

Calorimetric investigations on As–Te–Se and Ge–As–Se glasses

K NANDAKUMAR and J PHILIP

Department of Physics and Instrumentation Centre, Cochin University of Science and Technology, Cochin 682 022, India

MS received 15 October 1993; revised 2 April 1994

Abstract. Results of calorimetric investigations performed on two groups of glasses, viz. As–Te–Se and Ge–As–Se, are described. The glass transition temperature T_g and specific heat at constant pressure C_p of these two families of glasses have been determined using a differential scanning calorimeter. The composition dependence of glass transition temperature and variation of heat capacity during transition are discussed.

Keywords. Calorimetric investigations; As–Te–Se; Ge–As–Se.

1. Introduction

Due to their interesting electronic and optoelectronic properties, glassy chalcogenide semiconductors have been studied extensively. Since in many of these applications the materials are activated by light or an electrical signal, a thorough understanding of their optical and electrical properties is necessary. A good knowledge of their thermodynamic properties is also important from fundamental and application points of view. Little effort has so far been devoted to determination of the thermodynamic properties of these materials. Since glassy materials are not in equilibrium, their properties strongly depend on the thermal history of the samples. In the glass transition region, the physical properties are dependent on time because, in this region, the experimental time scale becomes comparable to the time scale for structural rearrangements, the material will relax towards equilibrium and most of the physical properties do exhibit anomalous changes near glass transition temperature.

During the past few years a number of models have been proposed to explain the features observed in the composition dependence of the various physical properties of network glasses. The topological models based on constraints theory (Phillips 1979, 1981; Thorpe 1983; Phillips and Thorpe 1985) and structural dimensionality (Tanaka 1989) have been very successful in this regard. In these models the physical properties are discussed in terms of the average coordination number $\langle r \rangle$, which does not depend on the species of the valence bond. In several chalcogenide glasses two topological thresholds, one at $\langle r \rangle \simeq 2.40$ and the other at $\langle r \rangle \simeq 2.67$, have been established; the first corresponding to a mechanical threshold at which the network moves over from an elastically floppy type to a rigid type and the second corresponding to the transition from an essentially layered structure to a three-dimensional network due to cross-linking. In many chalcogenide glasses, especially ternary systems, it is still not very clear whether $\langle r \rangle = 2.40$ or $\langle r \rangle = 2.67$ corresponds to the rigidity percolation threshold, even though substantial work has been done on binary and ternary systems. It is possible that anomalies in the properties occur at both $\langle r \rangle = 2.40$ and $\langle r \rangle = 2.67$. Anomalies at both these $\langle r \rangle$ values in glass transition temperature and mean atomic volume have been reported in Ge–In–Se, Ge–Sb–Se and Ge–Ga–Se glasses (Giridhar and Mahadevan 1991; Mahadevan and Giridhar 1992, 1993). More

experimental data on different physical properties and on more systems are necessary to establish this argument. This work aims at providing experimental data on glass transition temperature and specific heat on two ternary systems and analysing them in the light of the above models.

In this work we report the results of the calorimetric measurements on samples belonging to the As–Te–Se and Ge–As–Se systems. The composition dependence of glass transition temperature (T_g) and heat capacity (C_p) during glass transition have been studied. In the As–Te–Se system the compositions studied can be represented as $As_xTe_5Se_{95-x}$, $As_xTe_{10}Se_{90-x}$ (with $x = 30, 35, 40, 45$ and 50) covering an average coordination number $\langle r \rangle$ in the range 2.3 to 2.5, and $As_{40}(Te, Se)_{60}$ with Te concentration varying from 0 to 20 at.% which are the stoichiometric compositions of the As–Te–Se system. In the Ge–As–Se system, compositions studied can be categorized into two sets as $Ge_xAs_{10}Se_{90-x}$ (with $x = 5, 10, 15, 20, 25, 28.5, 30, 35$ and 40) and $(Ge_{0.5}As_{0.5})_xSe_{100-x}$ (with $x = 10, 20, 26.7, 30, 40, 44, 50$ and 60) covering an average coordination number $\langle r \rangle$ ranging from 2.15 to 2.9.

2. Experimental

Samples belonging to the As–Te–Se and Ge–As–Se systems were prepared by the well-established melt quenching technique. The amorphous nature of the samples was checked by X-ray diffractometry. The glass transition temperature T_g and specific heat at constant pressure C_p were determined using a Perkin-Elmer differential scanning calorimeter (DSC-7).

The initial calibration of the instrument was carried out using standard calibrants such as indium and zinc, over the temperature range 50°C to 450°C. Weighed samples in the form of powder were sealed in aluminium pans and scanned through their T_g .

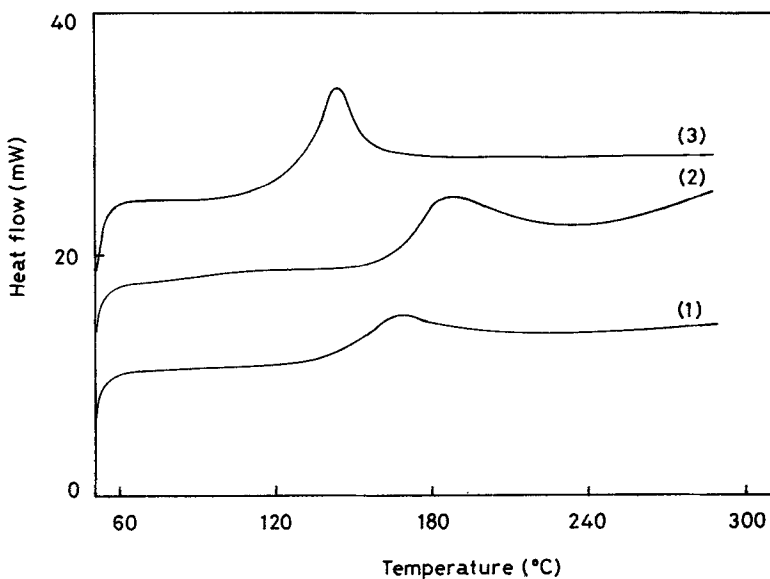


Figure 1. DSC curves of (1) $As_{30}Te_{20}Se_{40}$, (2) $As_{45}Te_{10}Se_{45}$ and (3) $As_{30}Te_5Se_{65}$.

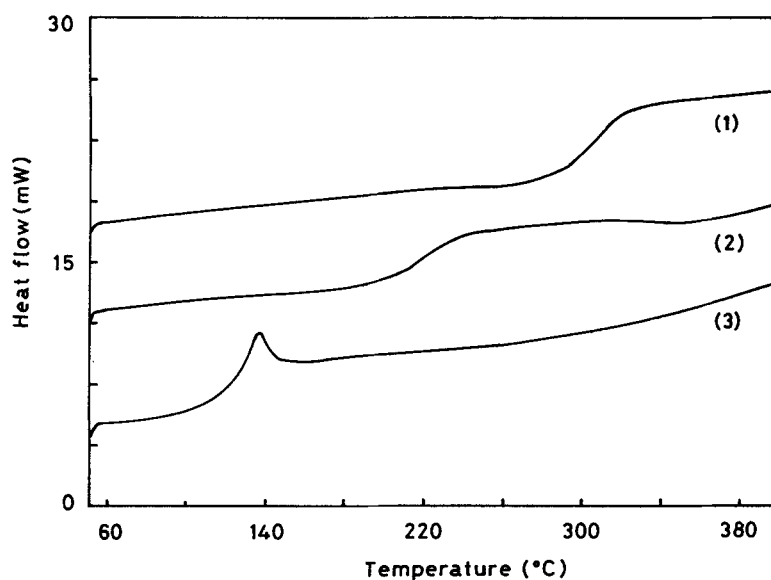


Figure 2. DSC curves of (1) $\text{Ge}_{25}\text{As}_{10}\text{Se}_{65}$, (2) $\text{Ge}_{20}\text{As}_{10}\text{Se}_{70}$ and (3) $\text{Ge}_{10}\text{As}_{10}\text{Se}_{80}$.

Table 1. The composition, average coordination number $\langle r \rangle$ and glass transition temperature T_g of As-Te-Se glasses.

Composition As-Te-Se	$\langle r \rangle$	T_g (K)
30:05:65	2.30	398
35:05:60	2.35	431
40:05:55	2.40	444
45:05:50	2.45	447
50:05:45	2.50	449
30:10:60	2.30	390
35:10:55	2.35	428
40:10:50	2.40	439
45:10:45	2.45	442
50:10:40	2.50	446
40:00:60	2.40	453
40:15:45	2.40	431
40:20:40	2.40	420

The heating rate used for all the samples was $20^\circ\text{C}/\text{min}$. The DSC curves of a few selected samples of As-Te-Se and Ge-As-Se glasses are shown in figures 1 and 2 respectively. The DSC curves do not show any trace of crystallization in any of the samples investigated suggesting that these glasses are highly glass-forming over a wide composition range. The glass transition temperature T_g is determined as the temperature corresponding to the onset of glass transition which appears as an endothermic baseline shift of the DSC curve, and is tabulated in tables 1 and 2. The

Table 2. The composition, average coordination number $\langle r \rangle$ and glass transition temperature T_g of Ge-As-Se glasses.

Composition Ge:As:Se	$\langle r \rangle$	T_g (K)
05:10:85	2.20	382
10:10:80	2.30	391
15:10:75	2.40	433
20:10:70	2.50	470
25:10:65	2.60	556
28.5:10:61.5	2.67	576
30:10:60	2.70	618
35:10:55	2.80	645
40:10:50	2.90	646
05:05:90	2.15	378
10:10:80	2.30	391
13.35:13.35:73.3	2.40	448
15:15:70	2.45	438
20:20:60	2.60	448
22:22:56	2.66	545
25:25:50	2.75	570
30:30:40	2.90	605

average coordination numbers $\langle r \rangle$ of the samples investigated are also given in these tables.

The specific heat at constant pressure C_p of all the samples was determined by the ratio method (O'Neill 1966). In this method, the baseline corresponding to the temperature range of interest is first obtained. After this, two independent DSC runs are performed under identical conditions; one with a weighed quantity of the standard reference sample (α -Al₂O₃) and the other with a weighed quantity of the experimental sample. Then the specific heat C_p of the sample can be calculated using the relation

$$C_p/C'_p = m'y/my',$$

where C'_p , m' and y' are the specific heat at constant pressure, mass and ordinate deflection of the reference standard respectively, and y and m are the ordinate deflection and mass of the experimental sample. Since the specific heat of α -Al₂O₃ is known from literature (Furukawa *et al* 1956), the C_p of each sample can be calculated using the above equation. The percentage error in C_p measurement using this technique is of the order of 5.

3. Results and discussion

The variation of T_g with average coordination number $\langle r \rangle$, i.e. with increase in As concentration, for As_xTe₅Se_{95-x} and As_xTe₁₀Se_{90-x} glasses is shown in figure 3. The glass transition temperature gradually increases as the As concentration is increased from 30 to 50 at.%. The rate of increase is higher for those with $x < 40$, in both cases. The variation of T_g with Te concentration for the stoichiometric com-

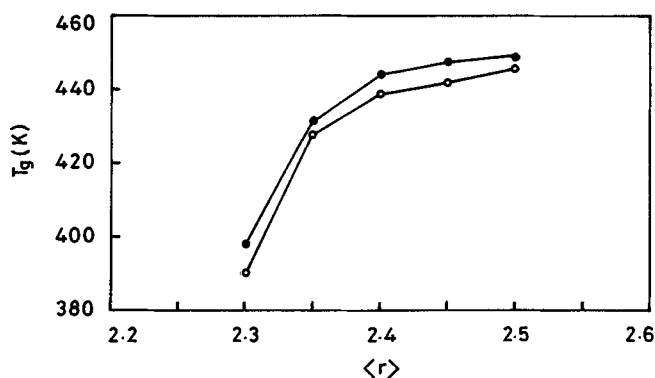


Figure 3. Variation of glass transition temperature T_g with average coordination number $\langle r \rangle$ of $As_xTe_5Se_{95-x}$ (●) and $As_xTe_{10}Se_{90-x}$ (○) glasses.

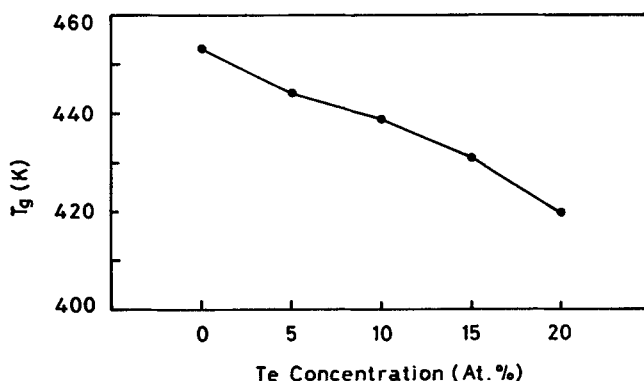


Figure 4. Variation of T_g with Te concentration for the stoichiometric compositions of the As-Te-Se glasses.

positions is shown in figure 4. The glass transition temperature gradually decreases as the Te concentration is increased from 0 to 20 at. %.

The variation of T_g with average coordination number $\langle r \rangle$ for $Ge_xAs_{10}Se_{90-x}$ and $(Ge_{0.5}As_{0.5})_xSe_{100-x}$ glasses are shown in figure 5. As the average coordination number $\langle r \rangle$ is increased, T_g also increases gradually and shows a saturation behaviour beyond $\langle r \rangle = 2.67$. Another important feature observed is that the T_g values for both glasses follow the same variation up to around $\langle r \rangle = 2.67$ and then deviate showing a saturation behaviour beyond $\langle r \rangle = 2.67$. There is no significant anomaly near $\langle r \rangle = 2.4$ but a change in the slope of the curve is observable at this $\langle r \rangle$ value.

The As-Te-Se system basically behaves like a binary system with As_2Se_3 and As_2Te_3 structural units. With the stoichiometric composition ($x = 40$) as reference, which corresponds to an average coordination number $\langle r \rangle = 2.4$, the T_g values increase more rapidly for the Se-rich glasses than for the As-rich glasses. Even though there is no sudden upturn in the $\langle r \rangle$ dependence of T_g to signal any threshold crossing, there is a clear slope change at $\langle r \rangle = 2.40$. T_g generally represents the strength or rigidity of the glass structure. As the average coordination number is increased, the system gradually undergoes a percolation transition from a polymeric glass state to

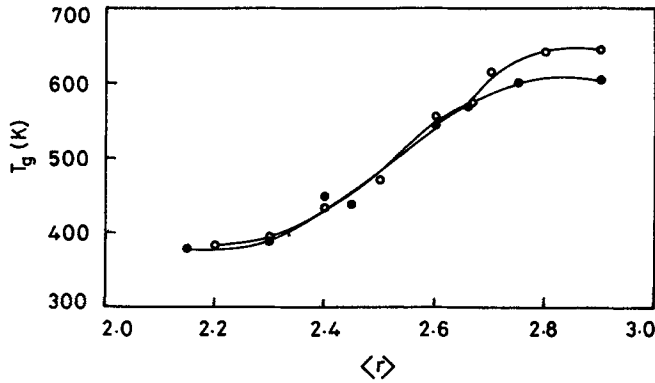


Figure 5. Variation of T_g with $\langle r \rangle$ of $\text{Ge}_x\text{As}_{10}\text{Se}_{90-x}$ (O) and $(\text{Ge}_{0.5}\text{As}_{0.5})_x\text{Se}_{100-x}$ (●) glasses.

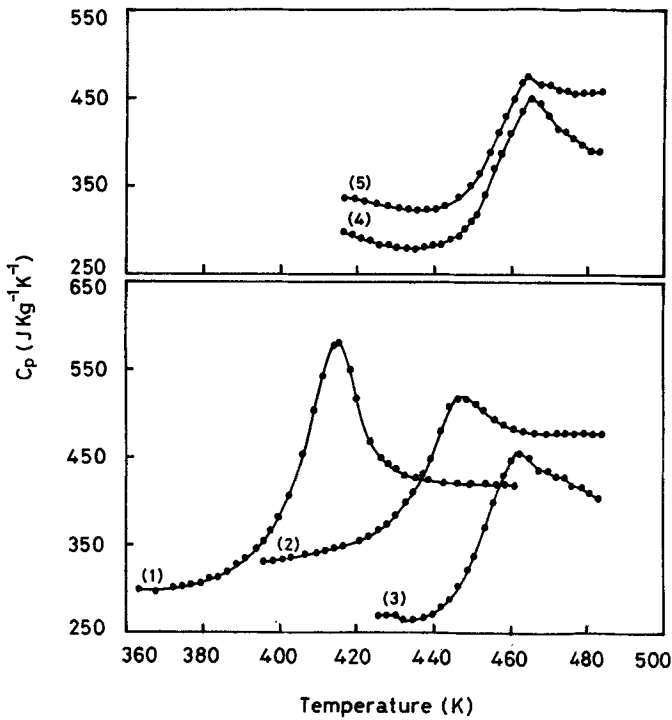


Figure 6. Variation of specific heat with temperature for (1) $\text{As}_{30}\text{Te}_5\text{Se}_{65}$, (2) $\text{As}_{35}\text{Te}_5\text{Se}_{60}$, (3) $\text{As}_{40}\text{Te}_5\text{Se}_{55}$, (4) $\text{As}_{45}\text{Te}_5\text{Se}_{50}$ and (5) $\text{As}_{50}\text{Te}_5\text{Se}_{45}$.

a rigid network structure registering a gradual increase in T_g for both As-Te-Se and Ge-As-Se glasses.

For the stoichiometric compositions of the As-Te-Se system, with increase in Te concentration more and more As_2Se_3 structural units will be replaced by As_2Te_3 structural units. Since Se and Te are isovalent, one cannot expect any drastic variation in T_g by the replacement of Se by Te. However, with increase in Te concentration,

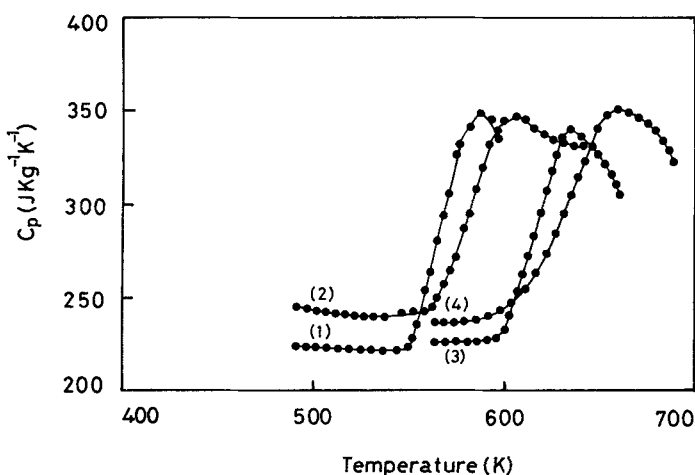


Figure 7. Variation of specific heat with temperature for (1) $\text{Ge}_{20}\text{As}_{20}\text{Se}_{60}$, (2) $\text{Ge}_{22}\text{As}_{22}\text{Se}_{56}$, (3) $\text{Ge}_{25}\text{As}_{25}\text{Se}_{50}$ and (4) $\text{Ge}_{30}\text{As}_{30}\text{Se}_{40}$.

the bond energy of the system on an average is reduced due to the replacement of As_2Se_3 structural units by As_2Te_3 units registering a gradual decrease in the glass transition temperature.

The features exhibited by Ge–As–Se suggest that the glass transition behaviour depends on the average coordination number and shows that T_g is a universal function of $\langle r \rangle$ up to and somewhat beyond the percolation threshold. Based on the above observations it can be concluded that the changes in the network topology with $\langle r \rangle$ can be interpreted in the light of the formation and development of layered structure in these glasses (Tanaka 1988, 1989). The present results also indicate that the mechanical threshold at $\langle r \rangle = 2.4$, predicted on the basis of short-range interactions (Phillips 1979; Thorpe 1983), is rather dormant and that alone is not sufficient to fully account for the structural properties of these glasses.

Heat capacity measurements in the transition region have been done at a heating rate of $20^\circ\text{C}/\text{min}$ on all the samples belonging to the As–Te–Se and Ge–As–Se systems covering a temperature range of 50°C to the region beyond glass transition. The variation of specific heat with temperature near glass transition in selected samples is depicted in figures 6 and 7 respectively. In all the samples, during glass transition a sharp increase in C_p is seen due to excess anharmonic contribution to the specific heat. The observed peak in these systems occurs because the structural relaxation times are of the same order as the time scale of the experiment (Schnaus *et al* 1970). In keeping with the general behaviour of chalcogenide glasses (Schnaus and Moynihan 1971; Schnaus *et al* 1972; Thornburg and Johnson 1975), it is observed that ΔC_p , the change in C_p during glass transition, is fairly large for the Se-rich glasses.

The variation of ΔC_p with average coordination number for the $\text{As}_x\text{Te}_5\text{Se}_{95-x}$ and $\text{As}_x\text{Te}_{10}\text{Se}_{90-x}$ glasses is shown in figure 8. In both groups ΔC_p gradually decreases as the average coordination number is increased from 2.3 to 2.5. The present result in As–Te–Se systems indicates that the total number of structural configurations available for the molecules decreases with increasing As concentration. A change in slope, as $\langle r \rangle = 2.40$ is approached, is clearly visible in these figures. This is supportive of the percolation transition of the network at this critical composition.

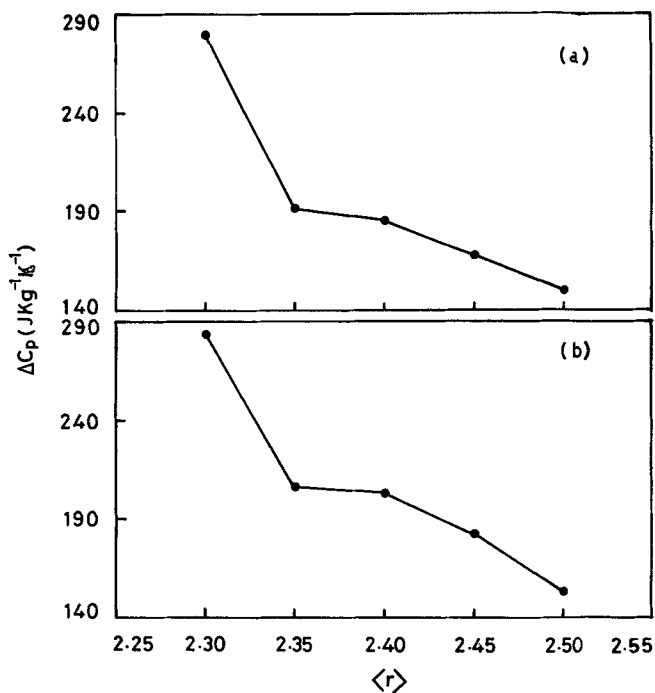


Figure 8. Variation of ΔC_p with average coordination number $\langle r \rangle$ for (a) $As_xTe_5Se_{95-x}$ and (b) $As_xTe_{10}Se_{90-x}$ glasses.

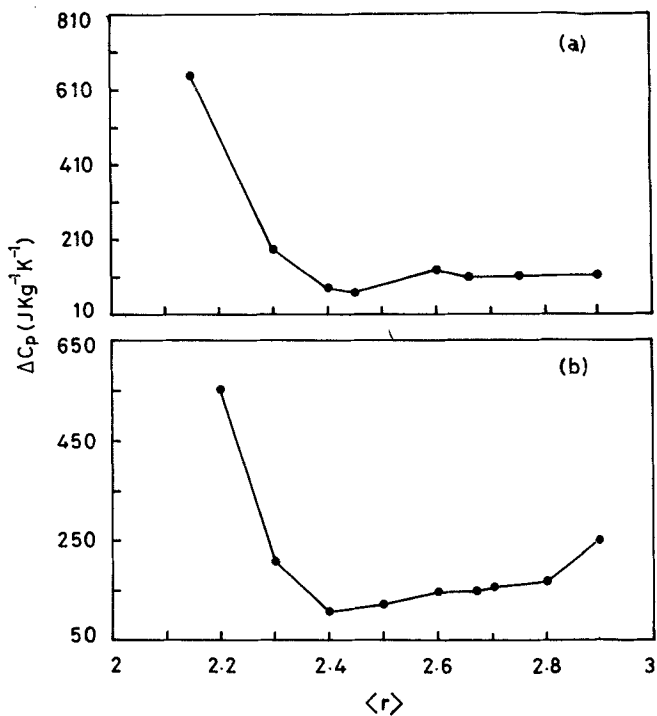


Figure 9. Variation of ΔC_p with average coordination number $\langle r \rangle$ for (a) $Ge_xAs_{10}Se_{90-x}$ and (b) $(Ge_{0.5}As_{0.5})_xSe_{100-x}$ glasses.

The variation of ΔC_p with average coordination number $\langle r \rangle$ for $(\text{Ge}_{0.5}\text{As}_{0.5})_x\text{Se}_{100-x}$ and $\text{Ge}_x\text{As}_{10}\text{Se}_{90-x}$ glasses is shown in figure 9. For both these systems the ΔC_p values decrease gradually and show a minimum around $\langle r \rangle = 2.4$, which corresponds to the mechanical threshold for these systems. The heat capacity jump at T_g in the vicinity of $\langle r \rangle = 2.4$ is very small and smeared out as the average coordination number is further increased. This implies a strong resistance to structural degradation in the liquid state and has been correlated to the minimum fragility in the overall viscous-liquid behaviour (Angell 1985). The source of ΔC_p at glass transition is generally taken to be configurational and the increase in the value of C_p above T_g is due to the addition of translational and/or rotational modes becoming available by the breakage of bonds forming the glass network (Jones 1971; Thornburg and Johnson 1975). Though a qualitative explanation for the observed variation in ΔC_p has not been possible, it is generally believed that ΔC_p arises from the thermal degradation of the network with increasing temperature.

4. Conclusions

The variation of the glass transition temperature and change in C_p at T_g in As-Te-Se and Ge-As-Se glasses indicate that in a pseudobinary system like As-Te-Se, the percolation transition takes place at $\langle r \rangle = 2.40$ whereas in a IV-V-VI ternary system like Ge-As-Se, features are seen at the topological thresholds of $\langle r \rangle = 2.40$ and $\langle r \rangle = 2.67$. This indicates that in these systems there is coexistence of the mechanical threshold at $\langle r \rangle = 2.40$ at which the network goes from an elastically floppy type to a rigid type and at $\langle r \rangle = 2.67$ at which a transition from an essentially layered structure to a three-dimensional network due to cross-linking takes place. More experimental data are required to confirm these findings.

Acknowledgements

One of the authors (KN) thanks CSIR for providing a senior research fellowship. The work has been supported by the Department of Atomic Energy.

References

- Angell C A 1985 *J. Non-Cryst. Solids* **73** 1
 Furukawa G T, Douglas T B, McCoskey R E and Ginnings D C 1956 *J. Res. Nat. Bur. Std.* **57** 67
 Giridhar A and Mahadevan S 1991 *J. Non-Cryst. Solids* **134** 94
 Jones G O 1971 in *Glass* (London: Chapman and Hall)
 Mahadevan S and Giridhar A 1992 *J. Non-Cryst. Solids* **143** 52
 Mahadevan S and Giridhar A 1993 *J. Non-Cryst. Solids* **152** 42
 O'Neill M J 1966 *Anal. Chem.* **38** 1331
 Phillips J C 1979 *J. Non-Cryst. Solids* **34** 153
 Phillips J C 1981 *J. Non-Cryst. Solids* **43** 37
 Phillips J C and Thorpe M F 1985 *Solid State Commun.* **53** 699
 Schnaus U E, Moynihan C T, Gammon R W and Macedo P B 1970 *Phys. Chem. Glasses II* **213**
 Schnaus U E and Moynihan C T 1971 *Mater. Sci. Eng.* **7** 268
 Schnaus U E, Marshall A and Moynihan C T 1972 *J. Am. Ceram. Soc.* **55** 180
 Tanaka K 1988 *J. Non-Cryst. Solids* **103** 149
 Tanaka K 1989 *Phys. Rev.* **B39** 1270
 Thornburg D D and Johnson R I 1975 *J. Non-Cryst. Solids* **17** 2
 Thorpe M F 1983 *J. Non-Cryst. Solids* **57** 355