

Rigidity transitions and molecular structure of $\text{As}_x\text{Se}_{1-x}$ glasses

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(Received 26 May 2000)

T -modulated differential scanning calorimetry measurements on bulk $\text{As}_x\text{Se}_{1-x}$ glasses show that the glass transition temperature $T_g(x)$ variation at $x < 0.12$ is linear with a slope $dT_g/dx = 4.1^\circ\text{C}/\text{at.}\%$ As, and the nonreversing heat flow, $\Delta H_{nr}(x)$ almost vanishes in the $0.291(1) < x < 0.37(1)$ composition range. These thermal results analyzed by agglomeration theory and constraint theory suggest that in addition to $\text{As}(\text{Se}_{1/2})_3$ units, quasitetrahedral $\text{Se}=\text{As}(\text{Se}_{1/2})_3$ units also serve to crosslink Se_q chains at $x < \frac{2}{5}$. The results also suggest that rigidity onsets at $r_c(1) = 2.29(1)$ and the transition to the stressed rigid phase occurs at $r_c(2) = 2.37(1)$, below the chemical threshold at $r_{ct} = 2.40$ (or $x = \frac{2}{5}$).

Since the pioneering scanning calorimetry work of Meyers and Felty¹ in 1967, the molecular structure of $\text{As}_x\text{Se}_{1-x}$ glasses at $x < \frac{2}{5}$ has been widely described as a random network of Se_q chain fragments crosslinked by pyramidal $\text{As}(\text{Se}_{1/2})_3$ units. The close parallels in the glass transition temperature $T_g(x)$ and the liquidus temperature $T_l(x)$ variation with x , and in particular the local maximum near $x = \frac{2}{5}$, corresponding to the stoichiometry of $c\text{-As}_2\text{Se}_3$ (isomorphous to $c\text{-As}_2\text{S}_3$; orpiment) have led to the idea that the crosslinking process saturates as x increases to $\frac{2}{5}$ when a network of corner-sharing pyramidal units is realized in the glass. Orpiment possesses a sheetlike structure with sheets built of 12 membered rings formed from 6 corner-sharing pyramidal $\text{As}(\text{S}_{1/2})_3$ units.¹ Although numerous structure investigations have been reported²⁻⁵ for the stoichiometric glass ($x = \frac{2}{5}$), nonstoichiometric glasses have received less attention. Notable in the latter are two reports. One report on the entropy of viscosity activation of melts $S_\eta(x)$ by Nemilov⁶ displayed distinct steps near $x = 0.15$ and 0.40 culminating in a *global minimum* of S_η in the $0.25 < x < 0.38$ composition range. Here S_η represents the slope dE_A/dT , where E_A is the activation energy for viscosity. Second, a comprehensive low- T specific heat investigation performed by Brand and Löhneysen⁷ showed a *global minimum* in the Debye term (bT^3) to the specific heat in the $0.22 < x < 0.35$ composition range.

We have performed T -modulated differential scanning calorimetry (DSC) measurements (MDSC) on $\text{As}_x\text{Se}_{1-x}$ glasses over the glass forming range $0 < x < 0.7$. In this Rapid Communication, we show that glass transitions become almost completely reversing in the $0.29(1) < x < 0.37(1)$ concentration range. We identify the thermally reversing window with the *intermediate phase* that separates the floppy glasses ($x < 0.29$) from the stressed rigid ones ($x > 0.37$). The onset of rigidity at $r_c(1) = 0.29(1)$ or a mean coordination number $\bar{r}_c(1) = 2 + x_c(1) = 2.29(1)$, and the extension of the stress-free rigid state up to $r_c(2) = 2.37(1)$ is a remarkable result for the large width [$\Delta r = 0.08(1)$] of

the *intermediate phase*. It is also an unusual result for its onset at $r_c(1) = 2.29$, significantly lower than the mean-field value of 2.40 for the observed⁸⁻¹⁰ onset of rigidity in several IV-VI glasses. We have used constraint counting algorithms to analyze the rigidity onset at $r_c(1)$, and stochastic agglomeration theory to analyze the x dependence of $T_g(x)$. These thermal results require that $\text{Se}=\text{As}(\text{Se}_{1/2})_3$ units in addition to pyramidal $\text{As}(\text{Se}_{1/2})_3$ units constitute the building blocks of $\text{As}_x\text{Se}_{1-x}$ glasses at $x < \frac{2}{5}$.

Glasses were synthesized by reacting stoichiometric As_2Se_3 with a requisite amount of Se or As to realize compositions in the $0 < x < 0.70$ range. The starting materials of 99.999% purity from Cerac, Inc., were reacted at 700°C for 72 h in evacuated fused quartz ampules with periodic shaking. Melts were equilibrated at 50°C above the liquidus prior to a water quench. The glasses were relaxed for several weeks prior to examining them in a model 2920 MDSC instrument from TA Instruments, Inc. All scans were taken at $3^\circ\text{C}/\text{min}$ ramp rate and $1^\circ\text{C}/100\text{ s}$ modulation rate. Figure 1 reproduces a typical scan of a glass sample at $x = 0.45$ in which the total heat flow rate (\dot{H}_t) is deconvoluted¹¹ into a

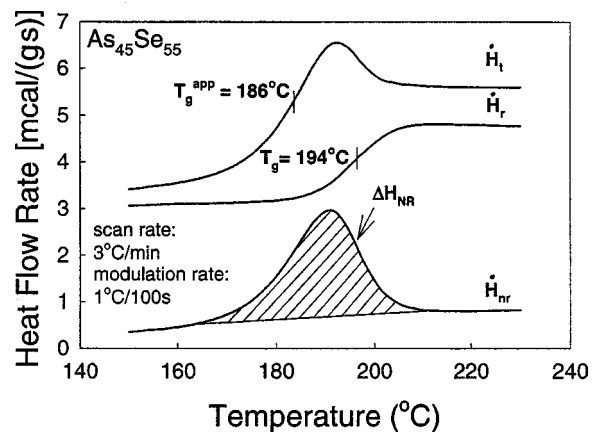


FIG. 1. MDSC scan of $\text{As}_{45}\text{Se}_{55}$ glass showing deconvolution of the \dot{H}_t into \dot{H}_r and \dot{H}_{nr} . See text for details.

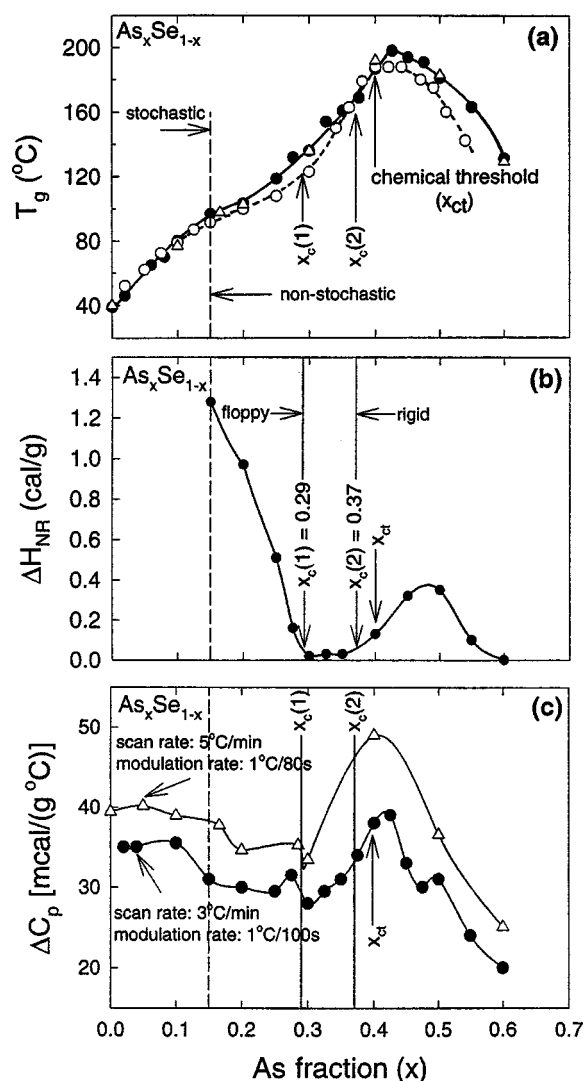


FIG. 2. Summary of present MDSC results on $\text{As}_x\text{Se}_{1-x}$ glasses showing (a) $T_g(x)$ variation, (b) $\Delta H_{nr}(x)$ variation, (c) $\Delta C_p(x)$ variation. The (Δ) data points are taken from Ref. 12, the (\circ) from Ref. 1, while the (\bullet) are the present results. The composition $x_{ct} = \frac{2}{5}$ corresponds to the chemical threshold defined by the stoichiometry of orpiment. The smooth curves through the data are merely to guide the eye.

reversing component (\dot{H}_r) that tracks the temperature modulations and a difference term, $\dot{H}_t - \dot{H}_r = \dot{H}_{nr}$ that does not. The area under the shaded curve in Fig. 1 represents the nonreversing heat flow, ΔH_{nr} . Frequency corrections to the ΔH_{nr} term were made the usual way.¹¹ The T_g was established as the inflection point of the reversing heat flow rate \dot{H}_r endotherm.

Figure 2 provides a summary of the MDSC results on the present glasses, where the observed $T_g(x)$ variation is displayed in panel (a), the $\Delta H_{nr}(x)$ variation in panel (b), and the changes in C_p at T_g , $\Delta C_p(x)$ from the \dot{H}_r endotherm in panel (c). The present $T_g(x)$ results are in excellent accord with the MDSC results reported by Wagner *et al.*,¹² and in reasonable accord with the DSC results of Meyers and Felty.¹ The consistently lower values of T_g s in the DSC measurements are not surprising since these T_g s are deduced from the \dot{H}_t endotherm, which is displaced to lower T in

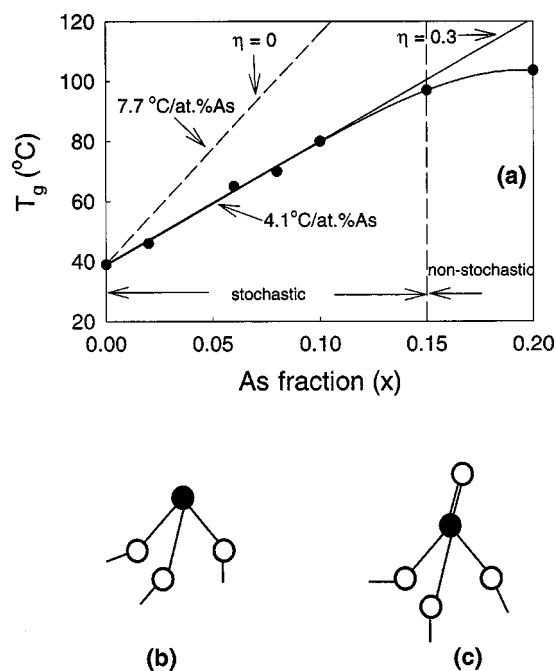


FIG. 3. (a) $T_g(x)$ variation in $\text{As}_x\text{Se}_{1-x}$ glasses at low x showing a linear regime, (b) pyramidal $\text{As}(\text{Se}_{1/2})_3$ unit, (c) quasitetrahedral $\text{Se}=\text{As}(\text{Se}_{1/2})_3$ unit.

relation to the \dot{H}_r endotherm (Fig. 1). Even though the thermal history of our glass samples and those of Wagner *et al.*¹² were qualitatively different, the T_g s deduced from the \dot{H}_r endotherms in both investigations *virtually coincide*. T_g s deduced in MDSC from the \dot{H}_r endotherm are largely immune from the state of relaxation of a glass.

Stochastic agglomeration theory^{13,14} provides an attractive framework to analyze the observed $T_g(x)$ trends in the low As content range. The theory identifies T_g with the temperature at which covalent agglomeration processes between local structural units are frozen. Thus, a Se chain-glass network stochastically crosslinked by three-fold coordinated As, should result in a linear increase of T_g [Fig. 3(a)] with the following slope:

$$\begin{aligned} dT_g/dx &= T_0/\ln(r_{\text{As}}/r_{\text{Se}}) \\ &= T_0/\ln(\frac{3}{2}) \\ &= 7.7 \text{ }^\circ\text{C/at.\% of As.} \end{aligned} \quad (1)$$

Here $T_0 = 40 \text{ }^\circ\text{C}$ or 313 K represents the glass transition of the Se glass and $r_{\text{As}}, r_{\text{Se}}$ designate the coordination numbers of As and Se. It has recently been shown¹⁵ that if a finite fraction η of the pnictide atoms were also four-fold coordinated as in a $\text{Se}=\text{As}(\text{Se}_{1/2})_3$ local unit, Eq. (1) acquires a more general form:

$$dT_g/dx = T_0/\ln(\frac{3}{2}(1-\eta)), \quad (2)$$

and the slope decreases [Fig. 3(a)]. The observed $T_g(x)$ variation in the present binary displays a linear regime, $0 < x < 0.12$, with a slope dT_g/dx of $4.1 \text{ }^\circ\text{C/at.\% As}$. At higher x the slope decreases and a mold plateau sets in the $0.15 < x < 0.20$ range, before increasing again at $x > 0.20$ to show a local maximum in T_g at $x = 0.42$. To quantitatively account

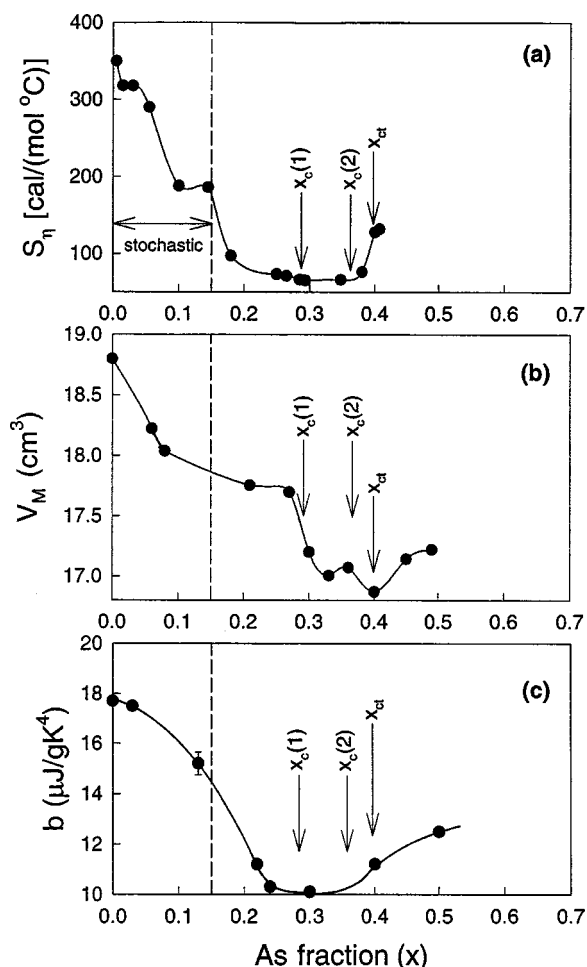


FIG. 4. (a) Activation entropy of $\text{As}_x\text{Se}_{1-x}$ melts taken from Ref. 6. (b) Molar volumes of $\text{As}_x\text{Se}_{1-x}$ glasses taken from Ref. 17. (c) Coefficient of the cubic term of the low- T specific heat taken from Ref. 7. All appear to be correlated to the thermally reversing window compositions.

for the observed slope of $4.1\text{ }^\circ\text{C/at.}\%$ As, we obtain $\eta=0.3$ from Eq. (2). The analysis of the $T_g(x)$ results [Fig. 3(a)] provides the first indication that at low x , a finite and measurable fraction of As atoms in Se glass are four-fold coordinated [Fig. 3(c)]. The result may be contrasted to a value of $\eta=0.5$ observed in the chemically isovalent P-Se binary glasses by NMR.^{15,16} The observed $T_g(x)$ variation is consistent with a stochastic crosslinking of Se_q chains by three- and four-fold coordinated As atoms up to $x\sim 0.15$, and a nonstochastic one at $x>0.15$, as extended range structural correlations evolve. The signature of this structural change apparently also manifests in the $S_\eta(x)$ variation, which shows a sharp step near $x=0.15$, as shown in Fig. 4(a).

The central result to emerge from the present work is the existence of a thermally reversing window that onsets at $x=x_c(1)=0.29(1)$ and extends up to $x=x_c(2)=0.37(1)$, as shown in Fig. 2(b). Before discussing these results, it may be relevant to note that the thermally reversing window coincides with a global minimum⁶ in S_η [Fig. 4(a)], a local minimum in molar volumes¹⁷ [Fig. 4(b)], and a global minimum in the cubic term⁷ to the low- T specific heat (Fig. 4). Glass compositions in the window are indeed quite special.

Thermally reversing windows were recently reported⁸⁻¹⁰ in the Si-Se and Ge-Se binary glasses, and the two endpoint compositions [$x_c(1)$ and $x_c(2)$] were found to coincide with thresholds in local elasticities inferred from Raman mode frequencies. The power-law variation of local elasticity at $x > x_c(2)$ in the Raman scattering measurement was supported by numerical simulations,¹⁸ and unambiguously showed such glasses to be rigid. The linear variation of mode frequencies at $x < x_c(1)$, on the other hand, suggested that such glasses are floppy. In analogy to these results, we must conclude that glasses in the present binary at $x < x_c(1)=0.29(1)$ are floppy while those at $x > x_c(2)=0.37(1)$ are rigid.

The near vanishing (~ 0) of the ΔH_{nr} term in the $x_c(1) < x < x_c(2)$ range also constitutes evidence that glasses in this compositional window are stress-free. The interpretation of the ΔH_{nr} heat-flow term was recently inferred by comparing the results of the ΔH_{nr} term in MDSC experiments¹⁹ with the relaxation of an external stress in flexural studies²⁰ in the $\text{As}_x\text{Ge}_x\text{Se}_{1-2x}$ ternary. The activation energy²⁰ $E_A(x)$ for an external stress to relax, and the $\Delta H_{nr}(x)$ term showed strikingly parallel compositional trends, and in particular global minima that onset and extend to identical glass compositions. These results suggest that while the flexural studies probe relaxation of an external stress, the ΔH_{nr} term provides a measure of intrinsic network stress. Glasses in the intermediate phase possess a backbone that is rigid but stress-free. This interpretation is independently suggested by recent numerical simulations²¹ in self-organized networks that show the existence of two transitions,²² one from a floppy to an unstressed rigid phase [$x_c(1)$] and a second one from an unstressed rigid to a stressed rigid phase [$x_c(2)$]. The presence of floppy modes²³ could not solely contribute to the ΔH_{nr} term since the heat flow term proliferates in the rigid phase where floppy modes vanish.

In the Se-rich region, if undercoordinated Se_q -chain ($n_c=2$, $r=2$) fragments and optimally coordinated ($n_c=3$, $\bar{r}=2.4$) $\text{As}(\text{Se}_{1/2})_3$ pyramids were the sole building blocks of the $\text{As}_x\text{Se}_{1-x}$ glasses, then rigidity would be expected to onset close to $x=\frac{2}{5}$ or $\bar{r}=2.40$, when the network largely comprises the corner-sharing pyramids as suggested by numerical simulations.²¹ Such a result is incompatible with a rigidity onset at $\bar{r}=2.29(1)$, and the observed slope dT_g/dx of $4.1\text{ }^\circ\text{C/at.}\%$ As near $x\rightarrow 0$. This result brings out a recurring theme in glass science which is that glasses differ from their crystalline counterparts in subtle ways, and the present binary glass system appears to be no exception. The onset of the thermally reversing window at $x_c(1)=2.29(1)$, when analyzed by constraint theory, independently suggest that in addition to Se_q chains and $\text{As}(\text{Se}_{1/2})_3$ pyramids [Fig. 3(b)] quasitrahedral $\text{Se}=\text{As}(\text{Se}_{1/2})_3$ [Fig. 3(c)] must also constitute building blocks of the Se-rich glasses as shown next.

It is instructive to enumerate the mechanical constraints associated with the quasitrahedral $\text{Se}=\text{As}(\text{Se}_{1/2})_3$ unit [Fig. 3(c)]. For this unit the number of average constraints/atom (\bar{n}_c) equals 3 even though its mean coordination number $\bar{r}=2.2857$, i.e., less than the magic number of 2.40. This is due to the terminal nature of the double bonded Se, for which only bond-stretching constraints need be considered since it is onefold coordinated.²⁴ Indeed, a binary As-Se glass network composed exclusively of such quasitrahedral

units would be rigid (optimally constrained; $\bar{n}_c=3$) at a composition $x=\frac{2}{7}$ or 0.2857. This may be seen directly from Eq. (3) below:

$$\bar{r}=2.40-0.4(n_1/N), \quad (3)$$

which represents²⁴ realization of rigidity onset, i.e., $\bar{n}_c=3$, for a glass network possessing a finite fraction n_1/N of one-fold coordinated atoms. For the quasitetrahedral unit [Fig. 3(c)], there are $N=3.5$ atoms in a formula unit, including one terminal Se($n_1=1$). Taking $n_1/N=\frac{1}{3.5}$, Eq. (3) is satisfied exactly at $\bar{r}=2.2857$ or at a glass composition $x=\frac{2}{7}$ in the present binary. Currently, there is no direct experimental evidence for four-fold coordinated As sites in $\text{As}_x\text{Se}_{1-x}$ glasses that we are aware of, although in principle, Raman scattering, nuclear quadrupole resonance (NQR), and diffraction experiment can provide the evidence. It may be pertinent to mention that in corresponding sulfide glasses there are two reports^{12,25} to suggest the existence of four-fold coordinates $\text{S}=\text{As}(\text{S}_{1/2})_3$ units. The challenge here derives in part from the fact that there are no model crystalline compounds in which such local units apparently occur. And this brings us to our final comment, namely that the fourfold coordinated As unit probably represents a low- P molecular structure that is populated in the glasses, when melts are structurally arrested at a lower density than in corresponding crystals.

The coefficient $b(x)$ of the T^3 term in the low- T specific heat⁷ provides a measure of the excess vibrational modes²⁶ in a glass in relation to the Debye term in a crystal. These excess vibrations²⁶ also contribute to the scattering at the boson peak, and are identified with strong scattering of

acoustic vibrations from structural heterogeneities intrinsic to a network glass. For glass compositions in the thermally reversing window, since the backbone is thought to be self-organized and stress-free, one may indeed expect the b coefficient to show a global minimum, as illustrated in Fig. 4(c). In both floppy and the rigid glasses, such structural heterogeneities can be expected to increase as network stress accumulates, and not surprisingly, the b coefficient acquires a larger magnitude. Glassy melts in the thermally reversing window also appears to be exceptional as well, as suggested⁶ by the global minimum of the activated entropy S_η . These results constitute evidence for an Arrhenius-like thermally activated viscosity in the window for which the activation energy E_A remains nearly T independent, thus leading to a minimum in $S_\eta=dE_A/dT$. Furthermore, one may regard glasses in the thermally reversing window to be strong and those outside the window to be fragile, a classification formally introduced²⁷ on the basis of S_η variation.

In conclusion, the present MDSC measurements show that the thermally reversing window in $\text{As}_x\text{Se}_{1-x}$ glasses occurs in the composition range $x_c(1)=0.29(1)<x<x_c(2)=0.37(1)$. The rigidity onset at $\bar{r}_c(1)=2.29(1)$, substantially below the usual mean-field value of 2.40, is suggestive of fourfold coordinated As [$\text{Se}=\text{As}(\text{Se}_{1/2})_3$] in addition to threefold coordinated As [$\text{As}(\text{Se}_{1/2})_3$] as building blocks of the Se-rich glasses. These ideas can motivate spectroscopic and diffraction measurements of local structure in these glasses in the future.

This work was supported by NSF Grant No. DMR-97-01289. LPTL is UMR 7600 of CNRS.

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