Modified Gibbs-DiMarzio equation applied to the Ge-Se-Fe and Ge-Se-In chalcogenide glasses

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The glass transition is a complex, non-equilibrium physical phenomenon and despite the numerous efforts expended in the last three decades, the mechanisms governing the glass transition continue to raise a lot of fundamental questions. Its study is of extreme importance from both academic and technological points of view. Several theoretical models have been developed to improve our understanding of the nature of the glass transition [1] but until today there is no consensus about which structural, kinetic and thermodynamic factors are decisive in determining T_g.

On the experimental side, many semi-empirical relationships have been proposed to fit the measured T_g s for particular systems [2]. Particularly, Gibbs and DiMarzio [3] and DiMarzio [4] have shown that for glass system, with some chain stiffness, the glass transition temperature is given by

$$T_g = \frac{T_o}{1 - \alpha X} \qquad (1)$$

where T_o is the glass transition temperature of the non-cross-linked initial polymeric chain, X is the cross-linking density, and α is a universal constant. At this point it must be stressed that Equation 1 is based on purely thermodynamic considerations and, therefore, it is well suited for the application to chalcogenide glasses because of the minor role played by kinetic factors in determining T_g for these materials.

Sreeram *et al.* [5] were the first to realize that Se-based polynary chalcogenide glasses satisfy the required conditions of Gibbs-DiMarzio equation, namely, the presence of Se polymeric chains which can be cross-linked by added atoms. They adapted Gibbs-DiMarzio equation by redefining the cross-linking density, X, as being equal to the mean coordination number of the glass, Z, less the coordination number of the initial chain and replacing the universal constant α, by a system constant β. Thus Gibbs-DiMarzio equation is rewritten as

$$T_g = \frac{T_o}{1 - \beta(Z - 2)} \qquad (2)$$

For Equation 2 to be physically meaningful, the values of $\beta(Z - 2)$ must lie between 0 and 1.

The importance of the mean-coordination number, Z, has been pointed out by Phillips [6] and is widely used for the description of the structure of network glasses. It is defined as the atom-averaged coordination of the compounds. For the ternary system $A_k B_l C_m$, Z is given by

$$Z = kCN(A) + lCN(B) + mCN(C) \qquad (3)$$

where $CN(A)$, $CN(B)$ and $CN(C)$ are the respective coordination numbers of atoms A, B, and C and k, l and m are the atomic concentrations of atoms A, B, and C, respectively.

Though the magnitude of the system parameter, β, is crucial in determining the value of T_g, its determination received little attention in the literature. Therefore, the aim of this work is to examine if the $T_g - Z$ variations for the studied systems could be modeled with Sreeram *et al.* relationship [5] and to obtain the values of T_o and β for these systems.

The procedure followed for the preparation of Ge-Se-Fe glasses is detailed elsewhere [7, 8]. Glasses
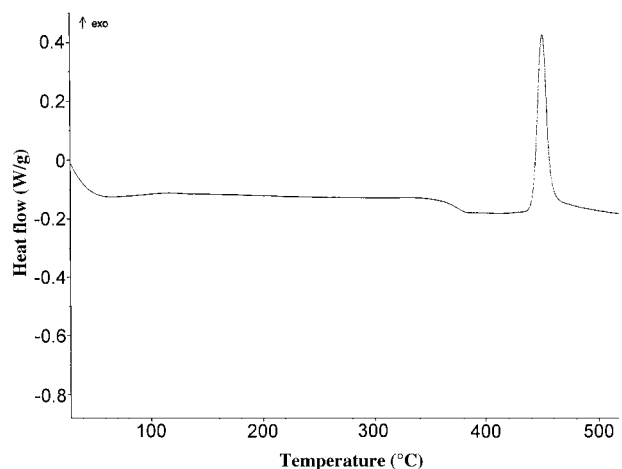

Figure 1 A DSC curve obtained on $Ge_{36}Se_{62}Fe_2$ glassy alloy.

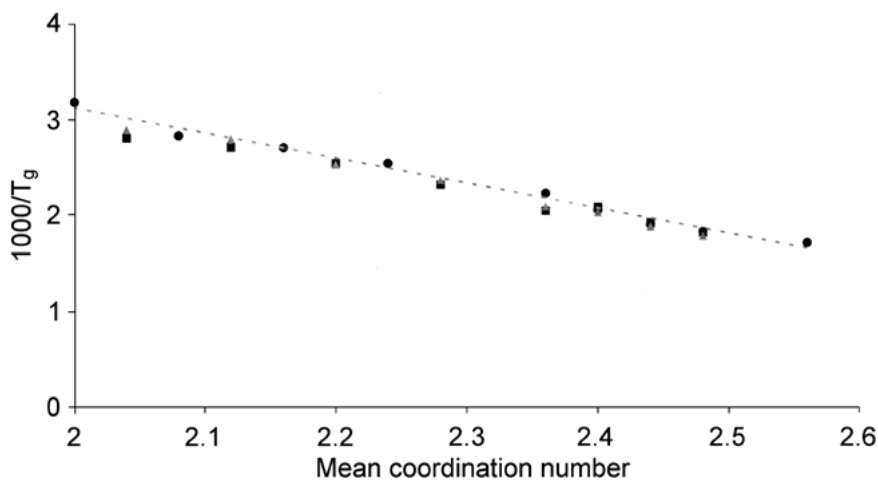*Author to whom all correspondence should be addressed.

Figure 2 Variations of $1000/T_g$ with the mean coordination number for Ge-Se-Fe system. The data points represented by circles, squares and triangles correspond to glassy alloys containing 2, 4, and 6% Fe, respectively.

containing 2, 4 and 6 at.% Fe were prepared in this system. The Ge-Se-In glasses, containing 6 and 12 at.% In, were prepared according to the melt-quench technique. The high purity (5 N) materials were accurately weighed according to their atomic percentages and sealed in silica ampoules (8 mm diameter, length 80 mm) in vacuum of $\sim 10^{-5}$ Torr. The ampoules were kept in a furnace where the temperature was first raised to 450 °C for 24 h and then to 850 °C for 48 h. The ampoules were frequently rocked at the maximum temperature to make the melt homogeneous. The quenching to 0 °C was done in an ice-water mixture.

The glass transition temperatures for Ge-Se-Fe glasses were measured by a differential scanning calorimeter (Netzsch DSC 404C) with a heating rate of 10 K/min. The samples with a mass of 50–75 mg were measured in evacuated and sealed silica tubes (length = 1.5 cm; diameter = 6.3 mm; wall thickness = 0.4 mm). An empty silica tube served as a reference. The system was calibrated with the melting points of gallium, indium, lead, antimony and zinc. The T_g s of Ge-Se-In glasses, at a scan rate of 10 K/min, were obtained by using a Setaram DSC 92 calorimeter and

sealed aluminum pans. The accuracy of the T_g measurements was better then ±1 K.

A DSC scan obtained on the $Ge_{36} Se_{62} Fe_2$ glassy composition is shown in Fig. 1. The first endothermic phenomenon is due to the glass transition whereas the second exothermic phenomenon corresponds to the crystallization reaction. From the DSC scans, the T_g s for Ge-Se-Fe and Ge-Se-In glasses were obtained.

For the evaluation of the mean coordination number, Z, one needs to know the coordination numbers of the individual atoms in the glassy alloy. It is well known that the coordination numbers of Ge and Se conform with Mott's $(8 - N)$ rule [9] where N is the number of outer shell electrons. Therefore, coordinations of 4 for Ge and 2 for Se were used in the evaluation of Z. A coordination number of 3, a value that was obtained form In K-edge extended X-ray absorption fine structure measurements [10], was used to evaluate Z for Ge-Se-In glasses. Because of the lack of any direct structural determination of the coordination number of Fe and as in previous investigations [7, 8], we used a coordination number of 2 for this element to evaluate Z for Ge-Se-Fe glassy alloys.
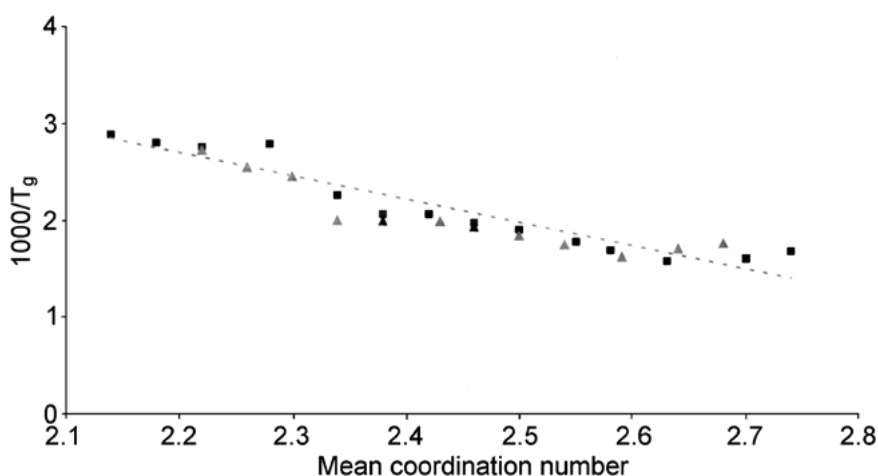

Figure 3 Variations of $1000/T_g$ with the mean coordination number for Ge-Se-In system. The data points represented by squares and triangles correspond, respectively, to glassy alloys containing 6 and 12% In.

TABLE I Values of β and T_o, obtained from least-squares fitting of the data of Figs 2 and 3. Correlation coefficients are also given

System	β	T_o (K)	Correlation coefficient
Ge-Se-Fe	0.84	319.5	-0.994
Ge-Se-In	0.76	313.5	-0.952

The glassy compositions prepared in the Ge-Se-Fe system covered a range of Z values between 2 and 2.56 whereas those prepared in the Ge-Se-In system covered a Z-range from 2.14 to 2.74.

According to Equation 2, we have plotted our data in terms of $1000/T_g$ versus Z. The results are shown in Fig. 2 and Fig. 3 for Ge-Se-Fe and Ge-Se-In, respectively. The values of β and T_o, obtained from least squares fitting of the data, for each glassy system are given in Table I. The results show that the condition $0 \leq \beta(Z-2) \leq 1$ is verified. Furthermore, our results on β for the studied systems fall within the range reported for multi-component chalcogenide glasses which varies from 0.55 for Ge-Sb-Se-Te [5] to 0.98 for Ge-Te-Sb [11]. The results also give T_o values which are very close to 318 K [12] and 315 K [13] which are the reported values for the glass transition temperature of pure Se.

In conclusion, we have shown that the $T_g - Z$ variations, for the studied systems, are well described by Sreeram *et al.* relationship [5] and that the values obtained for β and T_o are physical.

References

1. C. BIAO and C. ZHENHUA, *Physica* B **266** (1999) 152 and references therein.
2. L. TICHY and H. TICHA, *J. Non-Cryst. Solids* **189** (1995) 141.
3. J. H. GIBBS and E. A. DIMARZIO, *J. Chem. Phys.* **28** (1958) 373.
4. E. A. DIMARZIO, *J. Res. Nat. Bur. Stand.* **68A** (1964) 611.
5. A. N. SREERAM, D. R. SWILER and A. K. VARSHNEYA, *J. Non-Cryst. Solids* **127** (1991) 287.
6. J. C. PHILLIPS, *ibid.* **34** (1979) 153.
7. G. SAFFARINI, J. MATTHIESEN and R. BLACHNIK, *Physica* B **305** (2001) 293.
8. G. SAFFARINI and J. MATTHIESEN, *Appl. Phys.* A **73** (2001) 621.
9. N. F. MOTT, *Philos. Mag.* **19** (1969) 835.
10. J. LEDRU, J. M. SAITER, G. SAFFARINI and S. BENAZETH, *J. Non-Cryst. Solids* **232**–**234** (1998) 634.
11. M. BELHADJI, N. BENAMEUR, J. M. SAITER and J. GRENET, *Phys. Stat. Sol.* (b) **201** (1997) 377.
12. J. P. DENEUFVILLE and H. K. ROCKSTAD, in Proc. 5th Int. Conf. on Amorphous and Liquid Semiconductors, edited by J. Stuke and W. Brenig (Taylor and Francis, London, 1974) p. 419.
13. Z. U. BORISOVA, Glassy Semiconductors (Plenum Press, New York, 1981) p. 108.