JOURNAL OF MATERIALS SCIENCE **32** (1997) 5889–5893

Temperature-modulated differential scanning calorimetry studies of the structure of bulk and film $Ge_xAs_yS_{60}$ chalcogenide glasses

T. WAGNER*, S. O. KASAP
Electronic Materials Research Laboratories, Department of Electrical Engineering, University of Saskatchewan, Saskatoon, Canada S7N 5A9
K. PETKOV
Bulgarian Academy of Sciences, Central Laboratory of Photoprocesses, Sofia, Bulgaria

The recent novel temperature-modulated differential scanning calorimetry (TA Instruments MDSC^{TM}) technique has been applied to the measurement of thermal properties of $Ge_xAs_yS_{60}$ chalcogenide glasses in the glass transition region in bulk glasses and in their thin films. The reversing and non-reversing heat flows through the glass transformation region during both heating and cooling schedules were measured and the values of the parameters, T_g, ΔH, C_p and ΔC_p, which characterize the thermal events in the glass transition region, were determined. The structurally determined parameters, T_g, ΔH, C_p and ΔC_p, reveal significant changes with composition because in the $Ge_xAs_yS_{60}$ glasses the average coordination number, $\langle r \rangle$, increases from 2.4 to 2.8 with increasing x from 0 to 40 at% Ge. A maximum in T_g, ΔH and C_p and a minimum in the heat capacity change, ΔC_p, at T_g occur near the composition for which $x \approx 30$ at% Ge. These extrema which appear in both films and bulk glasses are ascribed to a change in the network function of Ge atoms replacing As atoms in a covalent network. Recent structural models for chalcogenide glasses have been considered to explain the observed thermal properties.

1. Introduction

Glasses in ternary systems Ge–As–X, where X is a chalcogen (S, Se or Te), are of considerable interest as infrared-transmitting materials [1]. The optimum compositions in terms of glass-forming ability, ease of fabrication, high softening temperature and strength are of considerable interest. Temperature-modulated differential scanning calorimetry (MDSC) is a new experimental method that has been described in more detail in the original papers [2–6] together with the results of measurements of various thermal events. The temperature-modulated differential scanning calorimeter operates essentially in the same way as a typical heat flux differential scanning calorimeter [7], but with an option that allows the sample temperature to be modulated sinusoidally about a constant ramp, i.e., the temperature, T, at time, t, is given by

$$T = T_0 + rt + A\sin\left(\frac{2\pi t}{P}\right) \qquad (1)$$

where T_0 is the initial (or starting) temperature, r is the heating rate (which may also be a cooling ramp, q), A is the amplitude of the modulation and P is the period. The resulting instantaneous heating rate, dT/dt, therefore varies sinusoidally about the average heating rate, r. The apparatus measures the amplitude of the instantaneous heat flow and the average heat flow (HF), called the total heat flow, and then by carrying out a suitable Fourier deconvolution of the measured quantities (also incorporating the sinusoidal temperature signal) it determines two quantities: reversing heat flow (RHF) and non-reversing heat flow (NHF). The reader is referred to the recent articles on the interpretation of MDSC and its application to various materials (see, for example, [8, 9]).

Recently there has been much interest in studying the changes in physicochemical, thermal, mechanical and optical properties of multicomponent chalcogenide glasses and thin films resulting from changes in the average coordination number, $\langle r \rangle$ (see, for example, [10–13]). Topological models, such as the constraints model [14, 15] and structural transition model [16], have been used in the interpretation of the compositional dependence of these properties. In an effort to elucidate the structure of these potentially important materials, T_g, ΔH, C_p and ΔC_p, in the pseudobinary system $Ge_xAs_yS_{60}$ (where $x + y = 40$

---

* On research leave from the Department of General and Inorganic Chemistry, Pardubice University, Pardubice, Czech Republic.

0022–2461 © *1997 Chapman & Hall*

and $x = 0$, 10, 20, 30 and 40 at%) were studied. The sulphur system was studied in preference to the corresponding Se and Te systems since the glass-forming range extends across the entire pseudobinary composition span. In recent papers we were able to show the usefulness of the MDSC technique in correlating the thermal properties obtained from RHF and NHF to the structure of the chalcogenide glasses, and in particular the average coordination number [17–19].

2. Experimental procedure

The glasses of the $Ge_xAs_yS_{60}$ systems, where $x = 0$, 10, 20, 30 and 40 at% Ge and $x + y = 40$, were prepared from pure elements. The elements Ge, As and S of purity 99.999% were weighed in a pre-cleaned and outgassed (heating under vacuum to 900 °C) quartz ampoules. Thus the ampoules were evacuated to a pressure of 1×10^{-3} Pa for 30 min and sealed. The synthesis was performed in the rocking furnace and exposed to a temperature of 900 °C for 24 h. Following heating, the ampoules with glass melt were quenched in water to a temperature of 273 K. Fragments of the bulk material were also used for thermal evaporation of the thin layers onto silica glass substrates in a 1×10^{-4} Pa vacuum at a rate of $1\ \mathrm{nm\,s^{-1}}$. The thickness of the evaporated layer was typically 1 μm. The composition of bulk materials and evaporated thin films were checked by X-ray micro-analysis. The film and bulk glass compositions agree within ± 1 at%.

The bulk samples were crushed into small pieces and the evaporated films were mechanically peeled from the substrates and immediately weighed into aluminium crimped pans and then sealed. Typical masses of the bulk and film sample were 20 mg and 18 mg, respectively.

First the samples were heated from $T_a = 20$ °C at a rate of 20 °C $\mathrm{min^{-1}}$ to a temperature, T_0, above their glass transformation region for that heating rate. The cell was stabilized at T_0 for 2 min and then a cooling scan was initiated at a rate of 5 °C $\mathrm{min^{-1}}$ down to the starting temperature, T_a. These schedules were performed in the non-modulated regime to ensure the same thermal history was set up. The value of T_g observed during a cooling scan is operationally defined in Fig. 1. The MDSC experiments were carried as described previously [19]. The modulated regime was applied to measure the modulated heat flow in heating and cooling schedules in the temperature region T_a–T_0. Typical MDSC thermograms showing HF, RHF, NHF and modulated heat flow (MHF) for $Ge_{10}As_{30}S_{60}$ glass are presented in Fig. 2. For the present experiments, r or $q = 5\,^\circ\mathrm{C\,min^{-1}}$, $A = \pm\,1.061$ °C and $P = 80$ s in Equation 1. The quantity ΔH refers to the observed enthalpy in the NHF in the glass transition region [20]. The specific heat capacity C_p was calculated from the RHF [20]. C_p, T_g and ΔC_p were determined from the step transition of heat capacity in the glass transition. A typical result for the glass of the composition $Ge_{10}As_{30}Se_{60}$ is shown in Fig. 3. The C_p value was established at $T_r = 0.9\,T_g$. For each composition, we carried out several experiments and all showed good reproducibility.

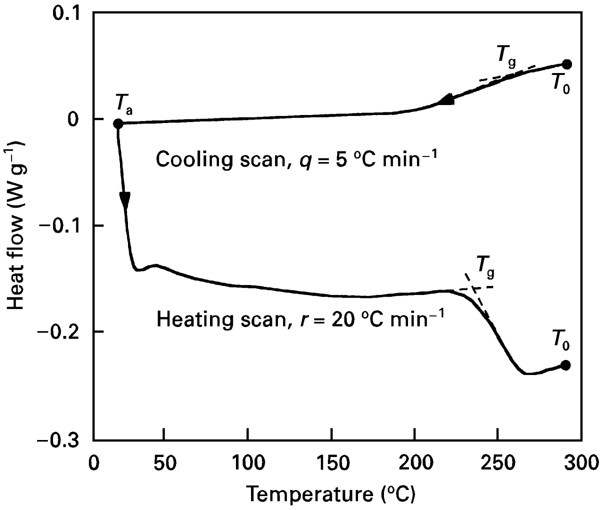

Figure 1 Typical heating and cooling scans that illustrate how each $Ge_{10}As_{30}S_{60}$ bulk sample was given the same thermal history.

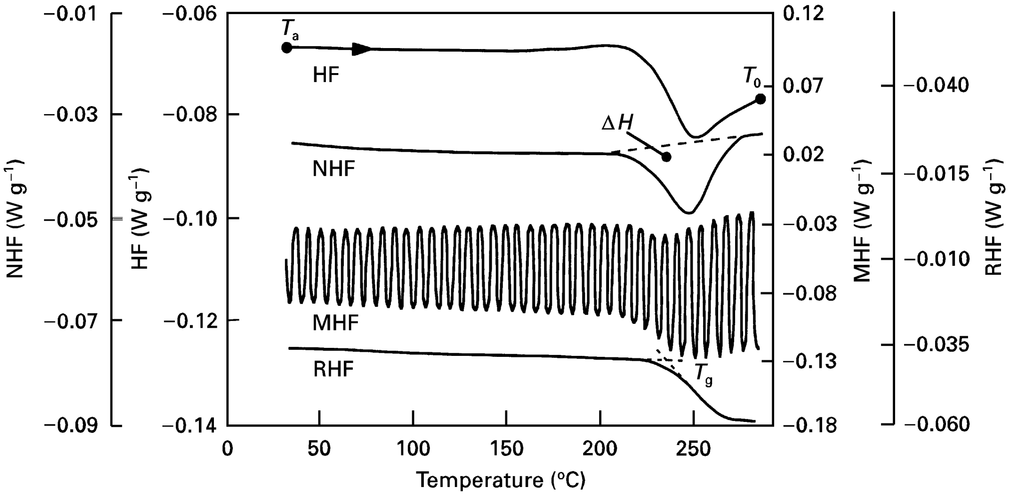

Figure 2 Typical conventional DSC (HF) and MDSC (MHF, NHF and RHF) results during a heating scan. NHF shows a relaxation peak which is separated out from MHF using RHF. HF, MHF, NHF and RHF are defined in the text. $Ge_{10}As_{30}S_{60}$ (bulk sample).

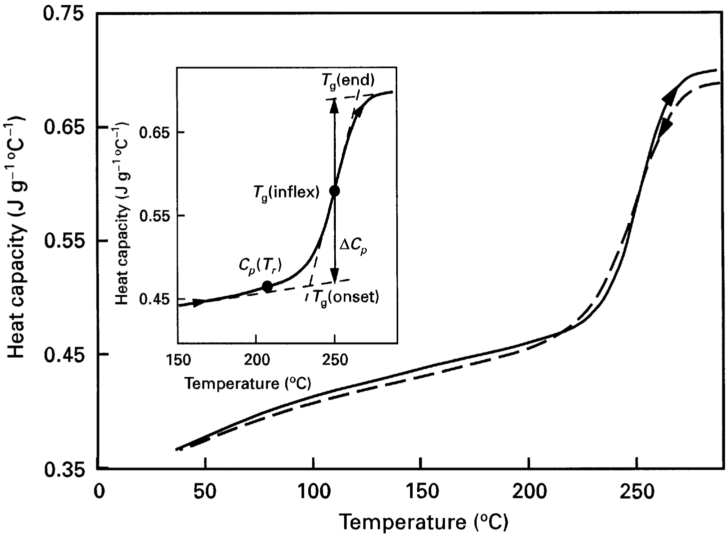

Figure 3 Typical specific heat capacity versus temperature behaviour in the glass transition region obtained from the RHF component in a MDSC experiment during a heating scan (—) and a cooling scan (– –). $Ge_{10}As_{30}S_{60}$ (bulk sample).

3. Results

Fig. 4 shows the dependence of the glass transition temperature, T_g, on the Ge concentration, x, of bulk and film $Ge_xAs_yS_{60}$ glasses. T_g increases monotonically with increasing Ge concentration up to $x = 30$ at% ($T_g = 450$ °C) and then decreases towards $T_g = 350$ °C at $x = 40$ at%, for both bulk and film samples. Fig. 4 also shows the Ge concentration dependence of the relaxation enthalpy, ΔH, for the $Ge_xAs_yS_{60}$ glasses (bulk and film) during glass transition. There is a maximum in ΔH at $x = 30$ at% Ge. The Ge concentration dependence of ΔH has a behaviour similar to that of T_g.

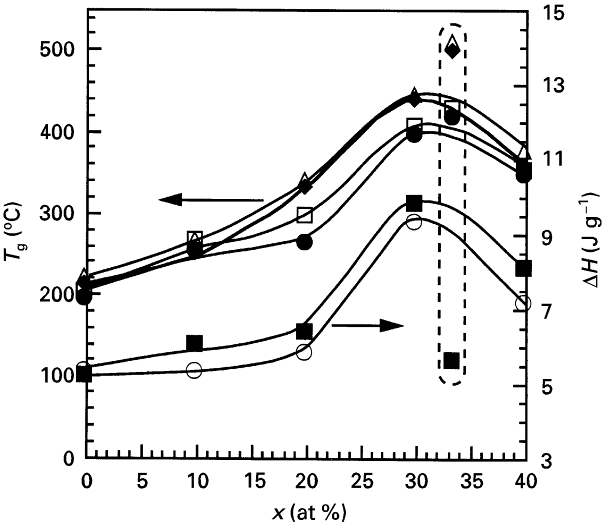

Figure 4 Glass transition temperature, T_g and relaxation enthalpy, ΔH, versus Ge concentration, x, in the $Ge_xAs_yS_{60}$ ($x + y = 40$) glasses from heating and/or cooling scans during MDSC experiments for bulk and film samples. (△), T_g cooling scan, bulk; (□), T_g, heating scan, bulk; (■), ΔH, heating scan, bulk; (◆), T_g, cooling scan, film; (●), T_g, heating scan, film; (○), ΔH, heating scan, film. Different T_g values are taken from C_p versus temperature curves. The points in the region outlined by a broken line are for $Ge_{33.3}S_{66.7}$.

The specific heat capacities, C_p, were measured by MDSC in both heating and cooling scans in the temperature region $T = 20$–450 °C. The C_p dependence on the Ge concentration of the $Ge_xAs_yS_{60}$ glasses at

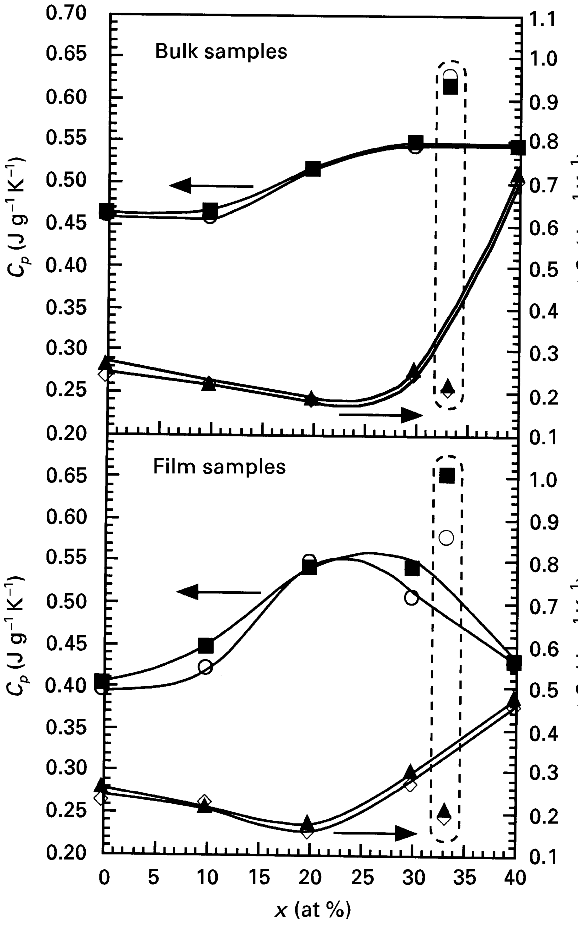

Figure 5 Specific heat capacity, C_p, and change ΔC_p, in the specific heat capacity, at the glass transition region versus Ge concentration for the $Ge_xAs_yS_{60}$ ($x + y = 40$) glasses from both heating and cooling scans during MDSC experiments for bulk and film samples. (○), C_p cooling scan; (■), C_p, (heating scan; (◇), ΔC_p, cooling scan; (▲), ΔC_p, heating scan. The points in the region outlined by a broken line belong to $Ge_{33.3}S_{66.7}$.

$T_r = 0.9\,T_g$ is shown in Fig. 5. C_p increases with increasing Ge content up to $x = 30$ at%, beyond which C_p is constant in the bulk glass whereas C_p decreases for film samples. The specific heat capacity difference, ΔC_p, occurring in the glass transformation was determined for all the $Ge_xAs_yS_{60}$ glass compositions and are plotted as a function of Ge concentration in Fig. 5. Initially, ΔC_p decreases slowly up to $x \approx 30$ at% Ge and then increases drastically towards $x = 40$ at% Ge in similar fashions for bulk and film samples.

4. Discussion

The notion that covalent bonding in glasses may be optimized when the average coordination number, $\langle r \rangle$, is 2.4 was advanced by Phillips [14] to explain the strong glass-forming propensity of some chalcogenide systems. It was subsequently further developed by Thorpe [15], who predicted, for the mean-field case, a sudden rise in bulk moduli as the composition in binary or multicomponent systems passes through the "rigidity percolation" (or vector percolation) threshold at this same coordination number. Taking into account not only the short-range constraints but also the constraints of medium-range order, Tanaka [16] predicted another structural transition. It is the transition from the two-dimensional layer-like structure to the three-dimensional cross-linked network. This transition is observed at $\langle r \rangle = 2.67$ and may be regarded as topological and has been observed through various physical properties (e.g., band-gap energy) in several chalcogenide glass systems [16] and their thin films [21].

On the basis of the structural units characteristic of binary glasses (as discussed in [22]), the structure in the region to As_2S_3–Ge_2S_3 should consist of a mixture of $AsS_{3/2}$ ($\langle r \rangle = 2.4$) and $GeS_{4/2}$ ($\langle r \rangle = 2.67$) units, interconnected either directly or through chalcogen atoms with a chain-like linkage. The infrared and Raman spectra of the pseudobinary glasses $(As_2S_3)_y(Ge_2S_3)_{1-y}$ correspond, as expected, to the superposition of vibrational spectra of the trigonal and tetrahedral units [22]. The structure of the glass with a composition close to Ge_2S_3 obviously consists primarily of $Ge_2S_{6/2}$ units, which contain a Ge–Ge bond each and are linked in a three-dimensional network through divalent $S_{2/2}$ atoms [22]. It is supposed that, in the $Ge_xAs_yS_{60}$ glasses with $x = 0$, 10, 20, 30 and 40 at%, the sulphur, arsenic and germanium atoms have coordination numbers of 2, 3 and 4, respectively. The coordination number and atomic concentration of each element in the glass allows us to calculate the average coordination number, $\langle r \rangle$ (or Z in [19]). For $Ge_xAs_yS_{60}$ glasses with $x = 0$, 10, 20, 30 and 40 at%, we obtained the average coordination numbers, $\langle r \rangle = 2.4$, 2.5, 2.6, 2.7 and 2.8, respectively. The introduction of Ge into the covalent glass structure increases $\langle r \rangle$ which is accompanied by an increase in T_g as shown for the film and bulk $Ge_xAs_yS_{60}$ glasses in Fig. 1.

It is reasonable to assume that the initial replacement of trivalent As with quadrivalent Ge in the $Ge_xAs_yS_{60}$ systems tends to cross-link two-dimensional sheets of $AsS_{2/3}$. This assumption accounts for the initial increase in T_g when As is replaced by Ge, since the onset of molecular mobility at T_g must involve bond breaking of some sort in these network glasses. To achieve the same degree of molecular mobility in a three-dimensionally cross-linked $Ge_xAs_yS_{60}$ liquid as in a two-dimensional $As_{40}S_{60}$ liquid requires the breaking of more bonds, so that T_g must be correspondingly higher. The dependence of T_g on composition can be explained by the empirical equation proposed by Tanaka [23]:

$$\ln T_g = 1.6Z + 2.3 \qquad (2)$$

where Z is the average coordination number ($2 < Z < 2.8$), and T_g is the glass transition temperature in kelvins. For example, $\langle r \rangle$ for the composition $As_{10}Ge_{30}S_{60}$ is 2.7 ($= 0.1 \times 3 + 0.3 \times 4 + 0.6 \times 2$), which agrees well with the value $Z = 2.67$ calculated from Equation 2 using the value of T_g from a cooling scan.

Figure 4 shows the variation in T_g in $Ge_xAs_yS_{60}$ glasses. It is not surprising that T_g passes through a maximum at an intermediate composition; this maximum occurs near $x = 30$ at%, where the S-to-Ge mole ratio becomes less than 2. This behaviour suggests that the glass consists of a GeS_2 network dissolving a moderate amount of elementary As near $x = 30$ at%. The maximum proportions are given by

$$5Ge_2S_3 + As_2S_3 \rightarrow 8GeS_2 + 2GeAsS$$

The network-making effect of replacing As with Ge evidently cannot continue across the entire composition range so that, when $x > 30$ at%, the GeS_2 network begins to be disrupted and T_g decreases. It should be noted that, at the other composition extreme, the $Ge_{40}S_{60}$ glass has a considerably different network structure. The Ge–Ge bonds in the $Ge_2S_{6/2}$ units are maintained only for the composition Ge_2S_3. T_g values are therefore reduced to those characteristic of vitreous Ge_2S_3 [22]. It can be seen that, in general, T_g increases with increasing interaction between the kinetic units; this behaviour is in agreement with that of the vaporization (or atomization) enthalpy in As_2S_3, GeS_2 and Ge_2S_3 glasses.

The enthalpic relaxation that takes place in the glass transition region [22] is represented by the endothermic heat, ΔH. The dependence of ΔH on the composition of film and bulk $Ge_xAs_yS_{60}$ glasses, shown in Fig. 4, follows the trend of the T_g dependence on composition. ΔH were obtained from MDSC heating scans of samples with the same thermal history (see Section 2). ΔH increases with increasing Ge content in $Ge_xAs_yS_{60}$ glasses. The increase in ΔH involved in the structural relaxation process (e.g., $\Delta H = 255.7\,\mathrm{J\,(mol\ As_{40}S_{60})^{-1}}$ and $\Delta H = 475.2\,\mathrm{J\,(mol\ Ge_{30}As_{10}S_{60})^{-1}}$) can be related to an increase in the dimensionality of the rearranging thermokinetic structural units.

As has been determined for other inorganic network glasses [24, 25], the heat capacities of the $Ge_xAs_yS_{60}$ glasses at high temperatures approach the high-temperature Dulong–Petit value of $3R$ ($=24.9\,\mathrm{J\,K^{-1}\,mol^{-1}}$) for the vibrational heat capacity of solids shown in Fig. 5. Hence, it may be assumed that heat capacities of the $Ge_xAs_yS_{60}$ glasses bellow T_g arise from thermal excitation of vibrational modes of the amorphous quasilattice. As found previously in the temperature range covered by the present experiments, the glass heat capacities can be approximated by the Debye function for C_V, since the difference between the constant-volume heat capacity, C_V, and the constant-pressure heat capacity, C_p, are negligible for these glasses. The Debye temperatures, Θ_D, of the $Ge_xAs_yS_{60}$ glasses for $x = 0$ (453 K), $x = 10$ (473 K), $x = 20$ (473 K), $x = 30$ (473 K) and $x = 40$ (453 K) agree reasonably well with values calculated from the vibrational frequency, ν_R of the characteristic structural unit present in these glasses. For example, for $AsS_{3/2}$, $\nu_R = 310\,\mathrm{cm^{-1}}$ and $\Theta_D = hc\nu_R/k = 446\,\mathrm{K}$ and, for $GeS_{4/2}$, $\nu_R = 367\,\mathrm{cm^{-1}}$ and $\Theta_D = hc\nu_R/k = 528\,\mathrm{K}$. The dependence of C_p on the composition follows the same trend as that of T_g, as shown in Fig. 5 and reveals a maximum at $x = 30$ at% Ge. Fig. 2 shows that ΔC_p of $Ge_xAs_yS_{60}$ glasses passes through a minimum which seems to correlate, within the limits of the experimental points, with the maximum in T_g, so that it is not unreasonable to assume that the two extrema are manifestations of the same structural phenomena discussed above.

5. Conclusions

The recent novel MDSC technique has been applied to the measurement of thermal properties of chalcogenide glasses of $Ge_xAs_yS_{60}$ (where $x + y = 40$ and $x = 0$, 10, 20, 30 and 40 at%) in the glass transition region in bulk glasses and its thin films. The RHF and NHF through the glass transformation region during both heating and cooling schedules were measured and the values of the parameters, T_g, ΔH, C_p and ΔC_p, which characterize the thermal events in the glass transition region, were determined. The structurally determined parameters, T_g, ΔH, C_p and ΔC_p, reveal significant changes with composition because in $Ge_xAs_yS_{60}$ glasses the average coordination number, $\langle r \rangle$, increases from 2.4 to 2.8 with increasing x from 0 to 40 at% Ge. A maximum in the T_g, ΔH and C_p and a minimum in the heat capacity change ΔC_p (at T_g) occur near the composition for which $x \approx 30$ at% Ge. These extrema which appear in both films and bulk glasses are ascribed to a change in the network function of Ge atoms replacing As atoms in a covalent network.

Acknowledgements

This project was made possible by financial support from the European Community under Grant ERBCIPA CT940107 and from the Natural Sciences and Engineering Research Council of Canada.

References

1. S. SATO, K. IGARASHI and M. TANIWAKI, *Appl. Phys. Lett.* **62** (1993) 669.
2. M. READING, *Trends in Polymers* **1** (1993) 248.
3. M. READING, D. ELLIOTT and V. L. HILL, *J. Therm. Anal.* **40** (1993) 949.
4. M. READING, A. LUGET and R. WILSON, *Thermochim. Acta* **238** (1994) 295.
5. B. WUNDERLICH, Y. JIN and A. BOLLER, *ibid.* **238** (1994) 277.
6. S. SAUERBRUNN and L. THOMAS, *Amer. Lab.* (1995) 19.
7. P. S. GILL, S. R. SAUERBRUNN and M. READING, *J. Therm. Anal.* **40** (1993) 931.
8. L. THOMAS, *North Amer. Therm. Anal. Soc. Sacramento, CA, Notes* **26** (1995) 48.
9. N. HASSEL, *ibid.* **26** (1995) 54.
10. A. N. STREEM, A. K. VARSHNEYA and D R. SWILER, *J. Non-Cryst. Solids* **130** (1979) 153.
11. E. VATEVA, E. SKORDEVA and D. ARSOVA, *Phil. Mag. B* **67** (1994) 225.
12. K. NANDAKUMAR and J. PHILIP, *Bull. Mater. Sci.* **17** (1994) 225.
13. U. SENAPATI and A. K. VARSHNEYA, *J. Non-Cryst. Solids* **185** (1995) 289.
14 J. C. PHILLIPS, *ibid.* **34** (1979) 153.
15. M. F. THORPE, *ibid.* **57** (1983) 355.
16. K. TANAKA, *Phys. Rev. B* **3** (1989) 1270.
17. S. O. KASAP, T. WAGNER and K. MAEDA, *Jpn. J. Appl. Phys.* **35** (1996) L1116.
18. T. WAGNER, S. O. KASAP and M. VLCEK, *Thin Solid Films* (1997) in press.
19. T. WAGNER and S. O. KASAP, *Phil. Mag. B* **74** (1996) 667.
20. "Modulated DSC™ compendium, basic theory and experimental considerations", (TA Instruments, Newcastle, DE, 1996) pp. 25–27.
21. D. ARSOVA, *J. Phys. Chem. Solids* **57** (1996) 1279.
22. A. FELTZ, "Amorphous inorganic materials and glasses" (VCH, Weinheim, 1993).
23. K. TANAKA, *Solid State Commun.* **54** (1985) 867.
24. U. E. SCHNAUS, A. MARSHALL and C. T. MOYNIHAN, *J. Amer. Ceram. Soc.* **55** (1972) 180.
25. R. BLACHNIK and A. HOPPE, *J. Non-Cryst. Solids* **34** (1979) 191.

Received 4 April
and accepted 29 May 1997