Topological phase transitions in Ge-In-Se glasses

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The investigation of the composition dependence of the various properties of chalcogenide glasses has increased in recent years for two reasons. The first one is scientific because this type of research provides new challenging fundamental problems for solid-state physicists. Second, many of these glasses have found applications in solid-state devices [1–3]. The Ge-In-Se system provides one member of these glasses and forms bulk glasses, by melt-quenching, over a wide range of compositions [4]. This makes it a suitable model system for the investigation of the composition dependence of its properties.

The composition dependence of the glass transition temperature [5, 6], the mean atomic volume [7], the macroscopic density [8] and the plasmon energy losses [9], for the Ge-In-Se glasses, was earlier reported by us. Composition dependence studies on other glassy alloys were reported for Ge-Se [10, 11], Ge-Se-Pb [12, 13], Ge-Se-Ga [14, 15], Ge-Se-As [16, 17], Ge-Se-Te [18], Ge-Se-Sb [19–25], Ge-Te-As [26], Ge-Se-Sb-Te and Ge-Se-Sb-As-Te [23–25], Ge-S-Sb [27, 28] and Ge-S-As [17].

In this paper, the variation of the crystallization temperature with composition, for glasses belonging to the Ge-In-Se system, is reported and discussed.

Glassy alloys within the composition range $6 \leq x \leq 34$ (x in at %), in the $Ge_x In_6 Se_{94-x}$ system, were prepared by the classical melt-quenching method. The method consisted of sealing, under a vacuum of $\approx 10^{-5}$ Torr, the appropriate atomic proportions of high purity Ge, In, and Se in cylindrical quartz ampoules. The ampoules were then placed in an electric furnace and heated to a temperature of $450\,°C$ for one day. Subsequently the temperature of the furnace was raised to $850\,°C$ and held at this temperature for two days. The ampoules at this temperature were continuously shaken to homogenize the melt. To obtain the glasses, the ampoules were quenched to $0\,°C$ in an ice-water mixture.

The differential scanning calorimetry (DSC) measurements were performed using a Setaram DSC 92 instrument with a scan rate of 10 K/min. The powdered samples (≈ 20–30 mg) were sealed in aluminum pans and compared with empty aluminum pans. The temperature calibration of the instrument was carried out using the well known melting temperature of high purity indium supplied with the instrument. The error in the measurement of T_p was estimated to be ± 1 K.

The composition of the glasses prepared and their corresponding peak crystallization temperatures are given in Table I. The average coordination number, m, was evaluated using the standard method [15, 29]. For $Ge_x In_y Se_z$, m is given by

$$m = 8 - \frac{[4x + 3y + 6z]}{100} \qquad (1)$$

where 4, 3, and 6 are the number of valence electrons in Ge, In, and Se, respectively, and x, y, and z are their respective concentrations in the glass composition. Equation 1 leads to a formula for m, for $Ge_x In_6 Se_{94-x}$ glasses under investigation, given by

$$m = 2.18 + 0.02\,x \qquad (2)$$

The variation of T_p with the amount of Ge content in the glass and with the average coordination number are shown in Fig. 1 and 2, respectively. In Fig. 2, a change in slope is observed at an m value equal to 2.4 (corresponding to the composition with $x = 11$ at %). This feature can be accounted for on the basis of Phillips-Thorpe's rigidity percolation model. Phillips [30], by considering short-range order structures only and equating the number of topological constraints per atom (N_c) to the number of degrees of freedom per atom (N_d), obtained an m value which is equal to 2.4 at which the glass possesses a mechanically optimized structure. This structural phase transition, at this m value, was also observed by Thorpe [31] from counting the number of zero frequency modes. In the glass-forming region (GFR) [31], networks with $m < 2.4$ (polymeric glasses) are referred to as underconstrained and contain large floppy or spongy regions with few rigid inclusions. For networks with $m > 2.4$ (amorphous solids), referred to as overconstrained, the rigid regions have percolated to

TABLE I Glasses prepared and their peak crystallization temperatures (T_p); compositions are in at % and T_p in K

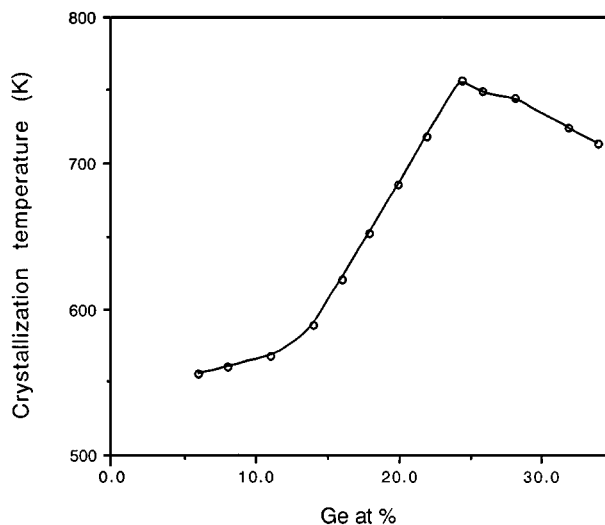| Glass number	Ge (at %)	Se (at %)	In (at %)	T_p (K) (± 1)	m
1	6	88	6	555	2.30
2	8	86	6	560	2.34
3	11	83	6	568	2.40
4	14	80	6	589	2.46
5	16	78	6	621	2.50
6	18	76	6	652	2.54
7	20	74	6	685	2.58
8	22	72	6	718	2.62
9	24.5	69.5	6	757	2.67
10	26	68	6	749	2.70
11	28.33	65.67	6	744	2.75
12	32	62	6	724	2.82
13	34	60	6	713	2.86

Figure 1 Variation of T_p with the amount of Ge at % present in the glass. Lines through data points are drawn as a guide for the eye.
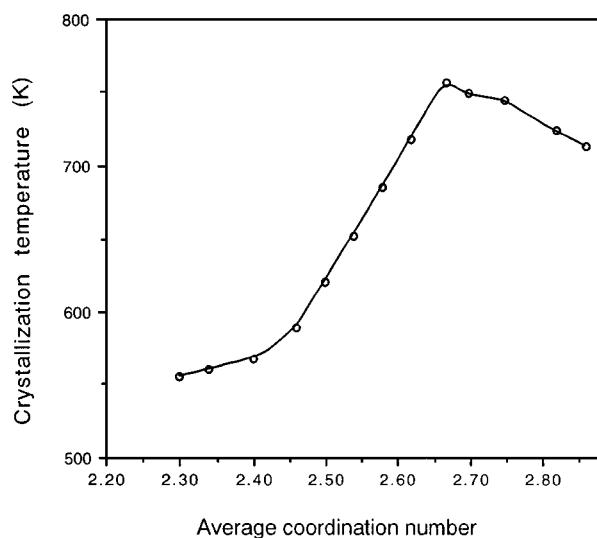

Figure 2 Variation of T_p with the average coordination number. Lines through data points are drawn as a guide for the eye.

form a rigid solid with a few floppy or spongy inclusions. The composition with $m = 2.4$ is a percolation threshold at which the transition from floppy-to-rigid network takes place. Therefore, the change in slope in the T_p-m dependence at $m = 2.4$, observed in the investigated networks, is attributed to the floppy-to-rigid transition.

Recently, Tanaka in a series of papers [32–34], showed that the inclusion of medium-range order structures into the Phillips-Thorpe balance condition, leads to the prediction of a threshold at $m = 2.67$. This threshold can be understood provided that the networks undergo a structural transition from two-dimensional (2-D) structures to three-dimensional (3-D) networks due to the increase in the number of cross-linked sites. The observed maximum in T_p at $m = 2.67$ (corresponding to the $Ge_{24.5}In_6Se_{69.5}$ composition), which coincides with Tanaka's prediction, is therefore attributed to the 2D $\rightarrow$ 3D transition taking place in these glasses. The reported topological thresholds, for the glasses under investigation, were also observed for other glassy systems [34].

In conclusion, the composition dependence of the peak crystallization temperatures, in Ge-In-Se glasses, reveals peculiarities at m values of 2.4 and 2.67. These peculiarities are caused by the Phillips-Thorpe's and Tanaka's topological transitions, respectively.

References

1. D. R. SIMONS, A. J. FABER and H. DE WAAL, *J. Non-Cryst. Solids* **185** (1995) 283.
2. K. WEI, D. P. MACHEWIRTH, J. WENZEL, E. SNITZER and G. H. SIGEL Jr., *J. Non-Cryst. Solids* **182** (1995) 257.
3. P. PRAKASH, S. ASOKAN and D. B. GHARE, *J. Phys. D: Appl. Phys.* **29** (1996) 2004.
4. Z. U. BORISSOVA, "Glassy Semiconductors" (Plenum, 1981).
5. G. SAFFARINI and A. SCHLIEPER, *Appl. Phys.* **A61** (1995) 29.
6. J. M. SAITER, J. LEDRU, G. SAFFARINI and S. BENAZETH, *Materials Lett.* **28** (1996) 451.
7. G. SAFFARINI and A. SCHLIEPER, *Phys. Stat. Sol.* (b) **191** (1995) 243.
8. *Idem., J. Mat. Sci. Lett* **15** (1996) 463.
9. G. SAFFARINI and M. NEUMANN, *Solid St. Commun.* **95** (1995) 577.
10. A. K. AGNIHOTRI, A. KUMAR and A. NIGAM, *Philos. Mag. Lett* **58** (1988) 63.
11. A. KUMAR, S. GOEL and S. K. TRIPATHI, *Phys. Rev.* **B38** (1988) 13432.
12. M. K. RABINAL, N. RAMESH, K. S. SANGUNNI and E. S. R. GOPAL, *Philos. Mag.* **B70** (1994) 89.
13. M. K. RABINAL, K. S. SANGUNNI, E. S. R. GOPAL and S. V. SUBRAMANYAM, *Physica* **B205** (1995) 403.
14. A. GIRIDHAR and S. MAHADEVAN, *J. Non-Cryst. Solids* **126** (1990) 161.
15. S. MAHADEVAN and A. GIRIDHAR, *ibid.* **152** (1993) 42.
16. D. ARSOVA, E. SKORDEVA and E. VATEVA, *Solid St. Commun.* **90** (1994) 299.
17. E. SKORDEVA and D. ARSOVA, *J. Non-Cryst. Solids* **192 & 193** (1995) 665.
18. R. GANESAN, A. SRINIVASAN, K. N. MADHUSOODANAN, K. S. SANGUNNI and E. S. R. GOPAL, *Phys. Stat. Sol.* (b) **190** (1995) K 23.
19. A. GIRIDHAR, P. S. L. NARASIMHAM and S. MAHADEVAN, *J. Non-Cryst. Solids* **37** (1980) 165.
20. *Idem., ibid.* **43** (1981) 29.
21. P. S. L. NARASIMHAM, A. GIRIDHAR and S. MAHADEVAN, *ibid.* **43** (1981) 365.
22. D. R. SWILER, A. K. VARSHNEYA and R. M. CALLAHAN, *ibid.* **125** (1990) 250.
23. A. N. SREERAM, D. R. SWILER and A. K. VARSHNEYA, *ibid.* **127** (1991) 287.
24. A. N. SREERAM, A. K. VARSHNEYA and D. R. SWILER, *ibid.* **128** (1991) 294.
25. *Idem., ibid.* **130** (1991) 225.
26. A. SRINIVASAN, K. RAMESH, K. N. MADHUSOODANAN and E. S. R. GOPAL, *Philos. Mag. Lett.* **65** (1992) 249.
27. E. SAVOVA, E. SKORDEVA and E. VATEVA, *J. Phys. Chem. Solids* **55** (1994) 575.
28. E. VATEVA and E. SAVOVA, *J. Non-Cryst. Solids* **192 & 193** (1995) 145.
29. J. Z. LIU and P. C. TAYLOR, *Solid St. Commun.* **70** (1989) 81.
30. J. C. PHILLIPS, *J. Non-Cryst. Solids* **34** (1979) 153.
31. M. F. THORPE, *ibid.* **57** (1983) 355.
32. K. TANAKA, *ibid.* **97 & 98** (1987) 391.
33. *Idem., ibid.* **103** (1988) 149.
34. *Idem., Phys. Rev.* **B39** (1989) 1270.