

# Fragility of Pb modified germanium chalcogenide glasses

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**Abstract** Bulk chalcogenide glasses with compositions  $Pb_xGe_{42-x}Se_{58}$  ( $3 < x \leq 15$ ) (series I),  $Pb_{10}Ge_xSe_{80-x}$  ( $17 \leq x < 24$ ) (series II),  $Pb_xGe_{42-x}Se_{48}Te_{10}$  ( $3 \leq x \leq 15$ ) (series III) and  $Pb_{20}Ge_xSe_{70-x}Te_{10}$  ( $17 \leq x \leq 24$ ) (series IV) were prepared by the melt quenching technique. The heat capacity jump at glass transition ( $\Delta C_p$ ) and the activation energy for viscous flow ( $E_\eta$ ) of the four series of glasses were obtained from differential scanning calorimetry (DSC) studies. The composition dependence of  $\Delta C_p$  and  $E_\eta$  of series I and III showed minima near the composition with  $x = 9$  at wt % Pb. Similarly the  $\Delta C_p$  and  $E_\eta$  data of series II and IV exhibited minimum near the composition with  $x = 21$  at wt % Ge. Since  $\Delta C_p$  and  $E_\eta$  could be associated with the fragility of the glass network, the data obtained have been used to understand the changes occurring in the glass network as a function of composition. The results have also been discussed in the light of the majority charge carrier reversal occurring at the specific compositions in the respective series of glasses.

**Keywords** Chalcogenide glasses, fragility, heat capacity jump, activation energy

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## 1. Introduction

Chalcogenide glasses are generally *p*-type semiconductors with the Fermi level pinned near the middle of the band gap by charged defects present in these glasses [1]. After the pioneering work by Toghe *et al* [2], it is now generally accepted that incorporation of appropriate amounts of either Bismuth (Bi) [2] or Lead (Pb) [3] in bulk Ge-Se glasses leads to the reversal of the majority charge carrier from *p*- to *n*-type. Attempts have been made to attribute the majority charge carrier reversal (MCCR) phenomenon in Bi modified Ge-Se glasses to percolation of Bi clusters [4], high degree of polarisation of Bi [5], existence of defect states [6], etc. The MCCR in Pb modified Ge-Se glasses has been attributed [7] to changes induced in electronic structure of the glass by the energetically disposed  $sp^3d^2$  band of Pb. Electrical properties of  $Pb_xGe_{42-x}Se_{48}Te_{10}$  glasses indicate

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[11] that MCCR occurs in this glass system at  $x \approx 9$  at. wt. of Pb. It is worthy to point out that calorimetric parameters of Bi and Pb modified chalcogenide glasses [8-12], such as glass transition temperature ( $T_g$ ) and crystallisation temperature ( $T_c$ ), heat capacity jump at glass transition, activation energies and thermal diffusivity [13, 14] consistently show anomalous features at the compositions at which the conduction type change occurs. Glass forming liquids are classified as 'fragile' or 'strong' on the basis of the magnitude of the heat capacity jump at  $T_g$  as well as from the extent of deviation of viscosity versus temperature Arrhenius plots [15]. However, the effect of compositional variation on glassy network has not been investigated in detail in Pb-Ge-Se(-Te) glasses. Differential scanning calorimetric (DSC) study of two series of Pb-Ge-Se and Pb-Ge-Se-Te glasses has been taken up to understand the changes occurring in the glassy network as a function of composition by evaluating the different factors contributing to the fragility of glass.

## 2. Experimental

The melt quenching technique was used to prepare bulk glasses with composition  $\text{Pb}_x\text{Ge}_{42-x}\text{Se}_{58}$  ( $0 \leq x \leq 15$ ) (series I),  $\text{Pb}_{20}\text{Ge}_x\text{Se}_{80-x}$  ( $17 \leq x \leq 24$ ) (series II),  $\text{Pb}_x\text{Ge}_{42-x}\text{Se}_{48}\text{Te}_{10}$  ( $0 \leq x \leq 15$ ) (series III) and  $\text{Pb}_{20}\text{Ge}_x\text{Se}_{70-x}\text{Te}_{10}$  ( $17 \leq x \leq 24$ ) (series IV). Appropriate amounts of high purity (99.999%) elements sealed in fused silica ampoules under a vacuum of  $10^{-5}$  mbar were slowly heated to 1300 K in a rotary furnace. After providing sufficient time for homogenisation at this temperature, the ampoules were suddenly dropped into cold water to form glass. The amorphous nature of as-quenched glass samples was verified by X-ray diffraction technique. The majority charge carrier type in each composition was determined from the sign of the Seebeck coefficient. Thermoelectric power measurements performed on thin slices of as quenched glasses established that the MCCR occurred at Pb concentration of ~9 at. wt. % in the series I and III, and at Ge concentration of ~21 at. wt. % in the series II and IV. Non-isothermal studies were performed with a Perkin-Elmer DSC 7 differential scanning calorimeter. Constant heating rates ranging from  $5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$  to  $25 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$  were used. All the DSC runs were performed using alumina sample pans under dry nitrogen atmosphere. The instrument was calibrated with indium and zinc melting point standards prior to data collection. Standard software supplied along with the DSC instrument was used for obtaining the characteristic temperatures and heat capacity data from the DSC curves.

## 3. Results and discussion

The kinetic parameters of glass transition and crystallisation can be estimated from the DSC data by several methods [16,17], which are based on the assumption that the temperature of a kinetically controlled reaction shifts with heating rate. According to one such method due to Bartenev [18],

$$d[\ln(\phi)]/d[1/T_g] = -E_\eta/R \quad (1)$$

where  $\phi$  is the heating rate,  $E_\eta$  is the activation energy of the kinetic reaction,  $T_g$  is the glass transition temperature and  $R$  is the universal gas constant. The activation energy

$E_\eta$  is also referred to [19] as the activation energy for viscous flow. The degree of fragility  $\langle m \rangle$  [20] of the glass at the glass transition is given by,

$$\langle m \rangle = E_\eta / (2.3R T_g) \tag{2}$$

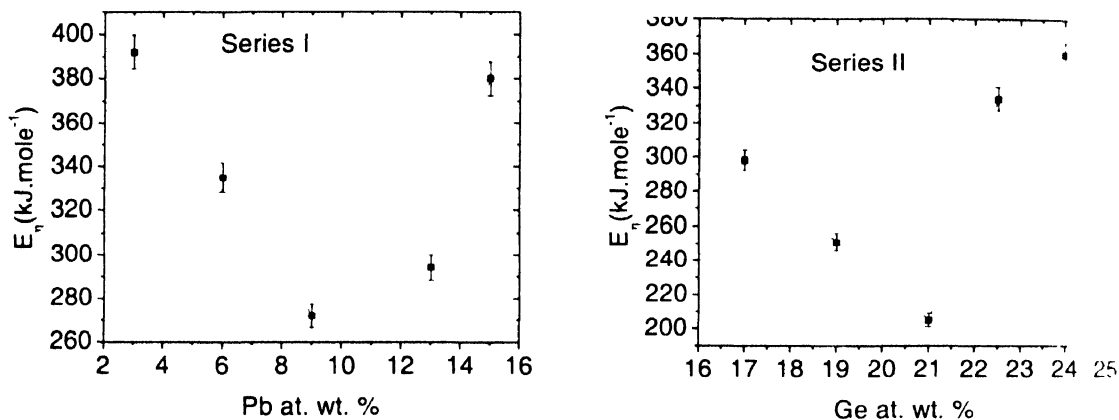
The activation energy of viscous flow ( $E_\eta$ ) estimated from the slope of the  $\ln(\phi)$  versus  $1000/T_g$  plots for two series of Pb-Ge-Se and Pb-Ge-Se-Te glasses are shown in Figure 1 and Figure 2, respectively.  $T_g$  values obtained at heating rates of 5, 10, 15, 20 and 25°C min<sup>-1</sup> from DSC measurements plotted and fitted using least squares fitting procedure for determining  $E_\eta$ . Since the kinetically controlled reaction is the glass transition and the estimated activation energy is a measure of the hindrance or resistance posed by the glassy network to the glass transition phenomenon, it can be concluded from the figures that the glass transition is least hindered for the glasses at  $x = 9$  at wt % Pb in series I and III, and at  $x = 21$  at wt % Ge in series II and IV. A minimum in the activation energy also implies that the glasses at these compositions undergo minimal configurational changes at the glass transition. The activation energy values obtained for the two series of glasses are tabulated in Table 1.

**Table 1** Activation energy of viscous flow ( $E_\eta$ ), glass transition temperature @ 20 °C min<sup>-1</sup> degree of fragility  $\langle m \rangle$  and heat capacity jump at  $T_g$  ( $\Delta C_p$ ) of various compositions of Pb-Ge-Se(-Te) glasses

Glass Composition	$E_\eta$ (kJ mole <sup>-1</sup> )	$T_g$ (K)	$\langle m \rangle$	$\Delta C_p$ (Jg <sup>-1</sup> K <sup>-1</sup> )	Glass Composition	$E_\eta$ (kJmole <sup>-1</sup> )	$T_g$ (K)	$\langle m \rangle$	$\Delta C_p$ (Jg <sup>-1</sup> K <sup>-1</sup> )
<b>Series I</b>					<b>Series II</b>				
Pb <sub>0.1</sub> Ge <sub>36</sub> Se <sub>58</sub>	392	544	37.7	0.44	Pb <sub>20</sub> Ge <sub>17</sub> Se <sub>63</sub>	298	495	31.5	0.45
Pb <sub>0.9</sub> Ge <sub>36</sub> Se <sub>58</sub>	335	527	33.3	0.19	Pb <sub>20</sub> Ge <sub>19</sub> Se <sub>61</sub>	251	533	24.6	0.17
Pb <sub>0.9</sub> Ge <sub>33</sub> Se <sub>58</sub>	272	524	27.2	0.16	Pb <sub>20</sub> Ge <sub>21</sub> Se <sub>59</sub>	205	544	19.7	0.15
Pb <sub>1</sub> Ge <sub>29</sub> Se <sub>58</sub>	294	527	29.2	0.20	Pb <sub>20</sub> Ge <sub>22.5</sub> Se <sub>57.5</sub>	334	535	32.7	0.19
Pb <sub>1</sub> Ge <sub>27</sub> Se <sub>58</sub>	380	530	37.5	0.28	Pb <sub>20</sub> Ge <sub>24</sub> Se <sub>56</sub>	360	524	35.9	0.45
<b>Series III</b>					<b>Series IV</b>				
Pb <sub>0.3</sub> Ge <sub>39</sub> Se <sub>48</sub> Te <sub>10</sub>	407	536	39.7	0.34	Pb <sub>20</sub> Ge <sub>17</sub> Se <sub>53</sub> Te <sub>10</sub>	298	496	31.4	0.20
Pb <sub>0.6</sub> Ge <sub>36</sub> Se <sub>48</sub> Te <sub>10</sub>	268	522	26.9	0.26	Pb <sub>20</sub> Ge <sub>19</sub> Se <sub>51</sub> Te <sub>10</sub>	213	510	21.9	0.18
Pb <sub>0.6</sub> Ge <sub>33</sub> Se <sub>48</sub> Te <sub>10</sub>	249	517	25.2	0.21	Pb <sub>20</sub> Ge <sub>21</sub> Se <sub>49</sub> Te <sub>10</sub>	208	518	21.0	0.13
Pb <sub>1.3</sub> Ge <sub>29</sub> Se <sub>48</sub> Te <sub>10</sub>	245	514	24.9	0.25	Pb <sub>20</sub> Ge <sub>22.5</sub> Se <sub>47.5</sub> Te <sub>10</sub>	303	516	30.7	0.18
Pb <sub>1.5</sub> Ge <sub>27</sub> Se <sub>48</sub> Te <sub>10</sub>	313	515	31.8	0.28	Pb <sub>20</sub> Ge <sub>24</sub> Se <sub>46</sub> Te <sub>10</sub>	329	508	33.9	0.20

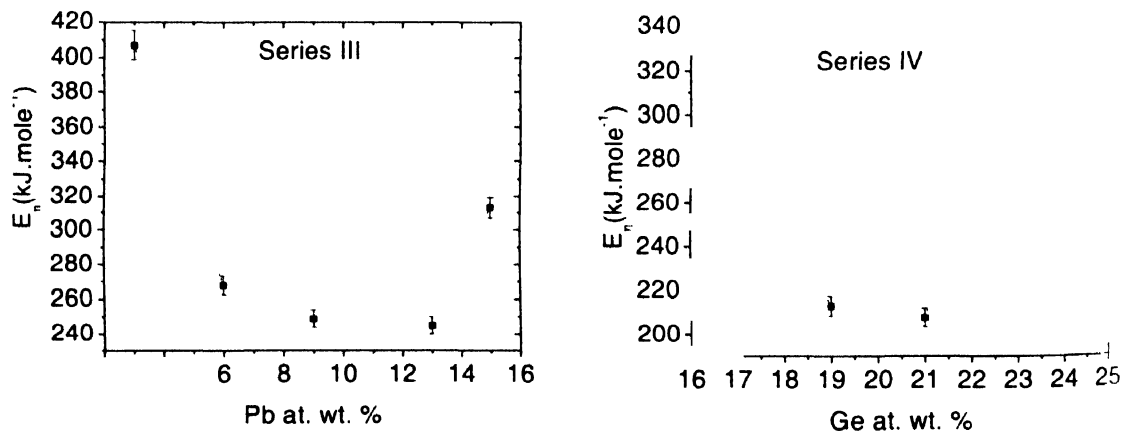
The degree of fragility values estimated for various glass compositions in the four series of glasses are listed in Table 1. The  $E_\eta$  and  $T_g$  values used for estimating  $\langle m \rangle$  are also listed in Table 1.  $\langle m \rangle$  varied between  $19.7 \pm 0.4$  and  $39.7 \pm 0.4$ . These low  $\langle m \rangle$  values are signatures of the 'strong' nature of covalently bonded chalcogenide glasses.

However, a consistent variation in  $\langle m \rangle$  value could be seen within each series with a minimum near at  $x = 9$  at. wt. % Pb in series I and III, and at  $x = 21$  at. wt. % Ge in series II and IV. Hence, one can conclude that  $\langle m \rangle$  values also indicate a minimum in fragility at the compositions at which the  $p$ - to  $n$ -type carrier change occurs in Pb-Ge-Se [3,21] and Pb-Ge-Se-Te [11,21] glasses. When  $\langle m \rangle$  is minimum, the glass and its high temperature crystalline phase have minimum configurational difference. This factor in combination with the directional nature of the covalent bond existing between the elements seems to provide a favourable situation for the electronic interaction leading to the unpinning of the Fermi energy level towards the conduction band [21].



**Figure 1.** Variation of activation energy of viscous flow ( $E_n$ ) as a function of composition of  $Pb_xGe_{42-x}Se_{58}$  ( $3 \leq x \leq 15$ ) (series I) and  $Pb_{20}Ge_xSe_{80-x}$  ( $17 \leq x \leq 24$ ) (series II) glasses. Dotted line merely connects adjacent data points

The heat capacity (specific heat at constant pressure) jump at the glass transition temperature is an inherent property of a glass [22]. The heat capacity jump (also referred to as the excess heat capacity at  $T_g$ ), is expressed as  $\Delta C_p = (C_{pl} - C_{pg})_{T-T_g}$ , where  $C_{pl}$



**Figure 2.** Variation of activation energy of viscous flow ( $E_n$ ) as a function of composition of  $Pb_xGe_{42-x}Se_{48}Te_{10}$  ( $3 \leq x \leq 15$ ) (series III) and  $Pb_{20}Ge_xSe_{70-x}Te_{10}$  ( $17 \leq x \leq 24$ ) (series IV) glasses. Dotted line merely connects adjacent data points.

and  $C_{pg}$  are the heat capacity of the liquid and the glassy states across the glass transition. The value of the excess heat capacity reflects the amount of configuration change occurring in the network at the glass to liquid transition. According to Angell [23],  $\Delta C_p$  could be correlated [24] with the fragility of a glass. Fragile glasses exhibiting a large  $\Delta C_p$  undergo more configurational change at the glass transition. Strong glasses exhibit a small  $\Delta C_p$  and minimal configuration changes at  $T_g$ . The variation of the heat capacity jump at  $T_g$  ( $\Delta C_p$ ) of the four series of glasses is shown in Figure 3 and Figure 4, respectively. The

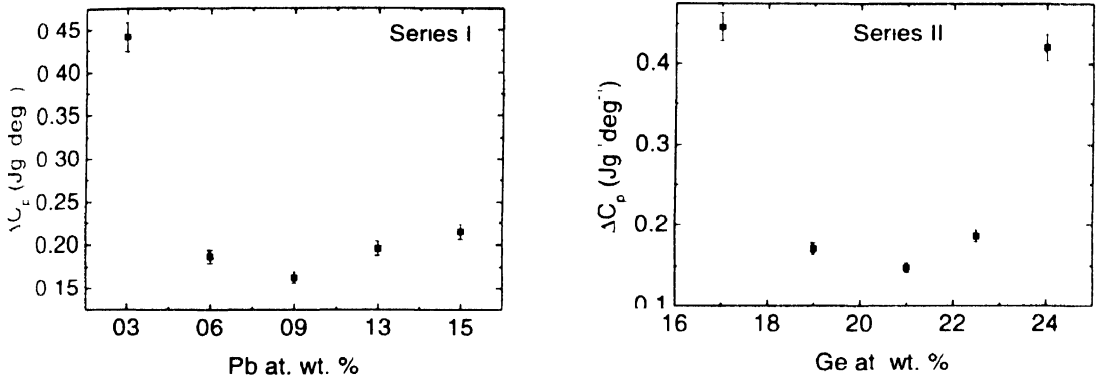


Figure 3. Variation of heat capacity jump at  $T_g$  ( $\Delta C_p$ ) as a function of composition of  $Pb_xGe_{42-x}Se_{58}$  ( $3 \leq x \leq 15$ ) (series I) and  $Pb_{20}Ge_xSe_{80-x}$  ( $17 \leq x \leq 24$ ) (series II) glasses. Dotted line merely connects adjacent data points

excess heat capacity at the  $T_g$  shows a minimum near the composition with  $x = 9$  at. wt. % Pb for series I and III, and  $x = 21$  at. wt. % Ge for series II and IV, which are the compositions at which the  $p$ - to  $n$ -type transition occurs [3,11,21]. Thus the minimum in fragility is associated with the composition at which MCCR occurs in these glasses. A small  $\Delta C_p$  is also a proof of a strong thermodynamic behaviour which indicates that the

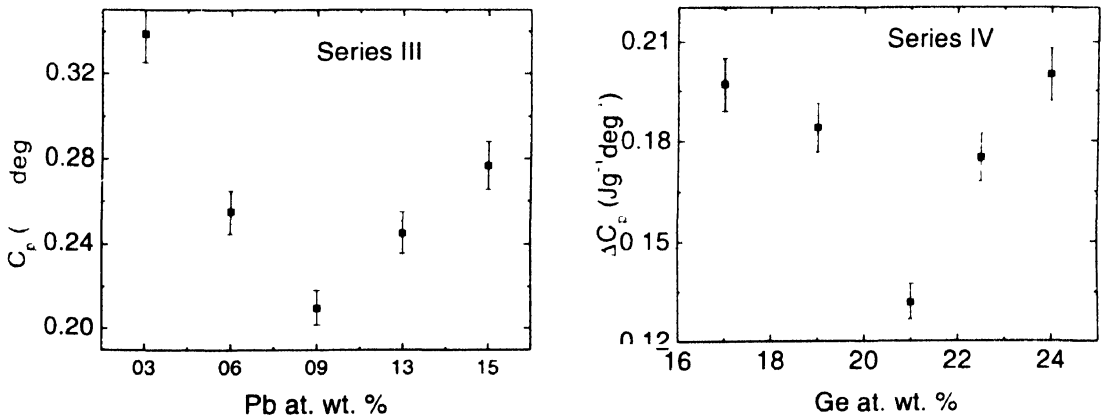


Figure 4. Variation of heat capacity jump at  $T_g$  ( $\Delta C_p$ ) as a function of composition of  $Pb_xGe_{42-x}Se_{48}Te_{10}$  ( $3 \leq x \leq 15$ ) (series III) and  $Pb_{20}Ge_xSe_{70-x}Te_{10}$  ( $17 \leq x \leq 24$ ) (series IV) glasses. Dotted line merely connects adjacent data points.

glass is not far away from its thermodynamic equilibrium. A minimum in  $\Delta C_p$  has been observed when glasses undergo a floppy to rigid transition [25,26] in Ge-As-Se [27] Ge-Sb-Se [28,29], Ge-As-Te and Si-As-Te [29] glasses. In the case of Pb-Ge-Se-Te glasses the composition dependence of  $T_g$  suggests the presence of a relatively large number of hetero-nuclear bonds near the compositions at which the p- to n-type transition occurs. This could give rise to an optimally coordinated 3-d structure, leading a rigid glassy network as reflected by the minimum in the excess heat capacity data.

#### 4. Conclusions

The composition dependence of  $E_n$ ,  $\langle m \rangle$  and  $\Delta C_p$  of two series of Pb-Ge-Se and Pb-Ge-Se-Te glasses has been obtained from DSC data. These parameters show subtle variation in their values among the different series of glasses. These variations are to be expected since the percentages of group IV and VI elements vary in each of these series of glasses, leading to variation in the nature of the bonding between the atoms. But within each series, the composition dependence of  $E_n$ ,  $\langle m \rangle$  and  $\Delta C_p$  consistently show a minimum at  $x = 9$  at. wt. % Pb and  $x = 21$  at. wt. % Ge, for both the Pb-Ge-Se and Pb-Ge-Se-Te glasses, which are the compositions at which the conduction type change occurs. This clearly shows evidence of a fragility change associated with the conduction mechanism change. Although the change in conduction mechanism is an electronic property, the current results clearly indicate that there is a structural basis to the electronic transition occurring at specific compositions in the lead modified chalcogenide glasses.

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