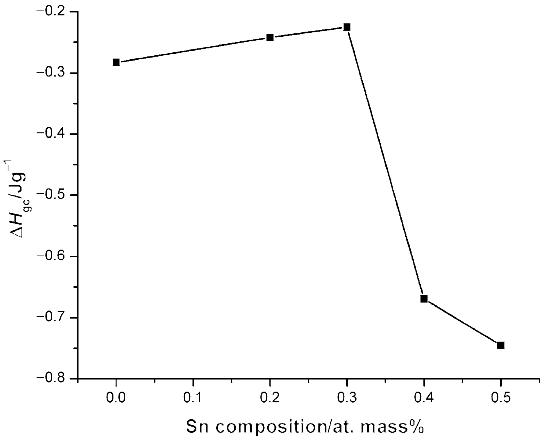

Fig. 2 The dependence of ΔH_{gc} against Sn composition of $Ge_{1-x}Sn_xSe_{2.5}$ $(0 \leq x \leq 0.5)$ glasses at a heating rate of 6 °C min^{-1}

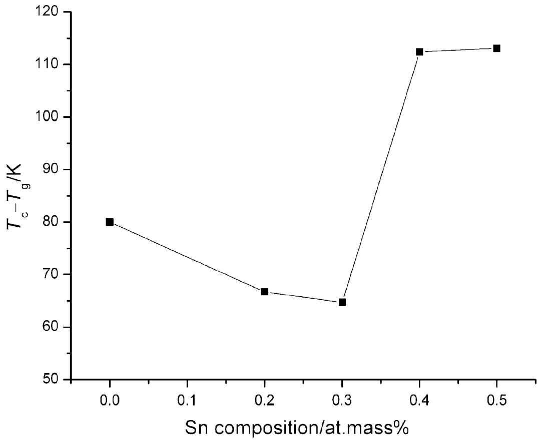

Fig. 3 Plot of $(T_c - T_g)$ against Sn composition at a heating rate of 6 °C min^{-1}

Entropy difference between metastable states in glassy region

Many amorphous glasses of practical importance are stable for extremely long time periods but may ultimately undergo a transformation, which may occur when a certain amount of energy is supplied. The amount of thermal energy absorbed by the glass in the glass transition region is given by $\Delta Q = T \cdot \Delta S$, where ΔS is the entropy difference between two metastable states in a certain temperature range. Experimentally, the amount of thermal energy absorbed by the system is calculated by measuring the area under the endothermic peak. The plot of ΔS as a function of temperature is shown in Fig. 4 for all the compositions of $Ge_{1-x}Sn_xSe_{2.5}$ glasses at a heating rate of 6 °C min^{-1}.

From Fig. 4, it is observed that entropy of the system is highest for the $Ge_1Se_{2.5}$ glass and decreases at 0.3 at. mass% of Sn and again increases for 0.4 at. mass% of Sn. The main characteristics of these plots are the sudden jump at T_g and a decreasing trend at a temperature where crystallization process begins. The jump in ΔS near T_g is due to increase in number of atomic arrays, which leads to increase in topological disorder in the system.

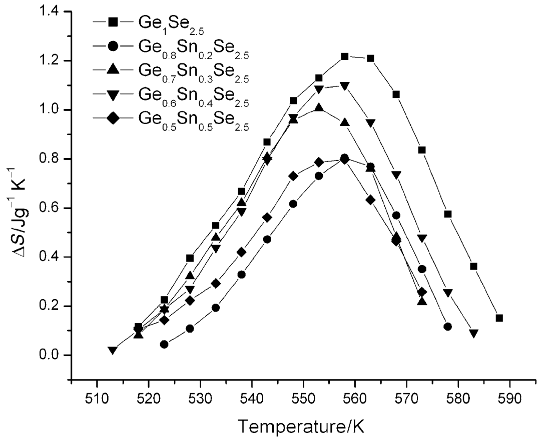

Fig. 4 The plot of ΔS as a function of temperature for all the samples of $Ge_{1-x}Sn_xSe_{2.5}$ series

Gibbs free energy

The Gibbs free energy difference (ΔG) between crystal and liquid means the driving force of crystallization and is a vital parameter in nucleation ratio and crystal growth. In an alloying system, the less ΔG means the less driving force of crystallization, the more stable is the supercooled liquid and better glass forming ability (GFA). So estimation of ΔG has played an important role in appraising the GFA of glassy systems.

Gibbs free energy difference between the glass and the corresponding crystalline phase (ΔG_{gc}) is given by:

$$\Delta G_{gc} = \Delta G_{g} - \Delta G_{c} \tag{3}$$

where, ΔG_g and ΔG_c represents the Gibbs free energy in the glassy and crystalline state respectively.

The Gibbs free energy difference in the glassy region is obtained using the following relation:

$$\Delta G_{g} = \Delta H_{g} - T \cdot \Delta S \tag{4}$$

where, ΔH_g denotes the heat released by the sample in the relaxation process and $T\Delta S = \Delta Q$, is the amount of thermal energy absorbed by the sample in the glassy region. However, when a transformation from glassy to crystalline state is considered, then ΔH represents the energy released by the glass during the crystallization process and is denoted by ΔH_c. The Gibbs free energy difference in this case is calculated using the relation:

$$\Delta G_{c} = \Delta H_{c} - T \cdot \Delta S \tag{5}$$

and the Gibbs free energy difference between the glassy and crystalline phases (ΔG_{gc}) at heating rate of 6 °C min^{-1} is calculated using Eq. 3. Figure 5 shows the plot of ΔG_{gc} against Sn composition.

From Fig. 5, it is observed that Gibbs free energy is highest for 0.3 at. mass% of Sn and lowest for 0.5 at. mass% of Sn. Since the number of nuclei available at any temperature decreases exponentially with the decrease of the free energy, therefore it is reasonable to suggest that at the composition of minimum free energy nucleation and growth process occurs sluggishly. Hence, it can be concluded that stability of the sample is minimum for 0.3 at. mass% of Sn and increases to maximum at 0.5 at. mass% of Sn.

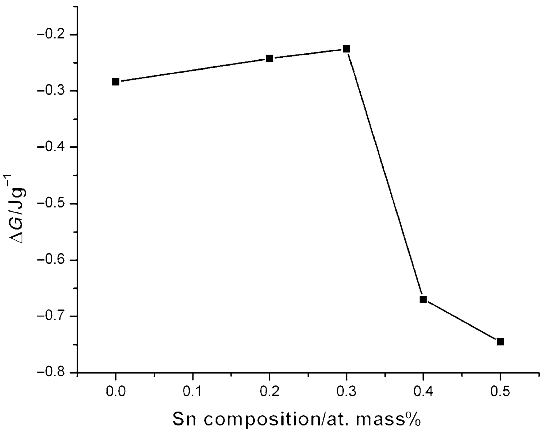

Fig. 5 The plot of ΔG_{gc} against Sn composition

Specific heat

Specific heat is very sensitive to the way in which atoms or molecules are dynamically bound in a solid [16]. Thus, the measurement of specific heat is regarded as one of the methods for the characterization of a material as a glassy substance. At T_g, an abrupt change in specific heat is the characteristic thermodynamic feature of all the glassy materials. Specific heat (C_p) of the samples could be easily evaluated using the DSC data from the following relation:

$$C_{p} = [m_{r}\Delta_{s}/m_{s}\Delta_{r}]C_{r} \tag{6}$$

where, m_r and m_s is the mass of the sample and reference material respectively and Δ_s and Δ_r are shifts for sample and reference materials with respect to base line, respectively, and C_r is the specific heat of the reference material, which was taken from the standard literature. Figure 6 shows the variation of C_p with temperature for all the samples under consideration.

It is clear from Fig. 6 that except for sudden jump in C_p at T_g, specific heat is weekly temperature dependent. However, after attaining a maximum value, C_p becomes stable above T_g, which is slightly higher than its stable value below T_g. At T_g, the glass becomes liquid and the abrupt jump in the specific heat is due to the additional configurational degrees of freedom of motion of the atoms so that the complete short-range order is formulated in the liquid state. The excess of specific heat above T_g is attributed to the fact that the supercooled liquid resembles that of the glass. Above T_c, the specific heat decreases abruptly and attains its minimum value at approximately the peak temperature of crystallization (T_p). This may be due to the vestiges of short-range order still remains above T_c and T_m, which may disappear, when the temperature is further raised [17].

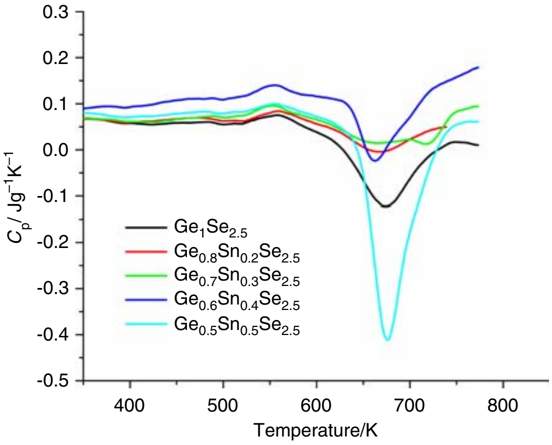

Fig. 6 The variation of C_p with temperature for $Ge_{1-x}Sn_xSe_{2.5}$ ($0 \leq x \leq 0.5$) compositions

Entropy difference between the glass and the crystalline states

The entropy difference between glass and crystalline state (ΔS_{gc}) is given by:

$$\Delta S_{gc} = \Delta S_{g} - \Delta S_{c} \tag{7}$$

where, S_g and S_c are entropy of glassy and crystalline state respectively.

The entropy of the glassy state 'S_g' is given by the following thermodynamical relation:

$$S_{g} = S_{conf.} + \int_{o}^{T} \left[C_{p}/T\right] \mathrm{d}T \tag{8}$$

where, $S_{conf.}$, is the configurational entropy and is defined as

$$S_{conf.} = -k \ln W$$

Here, W is the total number of different ways in which atoms can arrange themselves in a particular fashion and is given by [18]:

$$W = N!/\{(A_{Ge}N)!(B_{Se}N)!(C_{Sn}N)!\}$$

where, N is the total number of atoms present in the system. A_{Ge} is the fraction of Ge atoms, B_{Se} is the fraction of Se atoms and C_{Sn} is the number of Sn atoms. For the calculation of the entropy of the crystalline state we have taken the configuration entropy to be zero. This is because there is only one way to arrange the atoms in the correct ordered array ($W = 1$) [16]. Therefore, entropy of crystalline state can be written as:

$$S_{c} = \int_{o}^{T} \left[C_{p}/T\right] \mathrm{d}T \tag{9}$$

Figure 7a–e show the plot of entropy difference ΔS_{gc} against temperature difference ΔT for $Ge_{1-x}Sn_xSe_{2.5}$ ($0 \leq x \leq 0.5$) compositions (ΔT is taken as the difference between the temperature, where the crystallization has just started and onwards temperature till crystallization is completed, and the temperature which lies between T_g and T_{gp} in the glass transition region because entropy shows its maximum value in this temperature range). From Fig. 7–e, it is observed that

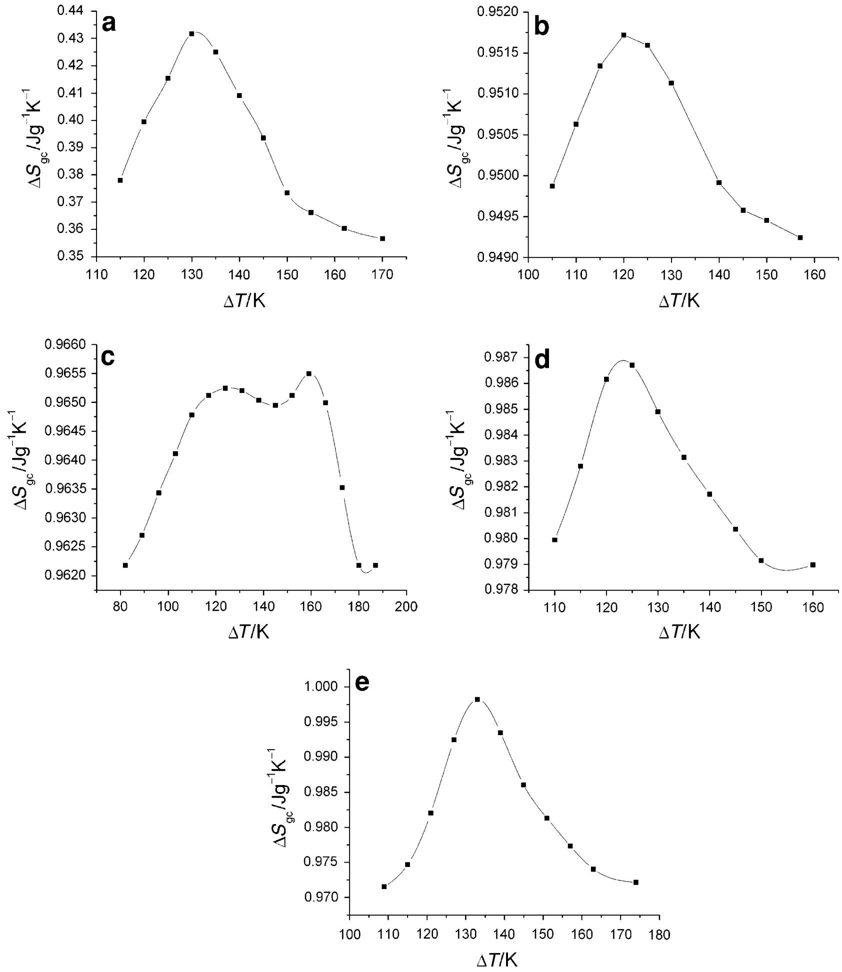

Fig. 7 **a** Plot of entropy difference ΔS_{gc} against ΔT for $Ge_1Se_{2.5}$ glass. **b** Plot of entropy difference ΔS_{gc} against ΔT for $Ge_{0.8}Sn_{0.2}Se_{2.5}$ glass. **c** Plot of entropy difference ΔS_{gc} against ΔT for $Ge_{0.7}Sn_{0.3}Se_{2.5}$ glass. **d** Plot of entropy difference ΔS_{gc} against ΔT for $Ge_{0.6}Sn_{0.4}Se_{2.5}$ glass. **e** Plot of entropy difference ΔS_{gc} against ΔT for $Ge_{0.5}Sn_{0.5}Se_{2.5}$ glass

entropy difference between glassy and crystalline state increases with the increase in Sn concentration. The maximum value of $\Delta S_{gc} = S_g - S_c$, is found to be for $x = 0.5$ at. mass% of Sn indicating that entropy is maximum in the glassy state. Meanwhile, in the crystalline state around T_c, ordering is minimum for this glass in comparison to other samples. Further, the difference in entropy goes on increasing upto certain temperature (around T_p), and after that attains approximately stable values.

Conclusions

1. Gibbs free energy difference between the glass and the corresponding crystalline phase 'ΔG_{gc}' is found to be highest for 0.3 at. mass% of Sn and lowest for 0.5 at. mass% of Sn, which suggests that stability of sample is minimum for 0.3 at. wt% of Sn and increases to maximum for 0.5 at. mass% of Sn.
2. Entropy difference between glassy and crystalline state increases with the increase in Sn concentration. The maximum value of ΔS_{gc} is found to be for $x = 0.5$ at. mass% of Sn indicating that entropy is maximum in the glassy state and is minimum in crystalline state therefore, the sample is most stable among the whole series.
3. The enthalpy released during transformation from glassy to crystalline phase and $T_c - T_g$ also favours the same fact.

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