

Glass structure, rigidity transitions and the intermediate phase in the Ge-As-Se ternary

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Abstract. – The non-reversing heat flow, $\Delta H_{nr}(x)$ near T_g in ternary $\text{Ge}_x\text{As}_x\text{Se}_{1-2x}$ glasses is examined by temperature-modulated differential scanning calorimetry. The $\Delta H_{nr}(x)$ term shows a deep minimum (which is almost zero) in the $0.09 < x < 0.14$ range, identified with the *intermediate phase*, and an increase, both at low x (< 0.09) in the *floppy phase* and at high x (> 0.14) in the stressed *rigid phase*. Expressed in terms of mean coordination number, $\bar{r} = 2 + 3x$, the large width, $\Delta\bar{r} = r_c(1) - r_c(2) = 0.15$, of the intermediate phase and its low onset value $r_c(1) = 2.27$ are shown to be consistent with the presence of Se = As($\text{Se}_{1/2}$)₃ units in addition to pyramidal As($\text{Se}_{1/2}$)₃ and tetrahedral Ge($\text{Se}_{1/2}$)₄ units in the stress-free backbone. The *vanishing* of $\Delta H_{nr}(x)$ in the *intermediate phase* is in harmony with the notion that the number of Lagrangian constraints/atom exhausts the three available degrees of freedom, and leaves the backbone in a *mechanically stress-free state*.

Introduction. – A floppy-to-rigid transition in network glasses was predicted [1, 2] in the early 1980's. The transition has enjoyed widespread interest in science, not only because the glass forming tendency is optimized near this transition, but also because it serves as a paradigm of percolative transitions in condensed matter [3], and computational complexity [4] in computer science (NP — complete problem). In *random* networks numerical calculations [2] have shown that a *solitary* floppy-to-rigid transition occurs when the connectivity or mean coordination number \bar{r} increases to 2.385, quite close to the predicted mean-field value of 2.40. Experimentally, new details of the transition have recently emerged [5–8] in binary (Ge or Si)_xSe_{1-x} glasses by Raman scattering and T -modulated Differential Scanning Calorimetry (MDSC). In contrast to numerical simulations on random networks [2], Raman optical elasticities provide evidence of *two* transitions, a *second-order* transition near $r_c(1) = 2.40$ from a floppy to an unstressed rigid phase, and a *first-order* transition near $r_c(2) = 2.52$ from an unstressed rigid to a stressed rigid phase. The unstressed nature of the intermediate

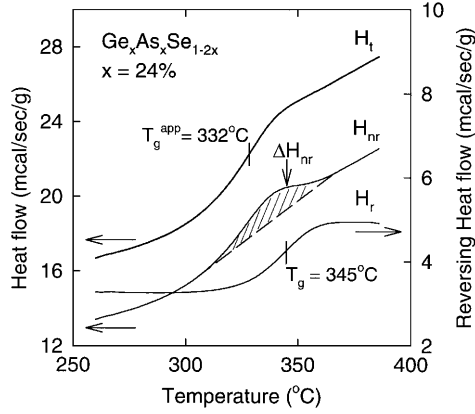


Fig. 1 – MDSC scan of indicated glass sample taken with a model 2920 instrument from TA Instruments, Inc., using a modulation of $1\text{ }^\circ\text{C}/100\text{ s}$, and a scan rate of $3\text{ }^\circ\text{C}/\text{min}$. \dot{H}_t , \dot{H}_{nr} and \dot{H}_r represent the total, non-reversing and reversing heat flow rates. The shaded area represents the non-reversing heat flow, ΔH_{nr} .

phase, $\bar{r}_c(1) < \bar{r} < \bar{r}_c(2)$, bounded by the two transitions emerges from T -Modulated Differential Scanning Calorimetry (MDSC) measurements [5–8] that reveal that glass transitions become almost thermally reversing in this compositional window. The potential of MDSC as a tool to probe the nature of T_g in chalcogenides goes far beyond DSC, and is illustrated in several recent publications [5–8]. These new experimental results are much closer to recent numerical simulations on self-organized networks [9] that predict *two* transitions.

In this work we report, for the first time, on the observation of a thermally reversing window in the $\text{Ge}_x\text{As}_x\text{Se}_{1-2x}$ ternary, which suggests that the backbone forms at $x_c(1) = 0.09$ or $\bar{r}_c(1) = 2.27$, while the transition to the stressed rigid state occurs at $x_c(2) = 0.14$ or $\bar{r}_c(2) = 2.42$. The large width ($\Delta\bar{r} = 0.15$) of the window and particularly its formation at a value substantially lower than the usual mean-field value [1, 2] of $\bar{r} = 2.40$, constitutes a new feature of the rigidity transition in the present ternary. The feature is suggestive of the presence of *optimally coordinated* quasi-tetrahedral $\text{Se} = \text{As}(\text{Se}_{1/2})_3$ units in addition to tetrahedral $\text{Ge}(\text{Se}_{1/2})_4$ and pyramidal $\text{As}(\text{Se}_{1/2})_3$ units in the backbone of the ternary glasses.

The $\text{Ge}_x\text{As}_x\text{Se}_{1-2x}$ ternary has been viewed as a paradigm of a Zachariasen glass consisting of a random network of As-pyramids and Ge-tetrahedra cross-linking Se_n -chain fragments. The connectivity of these glasses can be changed in a continuous fashion by changing the cation concentration x . Assuming Ge, As and Se to possess coordination numbers of 4, 3, and 2, respectively, one obtains the mean coordination number [10]

$$\bar{r} = 4x + 3x + 2(1 - 2x) = 2 + 3x, \quad (1)$$

which spans the range $2.0 < \bar{r} < 3.0$ as x changes in the $0 < x < 0.33$ concentration range.

Inelastic neutron scattering measurements [11] on this ternary have shown that the density of vibrational states at low frequencies ($0 < \omega < 10\text{ meV}$) depends exclusively on \bar{r} , a result that has been described as the vibrational isocoordinate rule. The topological rule apparently also describes trends in vibrational lifetime of a water guest molecule [12] in spectral hole-burning experiments. Furthermore, relaxation of an external stress in flexural studies has revealed [13] that the activation energies $E_Y(\bar{r})$ show a global minimum in the $2.30 < \bar{r} < 2.42$ range.

Experimental results. – The glasses were synthesized [4–8] in the usual way by quenching homogeneously alloyed melts in water. The glass transition endotherms were deconvoluted into reversing and non-reversing heat flow terms the usual way using a model 2920 MDSC from TA Instruments, Inc. Figure 1 displays an actual scan of a sample at $x = 0.24$ in the present ternary showing the convolution. Figure 2 provides a summary of the present MDSC results. The T_g 's deduced from the inflection point of the reversing heat flow rate are plotted in fig. 2a, the non-reversing heat flow term, $\Delta H_{nr}(x)$, is plotted in fig. 2b, and the change $\Delta C_p(T_g)$ from the reversing heat flow rate is plotted in fig. 2c. T_g 's are found to increase with x , as the connectivity of the backbone increases as also recognized earlier in DSC measurements [14]. The central result to emerge from the MDSC measurements is the deep global minimum in $\Delta H_{nr}(x)$ for $0.09 < x < 0.14$. Frequency corrections to ΔH_{nr} were made in the usual way [15] by first scanning up and then down in T across T_g . To facilitate a comparison of the present MDSC results with flexural studies [13], we plot $\Delta H_{nr}(\bar{r})$ variation as a function of $\bar{r}(= 2 + 3x)$ in fig. 3a, and have reproduced the activation energy for an external stress relaxation, $E_Y(\bar{r})$, reported by Bohmer and Angell [13] in fig. 3b. There is a striking similarity in the compositional trends of these two observables.

Discussion. – The Ge-As-Se ternary represents a benchmark test of agglomeration theory which provides a means to predict T_g -variation as a function of network connectivity as shown by one of us [16,17]. According to this theory, a glassy liquid is visualized to be composed of well-defined structural units in which the agglomeration of units is thermally activated and proceeds over finite time steps in a stochastic fashion. The glass transition temperature is identified with the temperature at which the agglomeration processes are frozen in. At its simplest level of description (single-bond formation), the construction yields a random bond distribution, and in favorable cases, parameter-free predictions for T_g in terms of the concentration of the structural units, or glass chemical composition.

For the present Ge-As-Se ternary, one assumes tetrahedral $\text{Ge}(\text{Se}_{1/2})_4$ - and pyramidal $\text{As}(\text{Se}_{1/2})_3$ -units crosslink Se_q -chain fragments in a stochastic fashion, and the results [18] are shown as the smooth line in fig. 2a. The predicted curve is in reasonable accord with the observed $T_g(x)$ trend for $x < 0.14$. For $x > 0.14$, the departure between theory and experiment becomes qualitative, suggesting that the randomness of bonding between local structural units is apparently replaced by the presence of extended range structural correlations. It underscores the non-stochastic nature of the backbone emerging in overcoordinated glasses. Such glasses represent the stressed rigid phase of the present ternary. And it is striking indeed that the onset of this phase suggested by these $T_g(x)$ trends actually coincides with a large increase in the $\Delta H_{nr}(x)$ term, both independently showing (compare fig. 2a and 2b) that glasses at $x > x_c(2) = 0.14$ are rigid.

Constraint counting algorithms [1,2] provide a simple but elegant means to understand the thermal results on the present glasses. The glasses are viewed to be floppy at $\bar{r}_c < 2.27$, optimally constrained in the $2.27 < \bar{r} < 2.42$ range, and stressed rigid at $\bar{r} > 2.42$. Stressed rigid glasses [19] consist of mechanically overconstrained backbones in which the mean constraint per atom \bar{n}_c exceeds 3. Bond-stretching constraints of the backbone increase and exhaust the floppy modes of the Se matrix, thus pushing T_g 's up to 350 °C (fig. 2a). The high T_g 's assist in the relaxation of an external stress, and result in a smaller increase in $\Delta H_{nr}(\bar{r})$ and $E_Y(\bar{r})$ in the stressed rigid phase than in the floppy phase. In undercoordinated networks ($\bar{n}_c < 3$) cyclical modes [19,20] proliferate, and one would have expected $\Delta H_{nr}(\bar{r})$ and $E_Y(\bar{r})$ to steadily *decrease* as the number of floppy modes increases when \bar{r} is lowered to 2 from 2.4. However, one must remember that the presence of dihedral angle- and van der Waals- forces in floppy Se_q -chain segments upshifts the mean energy of floppy modes, \bar{E}_f , from

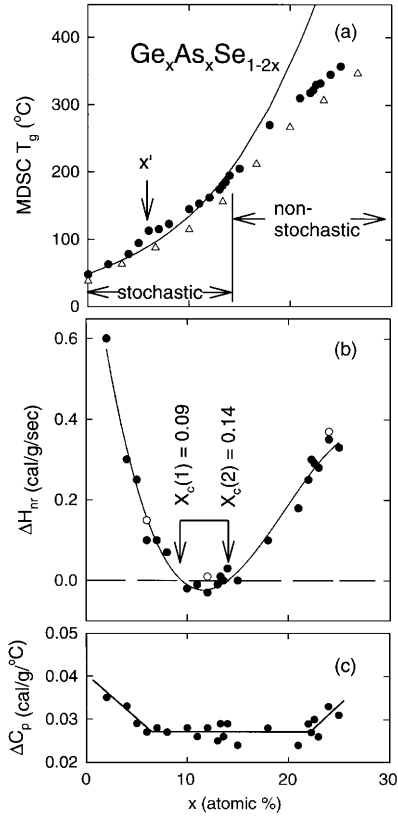


Fig. 2

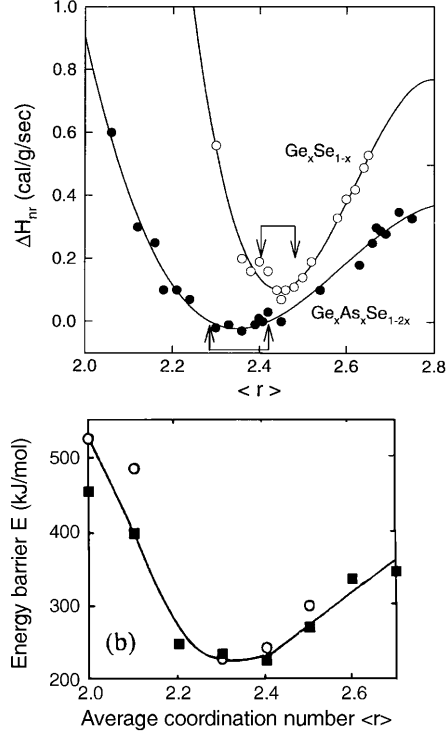


Fig. 3

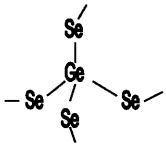
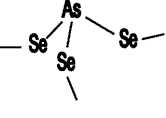
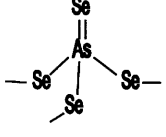
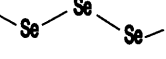
Fig. 2 – (a) $T_g(x)$ variation, (●) present MDSC results, (△) DSC results from ref. [13]. The continuous line is a calculation of $T_g(x)$ based on agglomeration theory, (b) $\Delta H_{nr}(x)$ and (c) $\Delta C_p(x)$ variation in the present ternary. In (b) the open circles represent results on finely crushed (10 μm) glass samples while the filled circles represent those on glass chips (2 mm).

Fig. 3 – (a) $\Delta H_{nr}(\bar{r})$ variation in $\text{Ge}_x\text{As}_x\text{Se}_{1-2x}$ ternary and $\text{Ge}_x\text{Se}_{1-x}$ binary, showing the intermediate phases. The results on the binary glass are taken from ref. [4]. (b) This figure taken from ref. [12] shows activation energies for viscosity (■) and activation energies for stress relaxation (○) in the present ternary.

zero to 5 meV, as shown by inelastic neutron scattering measurements [20]. Furthermore, since T_g 's monotonically decline to acquire values close to room temperature, $T_g \simeq 40^\circ\text{C}$ (fig. 2a) as $\bar{r} \rightarrow 2$, it becomes increasingly difficult for floppy glasses to soften or an external stress to relax unless the network is given enough heat of melting to overcome these internal stresses. The result of a monotonic increase in $\Delta H_{nr}(\bar{r})$ and $E_Y(\bar{r})$ as \bar{r} decreases to 2 in the floppy phase (fig. 2b) leads then to a *global minimum* of these observables when the network is optimally constrained. $\Delta H_{nr}(\bar{r})$ can thus be viewed as an *intrinsic measure of network stress* which increases due to *entropic* considerations in *undercoordinated* glasses, and due to *enthalpic* ones in the *overcoordinated* networks.

The absence of network stress in the $2.27 < \bar{r} < 2.42$ compositional window is both a *striking* and *unusual* result. It is striking for its large compositional width, $\Delta\bar{r} = 0.15$

TABLE I – *Building blocks of present ternary glasses and their mean coordination number, \bar{r} , and mean constraints/atom, \bar{n}_c .*

Building block	Mean coordination \bar{r}	Mean constraints \bar{n}_c
	2.67	3.67
	2.40	3
	2.285	3
	2.0	2

and it is unusual for its onset at $\bar{r}_c(1) = 2.27$. The latter is not consistent with bridging tetrahedral $\text{Ge}(\text{Se}_{1/2})_4$ and pyramidal $\text{As}(\text{Se}_{1/2})_3$ units as the *only* building blocks of the stress-free backbone in the glasses. These units possess (table I) a mean coordination of 2.67 and 2.40, considerably higher than the onset value of 2.27. The present observations are, however, consistent with existence of an optimally coordinated building block in the backbone, with a lower \bar{r} than in the pyramidal $\text{As}(\text{Se}_{1/2})_3$ units. Indeed, constraint counting algorithms show that the mean constraint per atom for a quasi-tetrahedral $\text{Se} = \text{As}(\text{Se}_{1/2})_3$ unit exactly equals 3 even though its mean coordination number $\bar{r} = 2.285$, because of the terminal [21] nature of the double-bonded Se. This can be seen by enumerating the total number (N_c) of bond-stretching ($n_\alpha = r/2$) and bond-bending ($n_\beta = 2r - 3$) constraints in a $\text{Se} = \text{As}(\text{Se}_{1/2})_3$ formula unit, and normalizing with respect to the number N ($= 3.5$) of atoms in such a unit to obtain \bar{n}_c :

$$\bar{n}_c = [N_c(\text{As}) + N_c(\text{b-Se}) + N_c(\text{nb-Se})]/N = [7 + 3 + 1/2]/3.5 = 3. \quad (2)$$

In calculating N_c above, we consider [21] bond-stretching constraints only for the non-bridging (nb)-Se, but both bond-stretching and bond-bending constraints for the bridging (b)-Se. The mean coordination number \bar{r} of the $\text{Se} = \text{As}(\text{Se}_{1/2})_3$ unit, then follows as

$$\bar{r} = [r(\text{As}) + (3/2)r(\text{b-Se}) + r(\text{nb-Se})]/N = [4 + 3 + 1]/3.5 = 16/7 = 2.285. \quad (3)$$

The intermediate phase [6] in binary $\text{Ge}_x\text{Se}_{1-x}$ glasses extends from $\bar{r}_c(1) = 2.40$ to $\bar{r}_c(2) = 2.52$ yielding a width, $\Delta\bar{r}$, of 0.12 (fig. 3a). The narrower width is due to the limited ways

a stress-free backbone [6] can form with only two building blocks; an overcoordinated one, $\text{Ge}(\text{Se}_{1/2})_4$ ($\bar{r} = 2.67$), and an undercoordinated one: Se_q ($\bar{r} = 2.00$). The down shift of the rigidity onset from the usual mean-field value [19] of $\bar{r}_c(1) = 2.4$ to $\bar{r}_c(1) = 2.27$ in the present ternary, most likely stems from the optimally constrained nature of the 4-fold coordinated As unit. This feature of structure probably also contributes to the width, $\Delta\bar{r} = 0.15$, of the intermediate phase, which derives from the high multiplicity of optimally coordinated units in the backbone. Thus, in addition to a combination of $\text{Ge}(\text{Se}_{1/2})_4$ tetrahedral units ($\bar{n}_c = 3.67$) and Se_q -chains ($\bar{n}_c = 2$), the existence of pyramidal ($\text{As}(\text{Se}_{1/2})_3$) units ($\bar{n}_c = 3$), and quasi-tetrahedral $\text{Se} = \text{As}(\text{Se}_{1/2})_3$ units ($\bar{n}_c = 3$) in the backbone substantially increases the number of ways in which a stress-free network can be realized in the intermediate phase. These ideas could be independently confirmed by molecular dynamic simulations of the intermediate phase in the present ternary. We are currently examining these glasses in Raman scattering measurements to establish vibrational signatures of the various building blocks.

It is possible that the small deviations between the calculated and observed T_g 's in the $0.02 < x < 0.08$ range are due to the presence of some 4-fold coordinated As units in the present ternary, which were excluded in our calculations. Fourfold coordinated P units ($\text{Se} = \text{P}(\text{Se}_{1/2})_3$) have been observed in the P-Se glass system [22] by NMR, where the ratio $\eta(r)$ of 4-fold to 3-fold coordinated P is found to decrease linearly with \bar{r} , starting from a value of 1.0 at $\bar{r} = 2$ to vanish at $\bar{r} = 2.40$. If such an $\eta(r)$ variation is also observed in the present ternary, the concentration of 4-fold As sites would show a maximum near $\bar{r} = 2.2$ corresponding to the composition $x = x' = 0.07$ (see fig. 2a). $T_g(x)$ calculations based on agglomeration theory including 4-fold coordinated As sites as well are currently being performed.

The $\Delta H_{\text{nr}}(x)$ results were typically obtained on glass samples of about 2 mm on an edge (filled circles in fig. 2a). Such measurements were also performed on finely crushed glass samples measuring about $10 \mu\text{m}$ on an edge, and gave the *same* $\Delta H_{\text{nr}}(x)$ trends as illustrated by the open circles in fig. 2a. These results are reminiscent of the neutron spin echo structural studies [23], and flexural studies of an external stress on Se glass [24], both of which gave identical Kohlrausch stretched exponent β of 0.45(2) even though the length scales probed in these two measurements differed by 12 orders of magnitude [25]. It thus appears that both the magnitude of internal stress (ΔH_{nr}) and its relaxation in time (β) near T_g scales over several orders in magnitude in linear dimension.

Conclusions. – MDSC experiments on the present ternary glasses show the existence of a rather wide thermally reversing window, $r_c(1) = 2.27 < \bar{r} < r_c(2) = 2.42$ with a low onset value at $\bar{r}_c(1) = 2.27$. The window is identified with the existence of a stress-free intermediate phase separating floppy from rigid compositions. The wide width and low onset of the intermediate phase is consistent with the presence of optimally coordinated $\text{Se} = \text{As}(\text{Se}_{1/2})_3$ units in these glasses, in addition to tetrahedral $\text{Ge}(\text{Se}_{1/2})_4$ and pyramidal $\text{As}(\text{Se}_{1/2})_3$ units. Glass network stress at T_g as measured by the non-reversing heat flow, $\Delta H_{\text{nr}}(\bar{r})$, appears to display scaling over several orders of magnitude in sample dimension.

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