

# Thermodynamics of Glass/Crystal Transformation in $\text{Se}_{58}\text{Ge}_{42-x}\text{Pb}_x$ ( $9 \leq x \leq 20$ ) Glasses

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This article reports the thermodynamics of  $\text{Se}_{58}\text{Ge}_{42-x}\text{Pb}_x$  ( $9 \leq x \leq 20$ ) glassy alloys determined from the heat of fusion and specific heat capacity measurements. A differential scanning calorimetry method has been employed for the determination of thermodynamic quantities such as entropy, enthalpy, and Gibbs free energy differences between the glassy and crystalline phase of these alloys as a function of temperature. An effort has also been made to determine the stability of these glasses using the data obtained from different thermodynamic quantities. This study reveals that stability of the samples increases with the increase of lead (Pb) content in the glassy alloys.

## Introduction

Thermodynamic properties of matter in the crystalline and liquid state have been well investigated and known for a long time, whereas amorphous substances and undercooled liquids are not so well studied yet. Glasses are amorphous solids that exhibit a more or less sudden change in the derivative thermodynamic properties, such as heat capacity and expansion coefficient, from crystal-like to liquid-like values.<sup>1</sup> One of the most significant feature of the glassy state is its deviation from thermodynamic equilibrium. Glasses are thermodynamically unstable relative to an (metastable) equilibrium liquid so that they tend to approach the latter state. This process, called stabilization, proceeds so slowly below the glass transition region that all properties of glasses seem to be almost fixed. To predict these transformations, when a system is driven away from equilibrium to a nonequilibrium state, the knowledge of thermodynamic properties of the undercooled liquid is essential. Glass formation entails slowing down continuously the particles in a liquid to such an extent that the structure of the liquid no longer changes over the duration of the macroscopic experiment. Such a situation is commonly achieved by cooling or compressing so as to avoid crystallization. It is well-known that the crystallization of glasses and undercooled melts occurs by a heterogeneous process of nucleation and growth of crystals. Glass transition is a phenomena that may easily be observed in most glasses by, for instance, differential scanning calorimetry (DSC). This is primarily due to the fact that, on heating, the heat capacity,  $C_p$ , of a glass increases suddenly by at least about half its original value in a very small temperature interval as the glass changes to a liquid. Usually, a characteristic temperature called glass transition temperature ( $T_g$ ) is defined at the inflection point in the  $C_p$  versus temperature curve.

Some effort have been made by the researchers to study the thermodynamics of glassy systems in the past decade. Z. Černošek et al. have studied the enthalpic relaxation of  $\text{As}_2\text{Se}_3$  glass and they found that enthalpies of metastable equilibria at temperatures below glass transition temperatures are higher than the ones obtained at the same temperatures by linear extrapolation of  $H(T)$  of a supercooled liquid.<sup>2</sup> Thermodynamics of

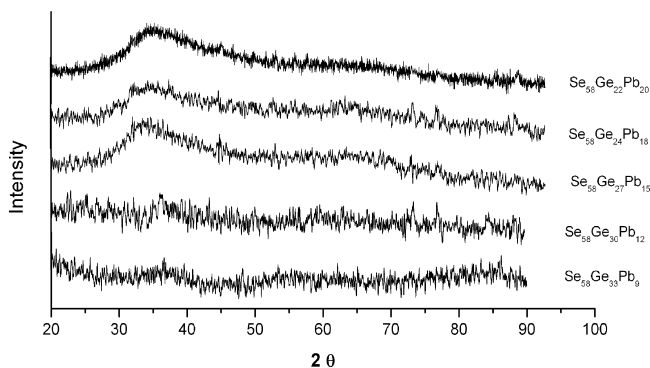
metallic glasses has been studied by Isabella Gallino et al. They investigated that the residual enthalpy of frozen-in glass is found to relax with stretching exponents approaching unity, which indicates rather strong glass behavior, reflected also by the high value of the fragility parameter and the small driving force of crystallization.<sup>3</sup> Jean A. Tangeman et al. have studied the thermodynamics and structure of single- and two-phase yttria–alumina glasses. Various quantities like heat capacities ( $C_p$ ) of the glasses and supercooled liquids, glass transition temperatures ( $T_g$ ), configurational heat capacities at  $T_g$  ( $C_p(T_g)$ ), and glass structures were investigated using differential scanning calorimetry (DSC) and  $^{27}\text{Al}$  MAS NMR spectroscopy. It was found that the  $T_g$  increases slightly with alumina content, from 1146 to 1156 K and  $C_p$  increases 60% at  $T_g$  to form a highly fragile supercooled liquid.<sup>4</sup> G. Shao et al. have studied the role of thermodynamics and transformation kinetics on phase selection in the nonequilibrium processing of materials. They demonstrated that the microstructural development of materials processed in nonequilibrium condition is controlled by the interplay between thermodynamic and transformation kinetics.<sup>5</sup> Xiulin Ji et al. have studied the Gibbs free energy difference in metallic glass forming liquids and proposed a hyperbolic variation of heat capacity difference of liquid and solid ( $\Delta C_p^{l-s}$ ) with temperature.<sup>6</sup> M. M. A Imran et al. have studied the thermodynamic properties of ternary  $\text{Se}_{80}\text{Te}_{20-x}\text{In}_x$  ( $x = 2, 4, 6, 8, \text{ and } 10$ ) chalcogenide glasses and their experimental observations and theoretical calculation showed that  $\text{Se}_{80}\text{Te}_{10}\text{In}_{10}$  is the most stable glass.<sup>7</sup>

In the present article, an effort has been made to determine the stability of  $\text{Se}_{58}\text{Ge}_{42-x}\text{Pb}_x$  ( $9 \leq x \leq 20$ ) glassy alloys through the study of various thermodynamic properties like entropy, enthalpy, and Gibbs free energy between the glassy and crystalline state.

## Experimental Methods

Glassy alloys of  $\text{Se}_{58}\text{Ge}_{42-x}\text{Pb}_x$  ( $9 \leq x \leq 20$ ) were prepared by melt-quenching technique. High purity (99.999%) of all constituent materials in appropriate atomic weight proportions were weighed into a quartz ampule. The content (4 g) of the ampule was sealed in a vacuum of  $10^{-5}$  Torr. The ampules are heated in two stages to avoid the sudden evaporation and deposition of the selenium to the inner wall of the quartz tube.

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**Figure 1.** X-ray diffraction pattern of the as-prepared samples of  $\text{Se}_{58}\text{Ge}_{42-x}\text{Pb}_x$  ( $9 \leq x \leq 20$ ) glassy alloys.

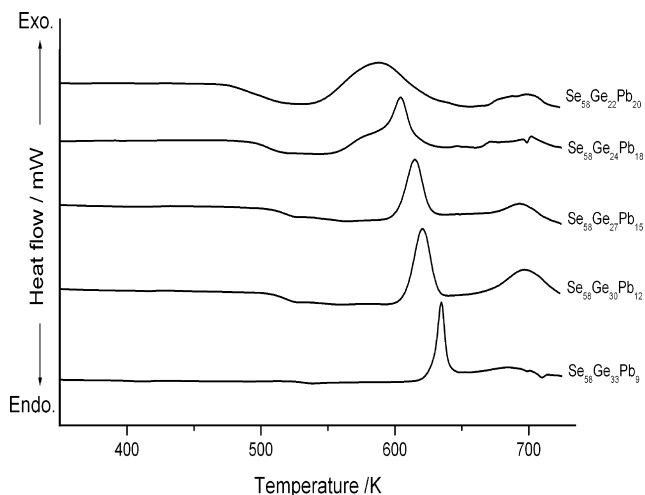
The ampules are heated slowly and maintained at 600 °C for about 6 h with continuous rotation. The temperature is then subsequently raised to 900 °C and kept under constant rotation for 30 h to facilitate the homogenization of the sample. The molten sample was rapidly quenched in ice-cooled water to get a glassy state. The ingot of so produced glassy sample was taken out of the ampule by breaking the ampule and then grinded gently in mortar and pestle to obtain powder form. The amorphous nature of the alloy was ascertained through X-ray diffraction pattern of the samples using Bragg-Brentano geometry on Panalytical X'pert Pro diffractometer in  $2\theta$  range of 20–90° with Cu  $K\alpha$  radiation source ( $\lambda = 1.5406 \text{ \AA}$ ). The X-ray tube was operated at 45 kV and 40 mA.

Differential scanning calorimetry (DSC) Rigaku Model 8230 is used to measure the caloric manifestation of the phase transformation under nonisothermal condition. The accuracy of heat flow measurement is  $\pm 0.01 \text{ mW}$  and the temperature precision as determined by the microprocessor of the thermal analyzer is  $\pm 0.1 \text{ K}$ . The DSC runs have been taken at a heating rate of 20 K/min on accurately weighed samples taken in aluminum pans. The temperature range covered in DSC was from room temperature (300 K) to 753 K.

## Results and Discussion

**Structural and Thermal Analysis.** Figure 1 shows the X-ray diffraction patterns of as-prepared  $\text{Se}_{58}\text{Ge}_{42-x}\text{Pb}_x$  ( $9 \leq x \leq 20$ ) glassy alloys. The absence of any sharp peak confirms the amorphous nature of these samples. Figure 2 shows the DSC curves of all of the as-prepared samples at a heating rate 20 K/min as a representative case. The characteristic features of the investigated thermal curves were as follows: first, the glassy alloys under consideration shows an endothermic step corresponding to its glass transition temperature ( $T_g$ ). Second, the crystallization process of the considered glassy alloys shows two exothermic crystallization peaks. The two exothermic peak represents the glass-crystal transformation. The glass crystallizes partially at the first crystallization and, when the temperature is further increased in DSC, it gets completely crystallized at the second crystallization. The appearance of double crystallization peak indicates phase separation occurring in these glassy alloys. The values of the glass transition temperature ( $T_g$ ), onset temperature of first crystallization ( $T_{c1}$ ), onset temperature of second crystallization ( $T_{c2}$ ), peak temperature for first crystallization ( $T_{p1}$ ), and peak temperature for second crystallization ( $T_{p2}$ ) are mentioned in Table 1.

For the confirmations of the remnant crystallization and identification of crystalline phases present in the samples, the samples were annealed at 2 h at temperature intermediate

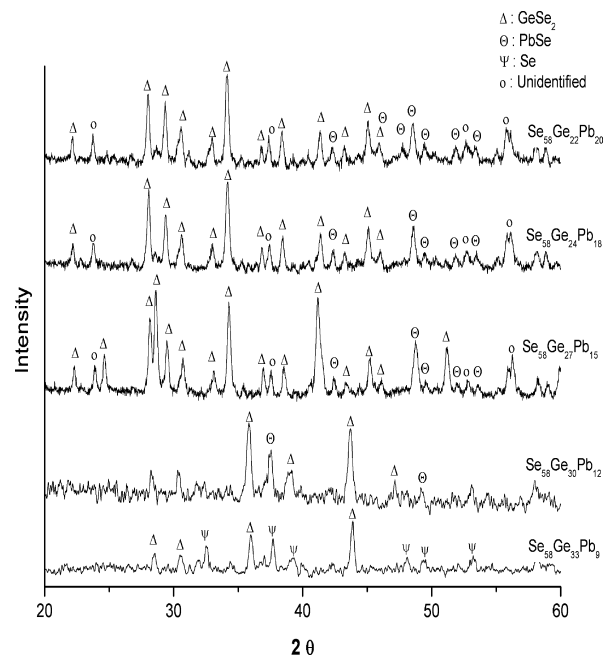


**Figure 2.** DSC thermograms of all the as-prepared samples at a heating rate of 20 K/min.

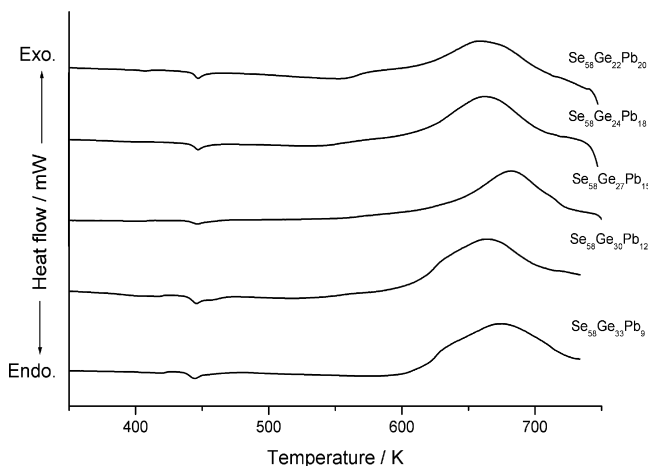
**TABLE 1: Values of the Characteristic Temperatures ( $T_g$ ,  $T_{c1}$ ,  $T_{c2}$ ,  $T_{p1}$ , and  $T_{p2}$ ) of All of the Samples of  $\text{Se}_{58}\text{Ge}_{42-x}\text{Pb}_x$  ( $9 \leq x \leq 20$ ) Glassy Alloys at a Heating Rate of 20 K/min**

sample	$T_g$ (K)	$T_{c1}$ (K)	$T_{p1}$ (K)	$T_{c2}$ (K)	$T_{p2}$ (K)	$T_a$ (K)
$\text{Se}_{58}\text{Ge}_{33}\text{Pb}_9$	$522.3 \pm 0.6$	$620.7 \pm 0.9$	633.7	$661.3 \pm 0.7$	685.5	640
$\text{Se}_{58}\text{Ge}_{30}\text{Pb}_{12}$	$507.6 \pm 0.8$	$601.6 \pm 0.8$	620.7	$653.8 \pm 0.6$	696.2	643
$\text{Se}_{58}\text{Ge}_{27}\text{Pb}_{15}$	$503.1 \pm 0.6$	$599.4 \pm 0.6$	614.3	$674.7 \pm 0.9$	693.4	648
$\text{Se}_{58}\text{Ge}_{24}\text{Pb}_{18}$	$492.6 \pm 0.7$	$556.8 \pm 0.7$	603.8	$666.5 \pm 1.0$	691.1	650
$\text{Se}_{58}\text{Ge}_{22}\text{Pb}_{20}$	$478.3 \pm 0.8$	$547.2 \pm 0.9$	586.8	$671.3 \pm 0.8$	694.2	655

between the first and second crystallization peaks. These intermediate temperatures ( $T_a$ ) for all of the samples of  $\text{Se}_{58}\text{Ge}_{42-x}\text{Pb}_x$  ( $9 \leq x \leq 20$ ) glassy alloys have been given in Table 1. The annealed samples were then subjected to XRD. Figure 3 shows the XRD pattern of annealed samples. The XRD pattern of annealed samples show sharp peaks at various diffraction angles. The  $d$  values corresponding to these peaks were matched with standard  $d$  values obtained from JCPDS card.



**Figure 3.** XRD pattern of annealed samples.



**Figure 4.** DSC thermogram of  $\text{Se}_{58}\text{Ge}_{42-x}\text{Pb}_x$  ( $9 \leq x \leq 20$ ) glassy alloys annealed at intermediate temperatures.

It was found that all the samples except  $\text{Se}_{58}\text{Ge}_{33}\text{Pb}_9$  crystallize in  $\text{GeSe}_2$  and  $\text{PbSe}$  phases, while  $\text{Se}_{58}\text{Ge}_{33}\text{Pb}_9$  crystallizes in  $\text{GeSe}_2$  and  $\text{Se}$  phases. The absence of  $\text{PbSe}$  phase at 9 at wt % is due to the fact that at 9 at wt % of  $\text{Pb}$ , the lead atoms go into the interstitial sites and do not contribute to the structure of the glass, whereas at  $\text{Pb}$  concentration beyond 9 at wt %, the  $\text{Pb}$  atoms start occupying the lattice sites and result in two phases, viz.  $\text{GeSe}_2$  and  $\text{PbSe}$ . Therefore, at 9 at wt % of  $\text{Pb}$ , only  $\text{GeSe}_2$  and  $\text{Se}$  phases are observed in the system, whereas at  $\text{Pb}$  concentration beyond 9 at wt %,  $\text{GeSe}_2$  and  $\text{PbSe}$  phases are found in the system. The  $\text{GeSe}_2$  phase is found to crystallize in the monoclinic structure with a unit cell defined by  $a = 7.016 \text{ \AA}$ ,  $b = 16.79 \text{ \AA}$ , and  $c = 11.83 \text{ \AA}$ . The  $\text{PbSe}$  phase crystallizes in the cubic structure with unit cell of  $a = 6.128 \text{ \AA}$ , whereas the  $\text{Se}$  phase crystallizes in the monoclinic structure with a unit cell defined by  $a = 15.01 \text{ \AA}$ ,  $b = 14.71 \text{ \AA}$ , and  $c = 8.789 \text{ \AA}$ .

Figure 4 shows the DSC thermogram of  $\text{Se}_{58}\text{Ge}_{42-x}\text{Pb}_x$  ( $9 \leq x \leq 20$ ) glassy alloys annealed at a temperature intermediate between first and second crystallization at a heating rate of 20 K/min. The thermogram shows an endothermic peak (glass transition region) and an exothermic peak (crystallization region). The occurrence of glass transition is due to the presence of some amorphous matrix in the annealed sample, whereas the exothermic peak observed is broader and seems to be a combination of the two peaks that were observed in the as-prepared sample. The appearance of a single exothermic peak confirms the fact that glass crystallizes completely at temperatures closer to second crystallization. This fact has also been confirmed by annealing the samples (obtained after annealing at intermediate temperatures) of  $\text{Se}_{58}\text{Ge}_{33}\text{Pb}_9$  and  $\text{Se}_{58}\text{Ge}_{22}\text{Pb}_{20}$  glasses beyond second crystallization temperature. The DSC scans (Figure 5) again show a single broader exothermic peak representing a mixed phase. This phase also crystallizes around temperatures closer to second phase of as-prepared sample. Therefore, it is suggested that the samples partially crystallize at first crystallization, whereas the remaining crystallization is completed on further heating the samples up to second crystallization temperature.

The phases obtained in XRD (Figure 6) of these samples are same as obtained before on annealing at intermediate temperatures with a small increase in the number of peaks of phases present in the samples. From Figures 4 and 5, it is also observed that the glass transition and crystallization temperatures shift toward the lower temperature side after annealing. A shift in the glass transition temperature and crystallization temperature

of the glass toward the lower temperature side on annealing is due to the fact that the annealing of glass will enhance the crystallization phenomenon of the glass and hence the crystallization of the glass will set at earlier or nucleation will start at lower temperature as compared to the as-prepared glasses. Consequently, on annealing, the glassy matrix will become less stable and hence amorphous to glass transition process is peaked out at a lower temperature.<sup>8</sup>

#### Thermodynamic Properties.

**Specific Heat.** Determination of specific heat,  $C_p$ , as a function of temperature provides an easy method for detection of glass transition under different compositions and heating rates. The sudden change in the specific heat at the glass transition temperature is one of the characteristics of all glassy materials.<sup>14</sup> Specific heat ( $C_p$ ) of the samples could be easily evaluated using the DSC data from the following relation:

$$C_p = [m_r \Delta_s / m_s \Delta_r] C_r$$

where  $m_s$  and  $m_r$  are the masses of the sample and reference material respectively and  $\Delta_s$  and  $\Delta_r$  are the shifts for sample and reference materials with respect to baseline respectively and  $C_r$  is the specific heat of the reference material, which was taken from the standard literature. All of the measurements of shifts and baseline for the determination of specific heats of different samples at different temperatures have been made at a heating rate of 20 K/min. Figure 7 shows the specific heat of  $\text{Se}_{58}\text{Ge}_{42-x}\text{Pb}_x$  ( $9 \leq x \leq 20$ ) glassy alloys in the entire range of temperature from 350 to 750 K. Figure 7 also shows  $C_p$  versus  $T$  plot within glass transition region in the insert.

From Figure 7, it is observed that the specific heat below the glass transition temperature ( $T_g$ ) is weakly temperature dependent for all the compositions. However, specific heats of the glassy samples show a compositional dependence in the entire range of temperature. 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 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 crystallization temperature ( $T_c$ ), 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 remaining above  $T_c$ , which may disappear when the temperature is further raised.<sup>15</sup>

**Composition Dependence of the Enthalpy Released During Transformation from Glass to Crystalline State.** The enthalpy released during phase transformation from glass to crystalline state ( $\Delta H_{gc}$ ) is an important parameter for the determination of stability of glasses. The enthalpy released during transformation from glass to crystalline state is given by:

$$\Delta H_{gc} = \Delta H_g - \Delta H_c \quad (1)$$

where  $\Delta H_g$  and  $\Delta H_c$  represent the enthalpy released during relaxation process and crystallization process, respectively.

The relaxation enthalpy  $\Delta H_g$  has been evaluated by determining the area under the curve of the specific heat versus temperature that is

$$\Delta H_g = \int C_p dT \quad (2)$$

whereas the crystallization enthalpy  $\Delta H_c$  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. Variation of  $\Delta H_{gc}$  as a function of  $\text{Pb}$  composition for phase transformation between glass and

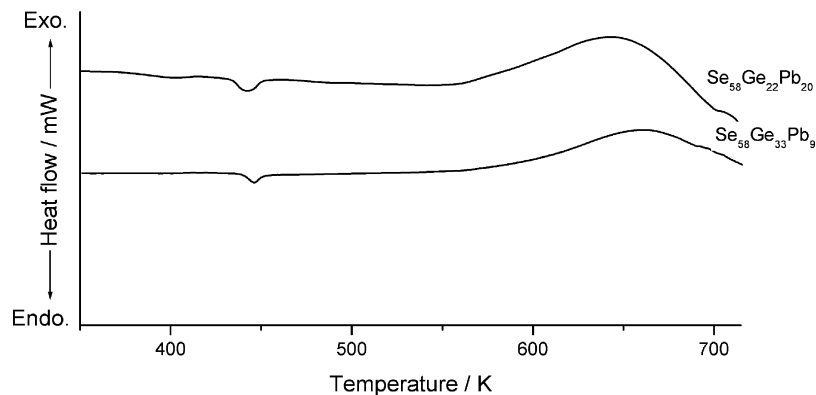


Figure 5. DSC thermogram of  $\text{Se}_{58}\text{Ge}_{33}\text{Pb}_9$  and  $\text{Se}_{58}\text{Ge}_{22}\text{Pb}_{20}$  glassy alloys annealed at the end of second crystallization temperature.

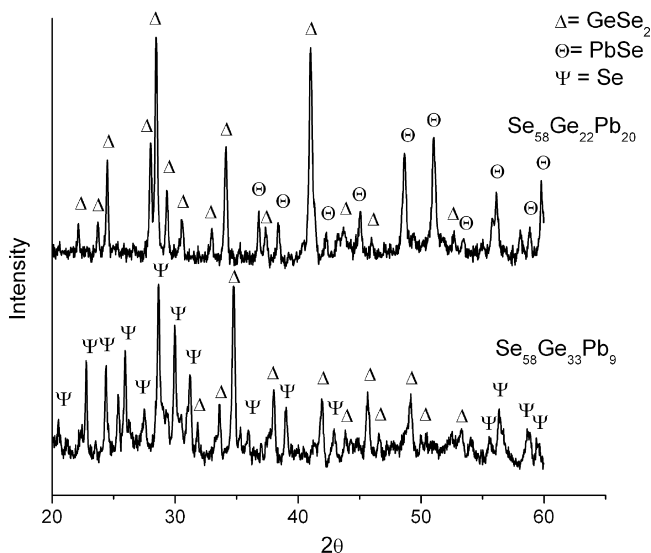


Figure 6. XRD pattern of  $\text{Se}_{58}\text{Ge}_{33}\text{Pb}_9$  and  $\text{Se}_{58}\text{Ge}_{22}\text{Pb}_{20}$  glassy alloys annealed at the end of second crystallization temperature.

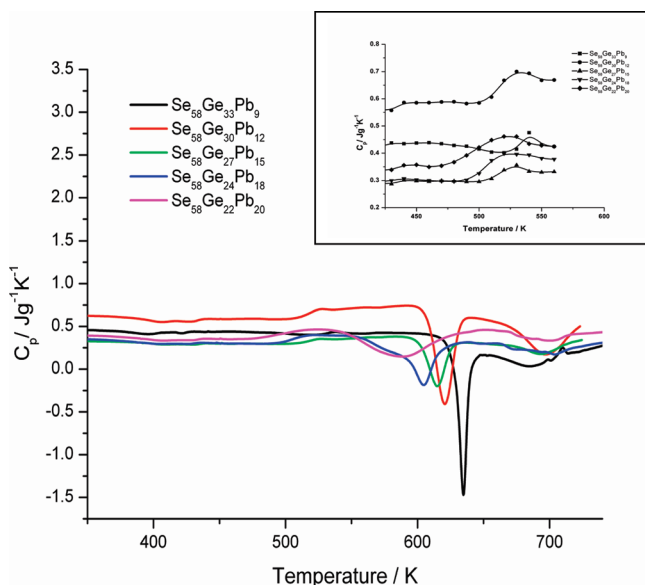


Figure 7. Plot of Specific heat ( $C_p$ ) vs  $T$  for  $\text{Se}_{58}\text{Ge}_{42-x}\text{Pb}_x$  ( $9 \leq x \leq 20$ ) glassy alloys. (The figure in the insert shows  $C_p$  vs  $T$  plot within glass transition region.)

first crystallization ( $\Delta H_{gc1}$ ) and glass and second crystallization ( $\Delta H_{gc2}$ ) has been shown in Figure 8. It is evident from Figure 8 that enthalpy released during phase transformation,  $\Delta H_{gc}$ , decreases with increase in Pb concentration. This enthalpy

released,  $\Delta H_{gc}$ , is associated with the stability of the glasses. A glass being in the metastable state tries to minimize its enthalpy as well as Gibbs free energy at every temperature by elementary atomic motions to gain stability. The most stable glass will release the least energy to gain stability as it already possesses a stable atomic configuration. Therefore, the most stable glass will have the least value of  $\Delta H_{gc}$ . Also, the least stable glasses, that is the glasses with maximum value of  $\Delta H_{gc}$ , will have the lowest value of  $(T_c - T_g)$ .<sup>9-11</sup> Therefore, it may be inferred that  $\text{Se}_{58}\text{Ge}_{22}\text{Pb}_{20}$  is the most stable glass among all of the samples of the series. Further, it is also observed that decrease of enthalpy ( $\Delta H_{gc2}$ ) is sharp in case of second phase, whereas  $\Delta H_{gc1}$  assumes an almost constant value in the case of first phase, which indicates the higher stability of second phase.

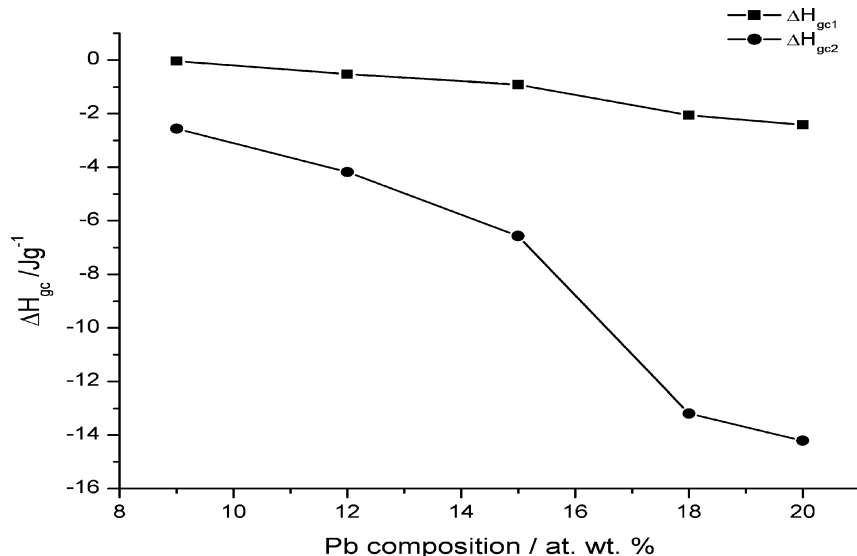
Figure 9 shows the trends of values of  $\Delta T_1(T_{c1} - T_g)$  and  $\Delta T_2(T_{c2} - T_g)$  with lead composition for the two phases of all of the samples of the series at a heating rate of 20 K/min. It has been observed that the values of  $\Delta T_1$  do not follow any trend (increase or decrease with lead composition) and hence cannot be taken as measure of determination of stability of the glasses. In view of this, the second phase that follows an increasing trend of  $\Delta T_2$  values is used for the determination of stability in terms of lead content in the glassy alloys. From the plot  $T_c - T_g$  against Pb composition, it is observed that  $\text{Se}_{58}\text{Ge}_{22}\text{Pb}_{20}$  glass has higher values of  $(T_c - T_g)$  and therefore it is most stable among all of the other studied samples. Plots of  $T_c - T_g$  against Pb composition confirm the results obtained from plots of  $\Delta H_{gc}$  against Pb composition.

This can also be explained on the basis of the bond energy of the system. In  $\text{Se}_{58}\text{Ge}_{42-x}\text{Pb}_x$  ( $9 \leq x \leq 20$ ) system, substitution of Ge with Pb atoms results in the reduction of Ge–Se bonds and an increase in Pb–Se bonds. The single-bond energy values<sup>12</sup> of Ge–Ge, Pb–Pb, and Se–Se bonds are 205.2, 85.7, and 206.1 kJ/mol respectively, whereas the single covalent bond energies of Ge–Se and Pb–Se bonds are 234.9 and 231.2 kJ/mol, respectively. With the increase in Pb content in Se–Ge system, more Pb–Se bonds are formed, resulting in reduction of total bond energy of the system<sup>13</sup> and ultimately leading to increase in the stability of system, hence the  $\text{Se}_{58}\text{Ge}_{22}\text{Pb}_{20}$  glassy alloy is found to be most stable among other samples of the series.

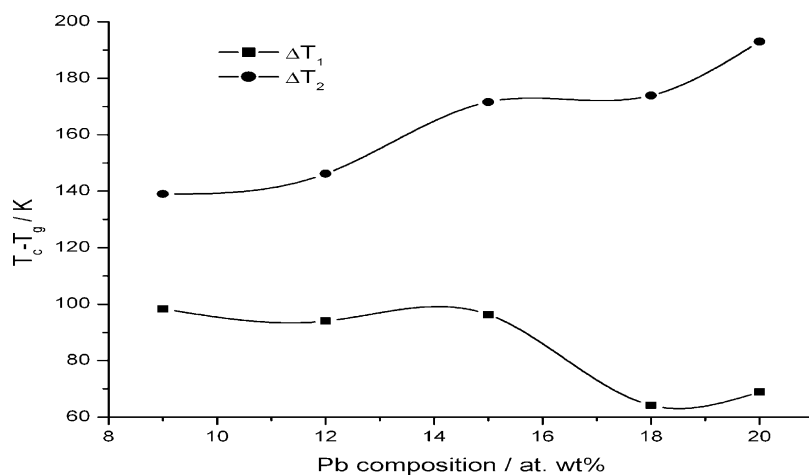
**Entropy Difference between Metastable States in Glassy Region.** The entropy difference,  $\Delta S$ , between metastable states in glassy region in a certain temperature range (i.e increase in temperature), can be obtained using the following relation:

$$\Delta S = \Delta Q/T \quad (4)$$

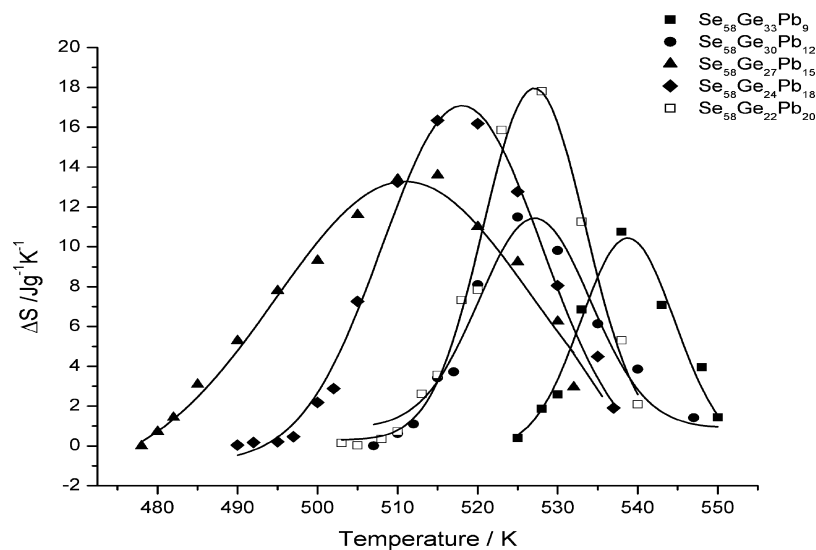
where  $\Delta Q$  is the amount of thermal energy absorbed by the glass in the glass transition region. Experimentally, the amount



**Figure 8.** Plot of  $\Delta H_{gc1}$  and  $\Delta H_{gc2}$  against Pb composition of  $\text{Se}_{58}\text{Ge}_{42-x}\text{Pb}_x$  ( $9 \leq x \leq 20$ ) glassy system.



**Figure 9.** Plot of  $\Delta T_1(T_{c1} - T_g)$  and  $\Delta T_2(T_{c2} - T_g)$  against Pb composition at a heating rate of 20 K/min.



**Figure 10.** Plot of  $\Delta S$  as a function of temperature.

of thermal energy absorbed by the system is calculated by measuring the area under the endothermic peak. Figure 10 shows the plot of  $\Delta S$  as a function of temperature.

From Figure 10, it is observed that entropy of the system increases with the increase in Pb concentration. Entropy of the

system is highest for  $\text{Se}_{58}\text{Ge}_{22}\text{Pb}_{20}$ , which indicates higher disorderness and hence more stability of this glassy composition. This is because of the fact that glass is a disordered solid and the addition of another element in the matrix increases the disorderness and hence the stability of the sample. When Pb is

introduced in Se–Ge system, it creates a compositional and configurational disorder in the glassy system and hence increases the stability of the glassy system. Thus, entropy, which represents the disorderness, is found to increase with the increase in lead (Pb) concentration in the Se–Ge glassy alloys.

The main characteristics of these plots is the sudden jump at  $T_g$  and a decreasing trend at a temperature where crystallization process begins. The jump in  $\Delta S$  near  $T_g$  is due to increase in number of atomic arrays, which leads to increase in topological disorder in the system.

**Gibbs Free Energy.** Gibbs free energy for the crystallization of undercooled liquid,  $\Delta G$ , is an important parameter in the study of crystallization kinetics. It is well-known that the exact temperature dependence of  $\Delta G$  can be calculated if the heat capacities of the liquid and crystalline solid are known as a function temperature. However, the heat capacity data of undercooled liquid is not available easily due to its metastable nature. Therefore, in the case of nonavailability of the specific heat data in the undercooled region, the functional dependence of  $\Delta G$  on undercooling must be estimated theoretically. Various expressions for  $\Delta G$  are available in the literature.<sup>16–21</sup> These expressions depend on some kind of assumption for the temperature dependence of the heat capacity.

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

Gibbs free energy difference between the glass and the corresponding crystalline phase is given by:

$$\Delta G_{gc} = \Delta G_g - \Delta G_c \quad (5)$$

where  $\Delta G_g$  and  $\Delta G_c$  represent 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:

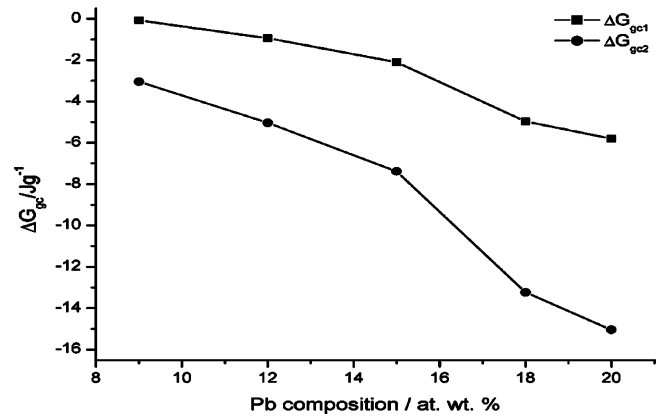
$$\Delta G_g = \Delta H_g - T\Delta S \quad (6)$$

where  $\Delta H_g$  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  $\Delta H$  represents the energy released by the glass during the crystallization process and is denoted by  $\Delta H_c$ . The Gibbs free energy difference in this case is calculated using the relation:

$$\Delta G_c = \Delta H_c - T\Delta S \quad (7)$$

and the Gibbs free energy difference between the glassy and crystalline phases ( $\Delta G_{gc}$ ) is calculated using eq 5. Figure 11 shows the plot of  $\Delta G_{gc}$  against Pb composition for phase transformation between glass and first crystallization ( $\Delta G_{gc1}$ ) and phase transformation between glass and second crystallization ( $\Delta G_{gc2}$ ) of  $\text{Se}_{58}\text{Ge}_{42-x}\text{Pb}_x$  ( $9 \leq x \leq 20$ ) glassy alloys.

It is evident from Figure 11 that the values of the Gibbs free energy difference between the glass and crystalline states of both first and second crystallization phases decrease with the increase in Pb concentration in the samples. Because 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



**Figure 11.** Plot of  $\Delta G_{gc1}$  and  $\Delta G_{gc2}$  against Pb composition of  $\text{Se}_{58}\text{Ge}_{42-x}\text{Pb}_x$  ( $9 \leq x \leq 20$ ) glassy alloys.

nucleation and growth process occurs sluggishly. Hence, one can infer that stability of the samples increases with an increase in Pb concentration in these glassy alloys. Further, it can also be concluded that the decrease in Gibbs free energy is more in the case of the second phase, and therefore the second phase is more stable than the first phase. The values of  $T_c - T_g$  and  $\Delta H_{gc}$  for both the phases also confirm the same fact.

**Entropy Difference between the Glass and the Crystalline States ( $\Delta S_{gc}$ ).** The entropy difference between the glass and crystalline states is given by the following relation:

$$\Delta S_{gc} = \Delta S_g - \Delta S_c \quad (8)$$

where  $\Delta S_g$  and  $\Delta S_c$  are the entropies of the glassy and crystalline states, respectively.

The entropy of the glassy state  $S_g$  is given by the following thermodynamical relation:<sup>22</sup>

$$S_g = S_{\text{conf}} + \int_0^T \left[ \frac{C_p}{T} \right] dT \quad (9)$$

where  $S_{\text{conf}}$  is the configurational entropy and is defined as

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

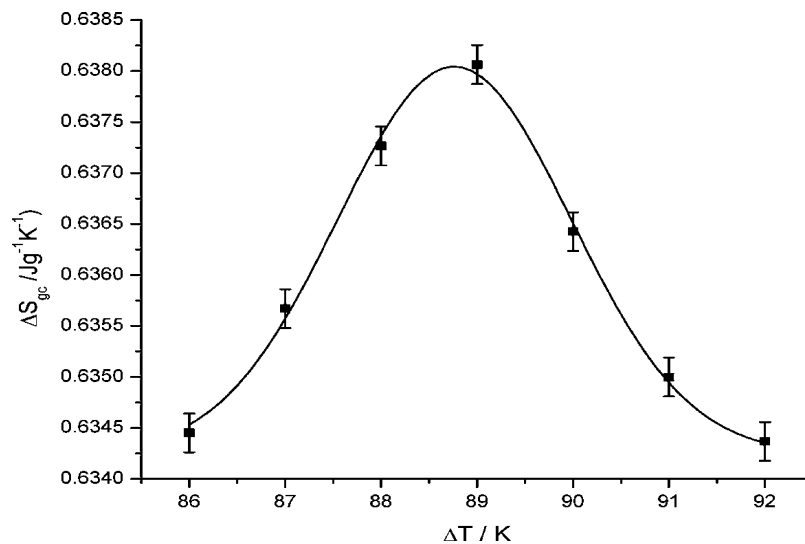
where  $W$  denotes the total number of different ways in which atoms can arrange themselves in a particular fashion and is given by:<sup>23</sup>

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

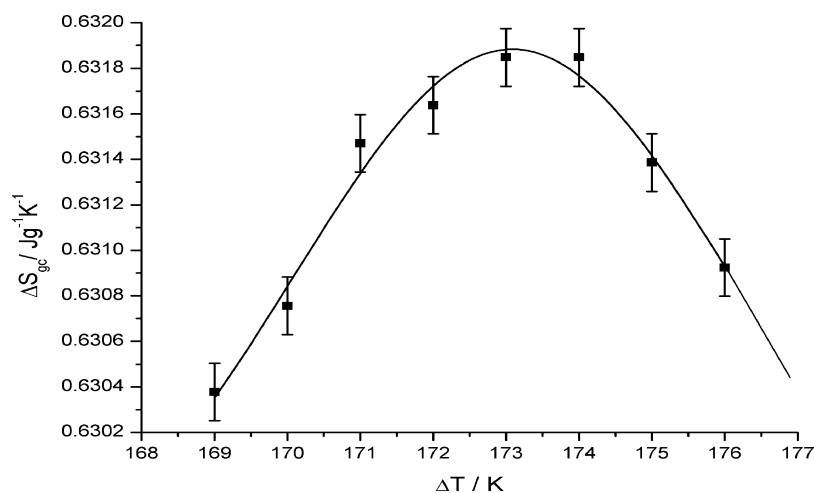
where  $N$  is the total number of atoms present in the system.  $A_{\text{Se}}$  is the fraction of Se atoms,  $B_{\text{Ge}}$  is the fraction of Ge atoms, and  $C_{\text{Pb}}$  is the number of Pb atoms. For the calculation of the entropy of the crystalline state, we have taken the configuration entropy to be zero. This is because there is only one way to arrange the atoms in the correct ordered array ( $W = 1$ ).<sup>22</sup> Therefore, the entropy of the crystalline state can be written as:

$$S_c = \int_0^T \left[ \frac{C_p}{T} \right] dT \quad (10)$$

Figures 12 and 13 show the plot of entropy difference  $\Delta S_{gc}$  against temperature difference ( $\Delta T$ ) for phase transformation between glass and first and second crystallization of  $\text{Se}_{58}\text{Ge}_{27}\text{Pb}_{15}$  glass respectively as a representative case.  $\Delta T$  is the difference of temperatures of the two crystallization regions and the glass transition region. It can be noted that the entropy shows its maximum in the vicinity of the glass transition peak beyond, which it decreases until the crystallization is completed.



**Figure 12.** Plot of entropy difference  $\Delta S_{gc}$  against temperature difference  $\Delta T$  for phase transformation between glass and first crystallization of  $Se_{58}Ge_{27}Pb_{15}$  glass.



**Figure 13.** Plot of entropy difference  $\Delta S_{gc}$  against temperature difference  $\Delta T$  for phase transformation between glass and second crystallization of  $Se_{58}Ge_{27}Pb_{15}$  glass.

The values of  $\Delta S_{gc}$  that is  $(\Delta S_g - \Delta S_c)$  for phase transformation between glass and first crystallization for  $Se_{58}Ge_{33}Pb_9$ ,  $Se_{58}Ge_{30}Pb_{12}$ ,  $Se_{58}Ge_{27}Pb_{15}$ ,  $Se_{58}Ge_{24}Pb_{18}$ , and  $Se_{58}Ge_{22}Pb_{20}$  glasses were found to be 0.586, 0.588, 0.638, 0.642, and 0.699 J/gK respectively, whereas the values of  $S_{gc}$  for phase transformation between glass and second crystallization for  $Se_{58}Ge_{33}Pb_9$ ,  $Se_{58}Ge_{30}Pb_{12}$ ,  $Se_{58}Ge_{27}Pb_{15}$ ,  $Se_{58}Ge_{24}Pb_{18}$ , and  $Se_{58}Ge_{22}Pb_{20}$  glasses were found to be 0.584, 0.585, 0.631, 0.634, and 0.689 J/gK, respectively. The values of  $\Delta S_{gc}$  for all of the compositions show that the entropy difference between the glassy and crystalline states increases with the increase in Pb concentration. The maximum value of  $\Delta S_{gc} = \Delta S_g - \Delta S_c$  is found to be for  $x = 20$  at wt % of Pb 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 up to certain temperature (around  $T_p$ ) and after that attains approximately stable values. The highest value of  $S_{gc}$  for  $Se_{58}Ge_{22}Pb_{20}$  glass again confirms that this glass is the most stable among the whole series.

## Conclusions

Investigation of various thermodynamic properties of  $Se_{58}Ge_{42-x}Pb_x$  ( $9 \leq x \leq 20$ ) alloys leads to the following conclusions:

1. The  $Se_{58}Ge_{42-x}Pb_x$  ( $9 \leq x \leq 20$ ) glassy systems exhibit single glass transition and double crystallization on heating, which is attributed to the phase separation during crystallization. The XRD study reveals that the  $Se_{58}Ge_{33}Pb_9$  glassy alloy crystallizes into GeSe<sub>2</sub> and Se phases with monoclinic structures, whereas all other glasses ( $Se_{58}Ge_{42-x}Pb_x$  ( $12 \leq x \leq 20$ )) in the series crystallizes into GeSe<sub>2</sub> and PbSe phases with monoclinic and cubic structures, respectively.

2. The most stable glass ( $Se_{58}Ge_{22}Pb_{20}$ ) is found to have maximum entropy in the glassy region. This maximum value of entropy is found to persist even in the crystalline region, indicating that growth and nucleation processes occur sluggishly.

3. Gibbs free energy difference between the glass and the corresponding crystalline phase  $\Delta G_{gc}$  is found to be highest for 9 at wt % of Pb and lowest for 20 at wt % of Pb, which suggests that stability of sample increases with the increase of Pb content in the glasses under investigation. The enthalpy released during transformation from glassy to crystalline phase and the values of  $T_c - T_g$  also favor the same fact.

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