

Thermal characterization of Ge–As–Se glasses by differential scanning calorimetry

R. P. Wang · C. J. Zha · A. V. Rode · S. J. Madden ·
B. Luther-Davies

Published online: 27 March 2007
© Springer Science+Business Media, LLC 2007

Abstract Differential scanning calorimetry (DSC) was performed at different heating rates under non-isothermal conditions to probe the glass transition kinetics of several Ge–As–Se glasses with different chemical compositions. The change of the glass transition temperature T_g with the heating rate and composition was investigated and the activation energy of the glass transition was estimated. The fragility index was calculated and the correlation to the mean coordination number of Ge–As–Se glasses was discussed.

1 Introduction

Chalcogenide glasses, typically non-oxide based glasses containing the chalcogen elements S, Se and Te, have received much attention for many applications. They exhibit many attractive optical properties including high refractive index, excellent transmission at 1.55 μm , large optical nonlinearity, ultrafast broad-band response, and low optical loss [1–3]. The low glass transition temperature T_g of the amorphous state of these twofold coordinated pure chalcogen elements can be increased by adding three-fold As and four-fold Ge coordinated elements [4]. Assuming Ge, As and Se to possess a coordination number of 4, 3 and 2 respectively, mean coordination number (MCN), which is

defined as a sum of their respective concentration times their coordination number, can be achieved [5]. For binary and ternary chalcogenide glasses, many physical properties have been found to correlate with the MCN. When the MCN increases to 2.4, Phillips and Thorpe [6, 7] predicted a floppy-to-rigid transition in the glass network which has been confirmed by Raman spectroscopy measurements [8]. Boolchand found an intermediate phase bound by the two transitions, revealing that the glass transition becomes almost thermally reversing in this composition window. This floppy-intermediate-stressed rigid phase transition is classified in terms of a structure-based approach to the elastic thresholds. Defining n_c as the count of Lagrangian bonding constraints per atom, intermediate phase consists of optimally constrained ($n_c = 3$) backbones that appear between mechanically floppy (under constrained, $n_c < 3$) and stressed rigid (over constrained, $n_c > 3$) phases [5–7]. The intermediate phase with a thermally reversing window is closely related to the ageing behavior, and thus is important for the application of the glasses.

In Ge–As–Se ternaries containing equal concentrations of As and Ge, nucleation of binary nanocrystalline phases is suppressed due to the same concentration of $\text{As}(\text{Se}_{1/2})_3$ pyramids and $\text{Ge}(\text{Se}_{1/2})_4$ tetrahedra [5, 8–11]. Therefore the so-called nanophase separation which is characteristic of the global maximum in T_g on a composition dependence plot, cannot be observed in $\text{Ge}_x\text{As}_x\text{Se}_{1-2x}$ system. However, a global maximum of T_g near MCN = 2.8 was found in ternary $(\text{Ge}_2\text{Se}_3)_x(\text{As}_2\text{Se}_3)_{1-x}$ glasses [12]. To resolve this difference, in this paper we investigated the glass transition kinetics of Ge–As–Se glasses with five different chemical compositions, $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$, $\text{Ge}_{22}\text{As}_{20}\text{Se}_{58}$, $\text{Ge}_{11}\text{As}_{22}\text{Se}_{67}$, $\text{Ge}_5\text{As}_{38}\text{Se}_{57}$ and $\text{Ge}_5\text{As}_{30}\text{Se}_{65}$. The activation energy of the thermal relaxation processes present in the glasses was also studied. The concentration of $\text{As}(\text{Se}_{1/2})_3$ pyramids and

R. P. Wang (✉) · C. J. Zha · A. V. Rode ·
S. J. Madden · B. Luther-Davies
Centre for Ultrahigh Bandwidth Device for Optical System
(CUDOS), Laser Physics Centre, Research School of Physical
Science and Engineering, Australian National University,
Canberra ACT 0200, Australia
e-mail: rpw111@rsphysse.anu.edu.au

$\text{Ge}(\text{Se}_{1/2})_4$ tetrahedra would not be equal in these five Ge–As–Se glasses. Therefore the investigation may provide further information regarding nanophase separation and whether the Boolchand's intermediate phase still exists since these five samples span a MCN from 2.4 to 2.8 which is characteristic of stressed-rigid glasses. Our preliminary results show a linear correlation between logistic T_g and MCN. By changing the heating rate, the activation energy of the glass transition was derived and the fragility index was calculated for each glass. The dependence of these two parameters on MCN seems to support the existence of a thermally reversing window. The possible physical origin of these results is also discussed.

2 Experiments

High purity germanium, arsenic and selenium metals were used as starting materials. They were weighed within a dry nitrogen-filled glove box, and then introduced into a pre-baked quartz ampoule before being sealed under vacuum. The sealed ampoule was placed into a rocking furnace, which was heated to 900 °C at a ramp rate of 3 °C/min. To obtain good homogeneity of the melt, the ampoule was rocked for 2 h and the melt liquid was then held statically in the furnace for 24 h. After the melt was removed from the furnace and quenched in air, the ampoule was subsequently annealed in another furnace for 15 h at a temperature slightly below T_g in order to reduce the internal stress. A detailed description of the sample preparation can be seen in our previous paper [13]. The glasses obtained were ground into fine powder for differential scanning calorimetry (DSC, Shimadzu DSC-50) measurement. Usually 15–20 mg powder was sealed into Al sample pans and then heated at constant heating rate, and the changes in heat flow with respect to an empty reference pan were measured. No devitrification or crystallization was observed for the samples in this study.

3 Results and discussion

The measured T_g of our five samples as a function of MCN, as well as the T_g of those samples with smaller MCN from [9] are shown in Fig. 1. The MCNs are evaluated using the standard procedure described by Tanaka, where the coordination numbers for Ge, As, and Se are 4, 3 and 2, respectively [11]. Thus for the glassy system $\text{Ge}_a\text{As}_b\text{Se}_c$ ($a + b + c = 1$), the value of MCN is given by:

$$\text{MCN} = 4a + 3b + 2c, \quad (1)$$

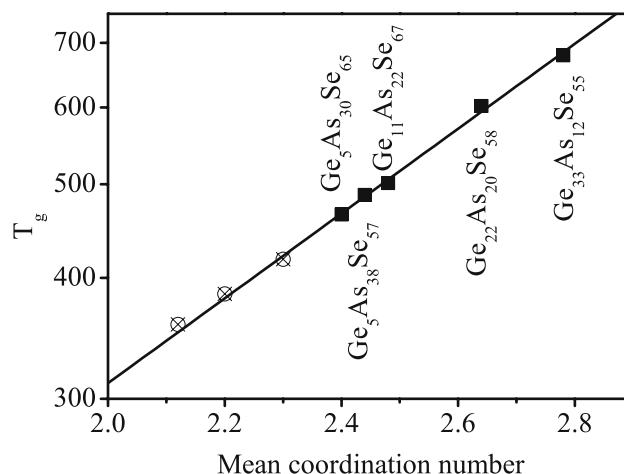


Fig. 1 T_g as a function of mean coordination number. The squares represent our five samples, and open circles are those from [9]

As previously mentioned, it is well established that T_g depends on the connectivity, and consequently on the rigidity of the vitreous network [4, 5]. Therefore adding an element with coordination number larger than two to a linear polymeric structure such as that exhibited by amorphous Se will result in a vitreous matrix with higher T_g proportional to the content of the added atom. In fact a linear correlation between logistic T_g and MCN has been proposed in chalcogenide glasses [14]. In this study absence of a global maximum in T_g indicates that there is no nanophase separation despite the different concentrations of $\text{As}(\text{Se}_{1/2})_3$ pyramids and $\text{Ge}(\text{Se}_{1/2})_4$ tetrahedra in these materials.

Figure 2 shows DSC curves of $\text{Ge}_{22}\text{As}_{20}\text{Se}_{58}$ samples with different heating rates, where T_g is simply defined as the temperature of the endothermic peak observed during heating. Clearly with increasing heating rate, a more intense endothermic relaxation peak can be observed. Based

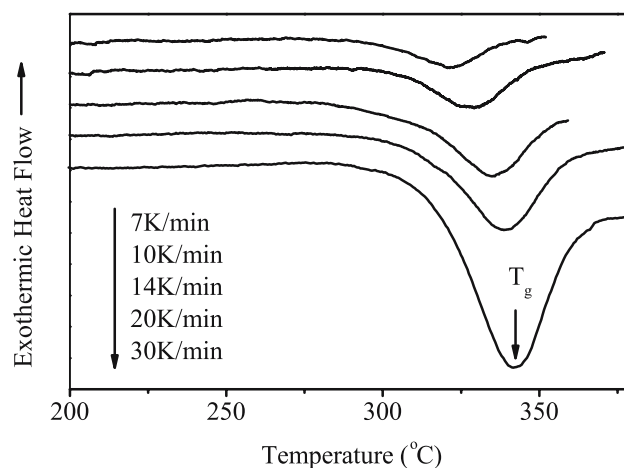


Fig. 2 T_g as a function of heating rate

on Ritland equation, T_g and the heating rate obey the relationship [15],

$$d(\ln(\beta))/d(1/T_g) = -\Delta H/R, \tag{2}$$

where β , ΔH and R are the heating rate, the apparent activation energy and the universal gas constant, respectively. The plots of $\ln\beta$ versus $1/T_g$ are shown in Fig. 3 for the five samples investigated in this paper. The apparent activation energy involved in the molecular motions and rearrangements around T_g can be extracted from the slope of each plot, and the results are shown in Fig. 4. It should be emphasized that ΔH is an apparent activation energy which normally depends on the thermal history and is generally smaller than the “true” glass transition activation energy obtained from cooling scans [16]. (The apparent activation energy depends on the product of partition parameter x and the actual activation energy as observed in cooling scans). Nonetheless, we can still use ΔH to examine how it changes with the composition and MCN.

The fragility indexes of these five samples were calculated using the relation of $F = \Delta H/(T_g \ln(10))$ in which ΔH is determined from heating scans vis-à-vis cooling scans expressed in units of temperature and T_g is glass transition temperature [17]. The calculated values are slightly lower than those obtained by viscoelastic shear compliance and modulus measurements in the tensile modes for $\text{Ge}_{10}\text{As}_{10}\text{Se}_{80}$ and $\text{Ge}_{13}\text{As}_{13}\text{Se}_{74}$ [17].

Since the works of Phillips [6] and Tanaka [11], it is well accepted that glassy covalent networks exhibit two topological thresholds. Describing these glassy structures by means of virtual atoms bonded together with a MCN,

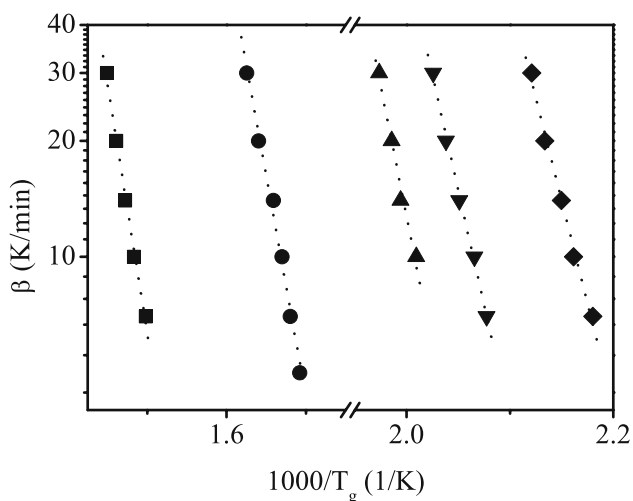


Fig. 3 Plots of T_g versus $\ln\beta$ for the five samples, $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ (■), $\text{Ge}_{22}\text{As}_{20}\text{Se}_{58}$ (●), $\text{Ge}_{11}\text{As}_{22}\text{Se}_{67}$ (▲), $\text{Ge}_5\text{As}_{38}\text{Se}_{57}$ (▼) and $\text{Ge}_5\text{As}_{30}\text{Se}_{65}$ (◆)

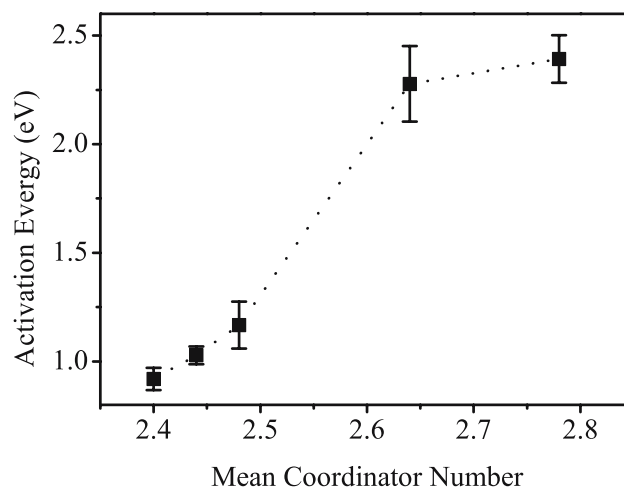


Fig. 4 Activation energy as a function of mean coordination number

these two thresholds appear at MCNs of 2.4 and 2.67, respectively, corresponding to the chemical composition dependence of floppy-intermediate-stressed rigid phase transition. On the other hand, instead of rigid transition involving a change in network dimensionality [11], nanoscale phase separation [12] was proposed to explain the network anomalies near $\text{MCN} = 2.6$ in $(\text{Ge}_2\text{S}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ systems. Absence of the global maximum of T_g in these preliminary results seems to rule out the possibility of nanoscale phase separation in our Ge–As–Se systems. A detailed investigation of the compositional dependence of T_g will be helpful to elucidate this point.

We note that a prerequisite condition to get the global maximum of T_g is the existence of As_4Se_4 monomers which can lead to a progressively loss of the $\text{As}(\text{Se}_{1/2})_3$ backbone and therefore a loss of global connectivity of network. For Ge–As–Se ternary glasses, the electronegativity difference between Ge(2.01) and Se(2.48) is larger than that between As(2.18) and Se(2.48) [18]. This suggests that Se will first select to covalently bond with Ge rather than As atoms to low free energy of all network structure. For the Se-rich glasses like $\text{Ge}_{11}\text{As}_{22}\text{Se}_{67}$ and $\text{Ge}_5\text{As}_{30}\text{Se}_{65}$, Se chains could be part of the backbone of the network except the tetrahedral $\text{Ge}(\text{Se}_{1/2})_4$ and pyramidal $(\text{AsSe}_{3/2})_2$ units. Moreover, optimally coordinated quasi-tetrahedral Se– $\text{As}(\text{Se}_{1/2})_3$ units could also be formed in Se-rich ternary glasses [9]. On the other hand, for the Se-poor glasses like $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ and $\text{Ge}_{22}\text{As}_{20}\text{Se}_{58}$, Ge–Ge and As–As bonds can incorporate into the backbone to suppress the formation of binary nanocrystal phase. It has also been found that in $\text{As}_x\text{Se}_{1-x}$ binary, ethylene-like $\text{As}_2\text{Se}_{(1/2)}_4$ units were firstly formed as a part of the network, and then gradually transformed into As_4Se_4 monomers at $x > 0.5$ [19]. If it is true for Se-poor ternary Ge–As–Se glasses, instead of forming As_4Se_4 monomers, As atoms will share Se atoms which have a priority to bond

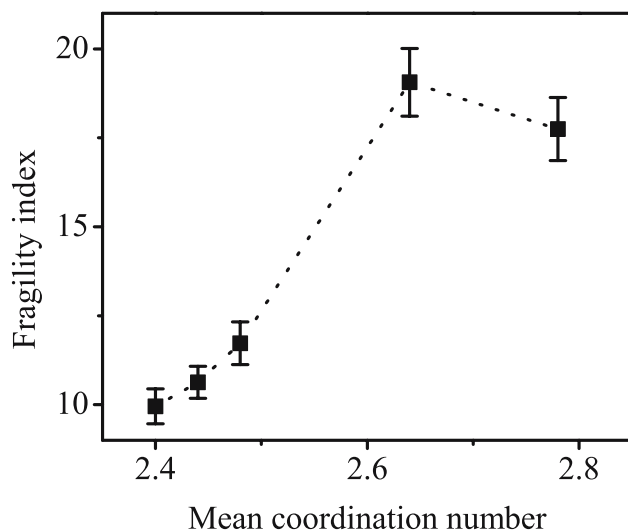


Fig. 5 Fragility index as a function of mean coordination number

with Ge atoms because of the difference of the electro-negativity. Therefore we conclude that for both Se-rich and -poor ternary glasses, the independent As_4Se_4 monomers are hardly formed. That is the reason why we cannot observe the global maximum of T_g .

Noteworthy is a discontinuous change of activation energy and fragility index at the MCN around 2.6 in Figs. 4 and 5, which is in good agreement with the rigidity transition around 2.67 predicted by the mean field theory. The MCN dependence of decreasing tendency of activation energy and fragility index is in qualitative agreement with those in [9], supporting the existence of Boolchand's intermediate phase in the glassy system.

4 Conclusion

In summary, DSC measurements were performed to investigate five Ge–As–Se glassy samples with different compositions. A linear correlation between logistic T_g and

could be explained by the formation tendency of the different structural units in the glassy backbones. The change of the glass transition temperature T_g with the heating rate and composition was investigated. The activation energy of the glass transition was derived and the fragility index was calculated. Their correlation to the MCN of Ge–As–Se glasses was discussed.

Acknowledgment This research was supported by Australian Research Council through its Centre of Excellence, Discovery and Federation Fellow Programs.

References

1. A. Schulte, C. Rivero, K. Richardson et al. *Opt. Commun.* **198**, 125 (2001)
2. A.C. Van Popta, R.G. DeCorby, C.J. Haugen, T. Robinson, J.N. McMullin, *Opt. Express* **10**, 639 (2002)
3. V.Q. Nguyen, J.S. Sanghera, J.A. Freitas, I.D. Aggarwal, I.K. Lloyd, *J. Non-Cryst. Solids* **248**, 103 (1999)
4. M.A. PoPescu, *Non-crystalline Chalcogenides* (Kluwer Academic Publishers, 2001)
5. P. Boolchand, *C.R. Chimie* **5**, 713 (2002)
6. J.C. Phillips, *J. Non-Cryst. Solids* **34**, 153 (1979)
7. M.F. Thorpe, *J. Non-Cryst. Solids* **57**, 355 (1983)
8. D. Selvanathan, W.J. Bresser, P. Boolchand, *Phys. Rev. B* **61**, 15061 (2000)
9. Y. Wang, P. Boolchand, M. Micoulant, *Europhys. Lett.* **52**, 633 (2000)
10. R. Bohmer, C.A. Angell, *Phys. Rev. B* **45**, 10091 (1992)
11. K. Tanaka, *Phys. Rev. B* **39**, 1270 (1989)
12. S. Mamedov, D.G. Georgiev, T. Qu, P. Boolchand, *J. Phys. Condens. Matter* **15**, 2397 (2003)
13. C.J. Zha, B.L. Davies, R.P. Wang, A. Smith, A. Prasad, R.A. Jarvis, S. Madden, A. Rode, in *Proceedings of ACOFT 2006*, Melbourne, Australia, 10–13 July 2006
14. R. Kerner, M. Micoulaut, *J. Non-Cryst. Solids* **210**, 298 (1997)
15. H. N. Ritland, *J. Am. Ceram. Soc.* **37**, 370 (1954)
16. S.O. Kasap, S. Yannacopoulos, *Phys. Chem. Glasses* **31**, 71 (1990)
17. R. Bohmer, K.L. Ngai, C.A. Angell, D.J. Plazek, *J. Chem. Phys.* **99**, 4201 (1993)
18. See <http://www.webelements.com/webelements>
19. B. Effey, R.L. Cappelletti, *Phys. Rev. B* **59**, 4119 (1999)