

Differential scanning calorimeter studies on Pb modified Ge–Se–Te glasses

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Bulk glasses $\text{Pb}_x\text{Ge}_{42-x}\text{Se}_{48}\text{Te}_{10}$ ($0 \leq x \leq 15$) and $\text{Pb}_{20}\text{Ge}_x\text{Se}_{70-x}\text{Te}_{10}$ ($17 \leq x \leq 24$) have been prepared by quenching the melt. The non-isothermal properties of these glasses have been determined using a Differential scanning calorimeter (DSC). The composition dependence of the glass transition temperature, crystallisation temperature, excess heat capacity at glass transition, glass forming tendency and activation energy of glass transition and crystallisation show anomalous features near the composition at which the p- to n-type transition occurs. These observations reflect the changes occurring in the chemical bonding and the nature of the glassy network in these glasses. The results have been interpreted in terms of existing models and the majority charge carrier reversal phenomenon occurring in these glasses. © 2003 Kluwer Academic Publishers

1. Introduction

Chalcogenide glasses are generally known to be 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 has been accepted that incorporation of appropriate amounts of either Bi [2] or Pb [3] in bulk Ge–Se glasses results in 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. It is a matter of interest 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] have consistently shown anomalous features at the compositions at which the conduction type change occurs. These thermal properties help in understanding the changes occurring in the glassy network near compositions at which the MCCR occurs apart from providing insight on the thermal stability of the glasses. A recent report [11] on the electrical properties of $\text{Pb}_x\text{Ge}_{42-x}\text{Se}_{48}\text{Te}_{10}$ glasses indicates that MCCR occurs in this glass system at $x \approx 9$ at. wt. of Pb. The Pb–Ge–Se–Te glass system has not been extensively studied. The differential scanning calorimeter (DSC) study of $\text{Pb}_x\text{Ge}_{42-x}\text{Se}_{48}\text{Te}_{10}$ ($0 \leq x \leq 15$) (series I) and $\text{Pb}_{20}\text{Ge}_x\text{Se}_{70-x}\text{Te}_{10}$ ($17 \leq x \leq 24$) (series II) glasses has been taken up to examine the thermal trans-

formations occurring in these glasses and to understand the changes occurring in the glassy network as a function of composition.

2. Experimental

Bulk glasses with composition $\text{Pb}_x\text{Ge}_{42-x}\text{Se}_{48}\text{Te}_{10}$ ($0 \leq x \leq 15$) (series I) and $\text{Pb}_{20}\text{Ge}_x\text{Se}_{70-x}\text{Te}_{10}$ ($17 \leq x \leq 24$) (series II) were prepared by the melt quenching technique. Appropriate amount of high purity elements sealed in fused silica ampoules under a vacuum of $\sim 10^5$ 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 in cold water to form glasses of respective compositions. 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 former (series I), and at a Ge concentration of ~ 21 at. wt% in the latter (series II). The non-isothermal studies were performed with a Perkin-Elmer DSC 7 Differential Scanning Calorimeter (DSC). Constant heating rates ranging from $5^\circ\text{C}\cdot\text{min}^{-1}$ to $20^\circ\text{C}\cdot\text{min}^{-1}$ were used. All the DSC runs were performed in 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 reported calorimetric parameters from the DSC curves.

3. Results and discussions

The thermal transformations observed in $\text{Pb}_x\text{Ge}_{42-x}\text{Se}_{48}\text{Te}_{10}$ and $\text{Pb}_{20}\text{Ge}_x\text{Se}_{70-x}\text{Te}_{10}$ glasses under a constant heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ are depicted in Fig. 1a and 1b respectively. The figure shows normalised heat flow curves obtained after baseline subtraction. All glasses exhibited an endothermic baseline shift at the glass transition temperature T_g followed by complex crystallisation exotherms and single/multiple melting endotherms. Glasses with $x \leq 9$ at. wt% Pb belonging to series I exhibited (Fig. 1a) three crystallisation peaks, whereas glasses with $x > 9$ at. wt% Pb exhibited two well resolved crystallisation peaks. It can be seen from Fig. 1b that the glass with $x = 21$ at. wt% Ge belonging to series II exhibited a sharp crystallisation exotherm and a single melting endotherm.

The variation of T_g and first crystallisation temperature T_{c1} of both the series of glasses as a function of composition are shown in Fig. 2a and b respectively.

In the case of the $\text{Pb}_x\text{Ge}_{42-x}\text{Se}_{48}\text{Te}_{10}$ (series I) glasses, T_g decreases sharply initially as Pb replaces Ge and after 9 at. wt% of Pb, there is no appreciable change in the value of T_g . As Pb content increases, more and more Pb–Se ($E_{\text{Pb-Se}} = 55.3$ kcal/mole) bonds have lower single bond energy [15] than Ge–Se ($E_{\text{Ge-Se}} = 56.2$ kcal/mole) bonds, the average bond energy (and hence T_g) of the glasses decrease as Pb replaces Ge. The insensitivity of T_g to addition of Pb after $x = 9$ at. wt% of Pb, may be due to the formation of more Pb–Pb ($E_{\text{Pb-Pb}} = 20.5$ kcal/mole) and other homo-nuclear bonds such as Se–Se ($E_{\text{Se-Se}} = 49.3$ kcal/mole) at these compositions. In the case of $\text{Pb}_{20}\text{Ge}_x\text{Se}_{70-x}\text{Te}_{10}$ glasses (series II) (Fig. 2b), T_g increases with increase in Ge concentration, attains a maximum near 21 at. wt% of Ge and then decreases. Such behaviour has also been observed [9, 12] in Pb–Ge–Se glasses. Bond counting calculations performed on $\text{Pb}_{20}\text{Ge}_x\text{Se}_{80-x}$ glasses showed [3] that maximum number of Ge–Se bonds

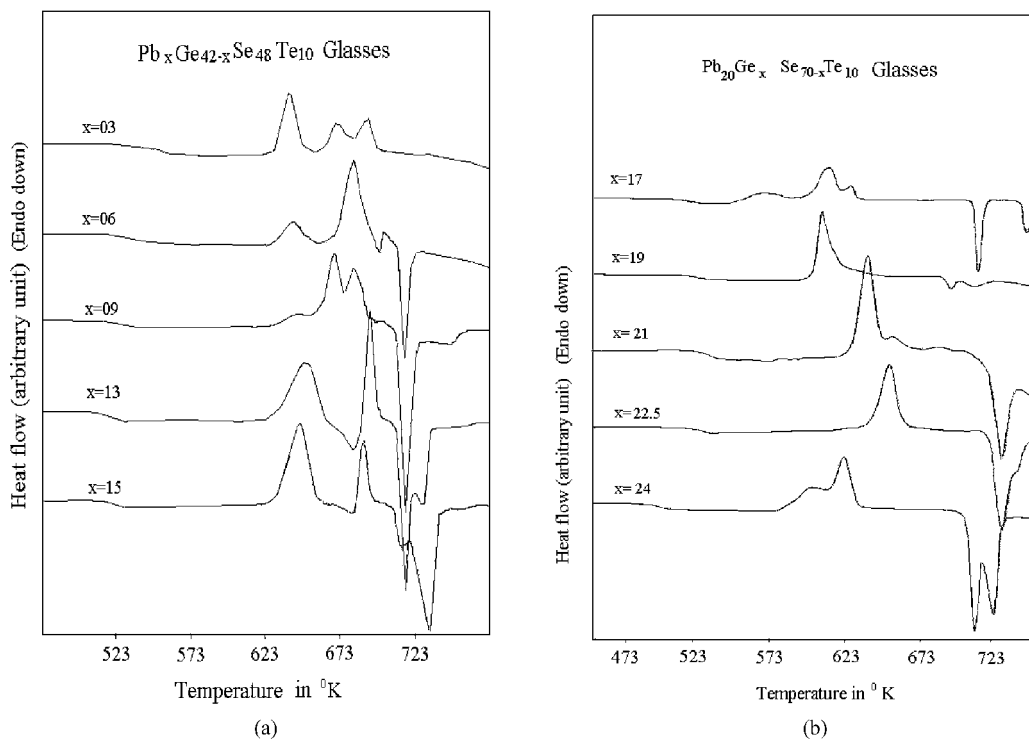


Figure 1 DSC curves of (a) $\text{Pb}_x\text{Ge}_{42-x}\text{Se}_{48}\text{Te}_{10}$ glasses, and (b) $\text{Pb}_{20}\text{Ge}_x\text{Se}_{70-x}\text{Te}_{10}$ glasses recorded at a constant heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$.

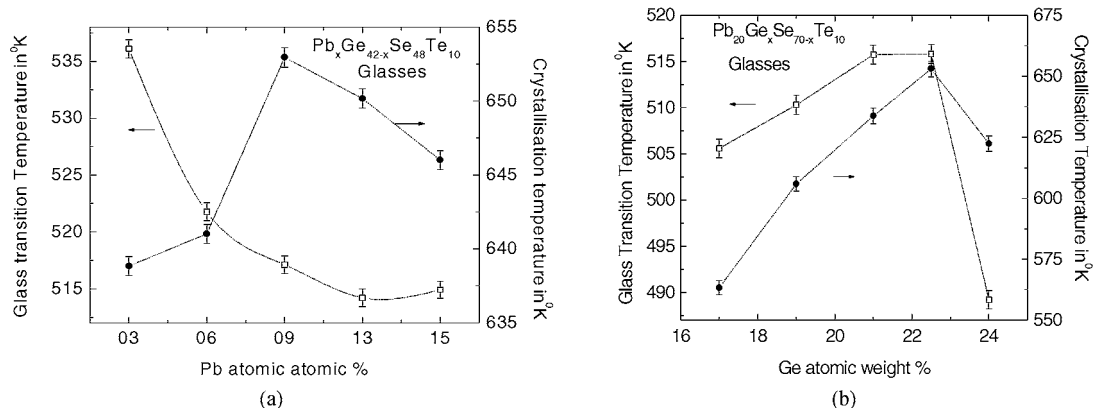
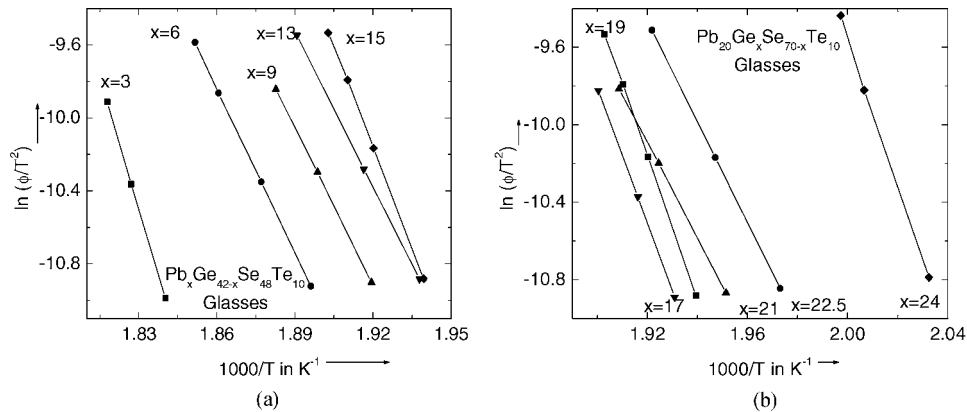


Figure 2 Glass transition temperature and crystallisation temperature as a function of composition of (a) $\text{Pb}_x\text{Ge}_{42-x}\text{Se}_{48}\text{Te}_{10}$ glasses, and (b) $\text{Pb}_{20}\text{Ge}_x\text{Se}_{70-x}\text{Te}_{10}$ glasses. The data correspond to DSC runs performed at a constant heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$.

TABLE I Calorimetric and kinetic parameters of Pb—Ge—Se—Te glasses

Glass composition	T_g (K)	T_{c1} (K)	ΔC_p ($Jg^{-1} deg^{-1}$)	K_{gl}	ΔE_g ($kJmole^{-1}$)	ΔE_{c1} ($kJmole^{-1}$)
Series I						
Pb ₀₃ Ge ₃₉ Se ₄₈ Te ₁₀	536	639	0.34	—	250	305
Pb ₀₆ Ge ₃₆ Se ₄₈ Te ₁₀	522	641	0.26	1.59	241	249
Pb ₀₉ Ge ₃₃ Se ₄₈ Te ₁₀	517	653	0.21	1.62	240	187
Pb ₁₃ Ge ₂₉ Se ₄₈ Te ₁₀	514	650	0.25	2.03	258	151
Pb ₁₅ Ge ₂₇ Se ₄₈ Te ₁₀	515	646	0.28	1.96	308	272
Series II						
Pb ₂₀ Ge ₁₇ Se ₅₃ Te ₁₀	506	563	0.20	0.38	217	155
Pb ₂₀ Ge ₁₉ Se ₅₁ Te ₁₀	510	606	0.18	1.08	206	284
Pb ₂₀ Ge ₂₁ Se ₄₉ Te ₁₀	516	634	0.13	1.28	199	332
Pb ₂₀ Ge _{22.5} Se _{47.5} Te ₁₀	516	653	0.18	1.76	292	266
Pb ₂₀ Ge ₂₄ Se ₄₆ Te ₁₀	489	622	0.20	1.46	317	248


 Figure 3 Kissinger's plots obtained for glass transition in (a) Pb_xGe_{42-x}Se₄₈Te₁₀ glasses and (b) Pb₂₀Ge_xSe_{70-x}Te₁₀ glasses.

occurred in the glass with $x = 20$ at. wt% Ge. The number of Pb—Se bonds remains constant throughout this series of glasses. Since Te bonds have lower single bond energy as compared to Se bonds, the above arguments could also be extended to explain the observed maximum in T_g near $x = 21$ at. wt% Ge in Pb₂₀Ge_xSe_{70-x}Te₁₀ glasses.

The variation of the first crystallisation temperature T_{c1} with composition in the two series of glasses is also shown in Fig. 2a and b. The discussion on the crystallisation phenomenon is limited to the first crystallisation peak since all glasses do not exhibit multiple crystallisation when heated at constant heating rate of $10^\circ C.min^{-1}$ or higher. It can be seen that the T_{c1} data shows a maximum near $x = 9$ at. wt% of Pb in series I and near $x = 21$ at. wt% of Ge in series II glasses. Similar trend in T_{c1} has been observed [9, 12] in Pb₂₀Ge_xSe_{80-x} glasses. A higher T_c signifies a higher inhibition to the nucleation and growth of a crystalline phase in such glass compositions. From Fig. 2a and b it can be concluded that the glass composition at $x = 9$ at. wt% Pb and 21 at. wt% Ge exhibit the highest inhibition to crystallisation.

Hruby [16] has proposed that the glass forming tendency K_{gl} (or thermal stability of the glass) could be estimated from the relation,

$$K_{gl} = (T_c - T_g)/(T_m - T_c) \quad (1)$$

Where T_c corresponds to the first crystallisation peak temperature and T_m the first melting temperature.

The K_{gl} values calculated for the two series of Pb—Ge—Se—Te glasses are tabulated in Table I. Higher values of K_{gl} imply higher thermal stability of the glass. It can be seen from the K_{gl} data that glasses with $x \geq 9$ at. wt% Pb in series I and glasses with $x \geq 21$ at. wt% Ge in series II have a higher thermal stability.

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

$$d[\ln(\dot{\theta}/T_r^2)]/d[1/T_r] = -E_r/R \quad (2)$$

(where $\dot{\theta}$ is the heating rate, E_r is the activation energy of the kinetic reaction, T_r is the reaction temperature and R is the universal gas constant). The Kissinger's plots obtained for the glass transition temperature in Pb_xGe_{42-x}Se₄₈Te₁₀ and Pb₂₀Ge_xSe_{70-x}Te₁₀ glasses are shown in Fig. 3a. and b respectively. The solid lines are least-squares fit to the data. The activation energy of glass transition (ΔE_g) estimated from the slope of the Kissinger's plots is shown in Fig. 5a and b respectively. Since the activation energy is a measure of the hindrance posed by the glassy network for the reaction, 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 at $x = 21$ at. wt% Ge in series II. A minimum in the activation energy also implies that the

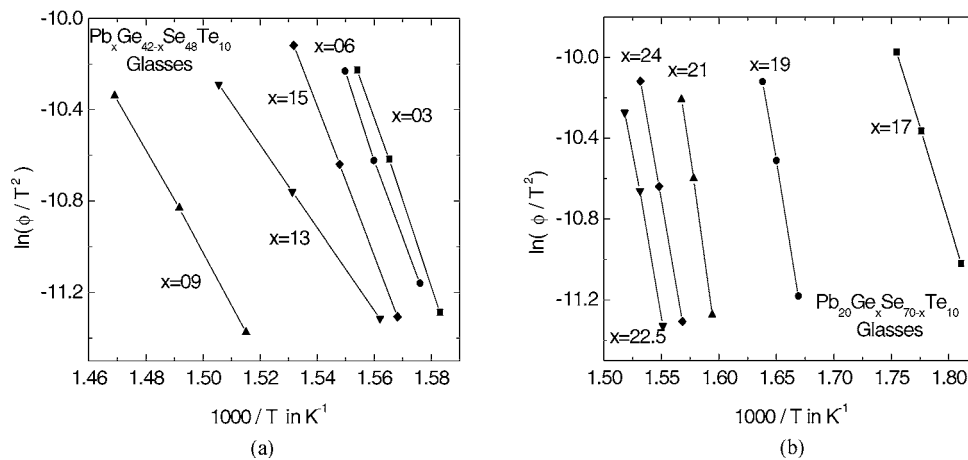


Figure 4 Kissinger's plots obtained for first crystallisation in (a) $\text{Pb}_x\text{Ge}_{42-x}\text{Se}_{48}\text{Te}_{10}$ glasses and (b) $\text{Pb}_{20}\text{Ge}_x\text{Se}_{70-x}\text{Te}_{10}$ glasses.

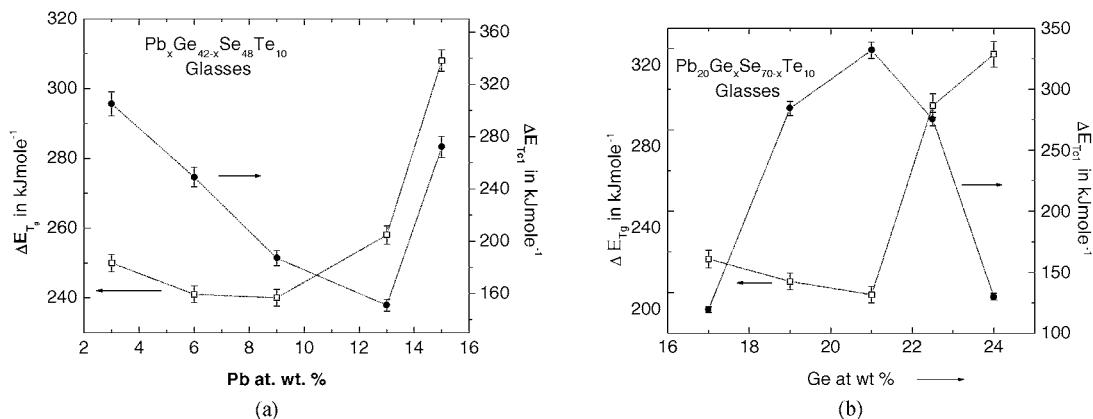


Figure 5 Variation of activation energy for glass transition and first crystallization peak in (a) $\text{Pb}_x\text{Ge}_{42-x}\text{Se}_{48}\text{Te}_{10}$ glasses and (b) $\text{Pb}_{20}\text{Ge}_x\text{Se}_{70-x}\text{Te}_{10}$ glasses.

glasses at these compositions undergo minimal configuration changes at the glass transition. It is interesting to note that activation energy increases sharply at the compositions at which the p- to n-type transition occurs. The Kissinger's plots corresponding to the first crystallisation are shown in Fig. 4a and b. The activation energy of crystallisation (ΔE_{c1}) for the two series of Pb—Ge—Se—Te glasses is also shown in Fig. 5a and b respectively. ΔE_{c1} plots for both the series of glasses exhibit inflexion points with a minimum for $x = 13$ at. wt% Pb in series I glasses and a maximum for $x = 21$ at. wt% Ge in series II glasses. The phase crystallising in series I glasses is most favoured at the composition with $x = 13$ at. wt% where as the crystalline phase nucleating in series II glasses is most hindered at the composition with $x = 21$ at. wt% Ge. The activation energy for glass transition and crystallisation obtained for the two series of glasses is tabulated in Table I.

The heat capacity (specific heat at constant pressure) jump at the glass transition temperature is an inherent property of a glass [19]. 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} 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 [20], ΔC_p could be correlated

with the fragility of a glass. Fragile glasses exhibiting a large ΔC_p undergo more configuration change at the glass transition. Strong glasses exhibit a small ΔC_p and minimal configuration changes at T_g . The variation of the heat capacity jump at T_g (ΔC_p) of the two series of glasses is shown in Fig. 6a and b respectively. The excess heat capacity at the T_g of both the series of glasses show a minimum near the composition with $x = 9$ at. wt% Pb (series I) and $x = 21$ at. wt% Ge (series II), which are the compositions at which the p- to n-type transition occurs. Thus the minimum in fragility is associated with the composition at which MCCR occurs in these glasses. A small ΔC_p is also a proof of a strong thermodynamic behaviour which indicates that the glass is not far away from its thermodynamic equilibrium [21]. It has been reported that a minimum in ΔC_p has been observed when glasses undergo a floppy to rigid transition [22, 23] in Ge—As—Se [24], Ge—Sb—Se [25, 26], Ge—As—Te and Si—As—Te [26] 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 co-ordinated 3d structure, leading a rigid glassy network, as reflected by the minimum in the excess heat capacity data.

The experimental data presented clearly indicates that the calorimetric parameters show anomalous behaviour at the composition at which the majority

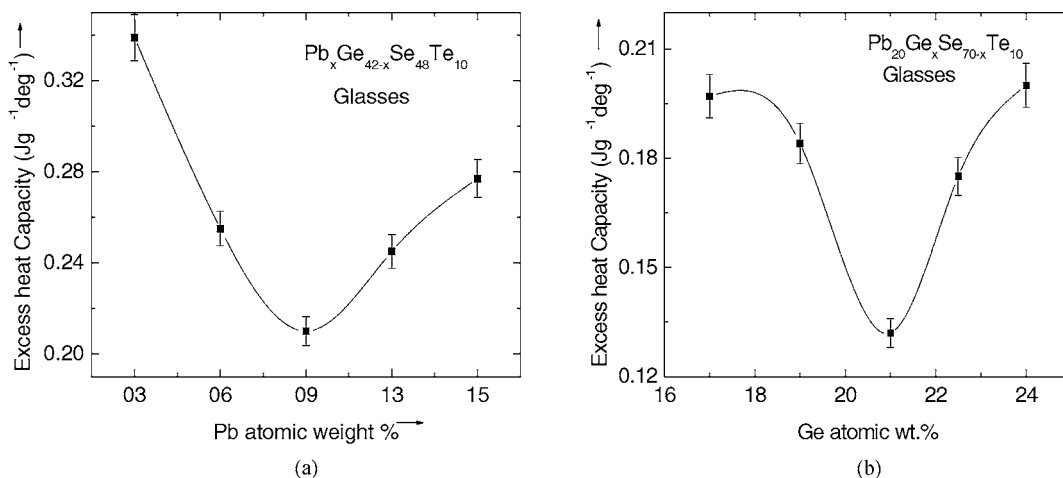


Figure 6 Variation of the heat capacity jump at glass transition of (a) Pb_xGe_{42-x}Se₄₈Te₁₀ glasses, and (b) Pb₂₀Ge_xSe_{70-x}Te₁₀ glasses.

charge carrier reversal occurs in both the series of Pb–Ge–Se–Te glasses. Interpretation of the composition dependence of T_g on the basis the average bond energy of the glasses predicts a preponderance of hetero-nuclear bonds at the compositions at which the carrier type reversal is observed. Analysis of the activation energy and the excess heat capacity at glass transition of these glasses shows that Pb₀₉Ge₃₃Se₄₈Te₁₀ and Pb₂₀Ge₂₁Se₄₉Te₁₀ glasses exhibit minimal configuration changes at the glass-to-super-cooled liquid transition. Other physical properties such as density, optical band gap and microhardness of Pb–Ge–Se–Te glasses consistently show [27] anomalous features at these compositions. These observations demonstrate that perceptible changes in bonding and network structure occur at the compositions at which the majority carrier type changes in Pb–Ge–Se glasses. Since the carrier reversal is brought about in these glasses by progressively changing the composition, a change in the bonding and network structure as a function of composition is to be expected. As already mentioned earlier, this is not a unique feature of Pb–Ge–Se–Te glasses alone, since DSC [7, 9, 12, 13, 14, 28] and density [29] studies on Pb–Ge–Se and Bi–Ge–Se glasses have also consistently shown such anomaly at the MCCR compositions. Since electrical properties are structure sensitive [30, 31], any physical property sensitive to changes in glassy network structure is bound to reflect the features observed in the electrical properties.

4. Conclusion

The non isothermal properties of two series of Pb–Ge–Se–Te glasses exhibiting p- to n-type charge carrier reversal has been reported in this paper. The present results on Pb₂₀Ge_xSe_{70-x}Te₁₀ glasses agree with the earlier reports on this series of glasses wherever such comparison is possible. The T_g behaviour of the two series of glasses have been interpreted in terms of the nature of chemical bonding and the change in the band structure of these glasses with composition. The composition dependence of T_g , T_{c1} , K_{gl} , ΔE_g and ΔC_p of both series of Pb–Ge–Se–Te glasses consistently show anomalous features at the compositions with $x = 9$ at. wt% Pb and $x = 21$ at. wt% Ge, which are

the compositions at which the conduction type change occurs. While the T_g data suggest the preponderance of hetero-nuclear bonds at these compositions, ΔE_g and ΔC_p suggest that these glasses undergo minimal configuration change at T_g . The present DSC study on two series of Pb–Ge–Se–Te glasses exhibiting MCCR phenomenon shows that changes in the chemical bonding and the nature of the glassy network occur at these compositions. These observations from a non-electronic property provides an insight on the influence of the network structure on the MCCR phenomenon in these glasses. Infrared spectroscopy may be of help in estimating the relative preponderance of Ge–Se and Pb–Se bonds in these glasses in support of the above arguments. X-ray diffraction study would throw light on the phases crystallising in the two series of Pb–Ge–Se–Te glasses at T_{c1} .

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