Coordination-number-induced morphological structural transition in a network glass

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Mössbauer electric field gradients, Raman vibrational modes, and crystallization temperatures exhibit threshold behavior near the composition $x = 0.20$ in binary Si$_x$Te$_{1-x}$ glasses. This threshold is evidence of a morphological structural change that may be driven by network connectivity or average coordination number. At $x \leq 0.20$, the network largely consists of Si-cross-linked Te$_x$ chain segments. At $x \geq 0.20$, Te$_x$ chains reconstruct with tetrahedral Si(Se$_{1/2}$)$_4$ units and nucleate a defect-ridden Si$_x$Te$_2$-like layered molecular fragment. These fragments represent the elastically rigid domains that percolate above the threshold.

I. INTRODUCTION

Current interest in elastic properties of glassy networks has been stimulated by the idea of rigidity percolation.\cite{1,2} Undercoordinated (or underconstrained) networks corresponding to a mean coordination number $\langle m \rangle = 2.40$ are pictured as elastically floppy because these networks are easily deformed under a shearing force. On the other hand, overcoordinated (or overconstrained) networks corresponding to $\langle m \rangle > 2.40$ are visualized as elastically rigid because such networks resist a change in shape under a shearing force. These ideas due to Phillips\cite{1} and Thorpe\cite{2} have led to the realization that at the threshold coordination number of $\langle m \rangle = 2.40$, a glass network constrained by bond-stretching and -bending forces sits at a mechanical critical point in which rigid regions are thought to percolate in a mean-field sense. In a glass $A_xB_{1-x}$ network composed of cations ($A = Ge, Si$) and anions ($B = S, Se, and Te$) that are, respectively, fourfold and twofold coordinated, the critical composition $x^* = x_c$ corresponding to vector percolation is given by

$$2(x_c + 1) = 2.40$$

yielding $x_c = 0.20$. Experimental evidence in support of mechanical thresholds in binary Ge-Se (Ref. 3) glasses and ternary Ge-As-Se glasses\cite{4} was recently provided using a macroscopic probe (ultrasonic elastic constant) of network rigidity. The structural consequences of mechanical thresholds were elucidated by Bresser et al.\cite{5} using Mössbauer site spectroscopy which was also correlated with Raman band spectroscopy.\cite{6}

In this paper we present experimental evidence for thresholds in $^{125}$Te electric field gradients, Raman vibrational modes, and crystallization temperatures each occurring very near the composition $x = 0.20$ in binary Si$_x$Te$_{1-x}$ glasses. These results appear to be consistent with the notion that molecular fragments based on the c-Si$_2$Te$_3$ structure are populated in the bulk glasses above the vector percolation threshold at $x \geq 0.20$. At $x \leq 0.20$, Te$_x$ chain segments and tetrahedral Si(Se$_{1/2}$)$_4$ units predominately occur in the glassy networks. The present experiments, along with those reported\cite{3-6} recently, appear to demonstrate that the so-called mechanically rigid regions present in overcoordinated glasses largely consist of compacted molecular fragments derived from corresponding crystals.

II. EXPERIMENTAL PROCEDURES

Binary Si$_x$Te$_{1-x}$ glasses were prepared by alloying the elements in vacuum followed by a water quench. 99.9999%-pure Si chunks and 99.9999%-pure Te chunks from Cerac Inc., Milwaukee, Wisconsin, were used as the starting materials. The elements in the desired proportion were sealed in 5-mm-inner-diameter fused-quartz ampules at a pressure of $5 \times 10^{-7}$ Torr using a CTI cryopump-based vacuum system. The melts, typically 0.5 g in size, were held at 1000°C for 5 d in a vertical configuration and periodically shaken to homogenize before quenching in water. This procedure yielded homogeneous glass samples in the composition range $0.10 < x < 0.25$ that displayed reproducible glass transition $T_g(x)$ and crystallization temperatures $T_c(x)$.

Our differential-scanning-calorimetry traces taken with a Perkin-Elmer model 2C instrument at selected compositions $x$ are displayed in Fig. 1. These results show the presence of two distinct crystallization temperatures, $T_{c1}$ and $T_{c2}$ at $x \leq 0.20$ but only one crystallization temperature at $x \geq 0.21$. Figure 2 displays the compositional dependence of $T_g(x)$, $T_{c1}(x)$, and $T_{c2}(x)$ taken at a 20-K/min scan rate.

Raman scattering from the bulk glass chips was obtained using the 7525-Å exciting line from a Kr-ion laser. Spectra were recorded as a function of laser power to understand the various steps leading to photo-crystallization both at $x < 0.20$ and at $x > 0.20$. Details of the experimental setup are described elsewhere.\cite{7} Figures 3(a) and 3(b) reproduce spectra observed at $x = 0.18$.
and 0.23. Reference spectra of the crystals in this binary compound (c-Te and c-Si$_2$Te$_3$) were also obtained for purposes of comparison. $^{125}$Te Mössbauer spectra of the glasses were taken at 4.2 K using a source of half-life 58 d, $^{125}$Te$^{m}$ in cubic GeTe. The spectra of the glasses display a quadrupole doublet whose splitting ($\Delta$) decreases with $x$ in a systematic fashion to display a cusp at $x = 0.20$ shown in Fig. 4. The spectrum of c-Si$_2$Te$_3$ was also studied for reference purposes. $^{125}$I emission spectra of the glasses and of c-Si$_2$Te$_3$ were also studied and will be discussed elsewhere.

III. DISCUSSION OF RESULTS AND GLASS MOLECULAR STRUCTURE

The glass-structure consequences of our calorimetric and spectroscopic results are discussed sequentially in this section.

A. Differential scanning calorimetry

Several years ago Cornet found that the compositional dependence of glass transition temperatures $T_g(x)$ and first crystallization temperatures $T_{c1}(x)$ in binary Si$_x$Te$_{1-x}$ glasses is linear in the composition range $0.10 \leq x \leq 0.25$. Our results confirm the linear variation of $T_g(x)$ and $T_{c1}(x)$ found earlier by Cornet. These results do differ qualitatively from those of Asokan, Parthasarathy, and Gopal, however, who observe a local minimum in both $T_g(x)$ and $T_{c1}(x)$ at $x = 0.20$. The difference between our results and those of Asokan et al. are probably related to different sample-preparation conditions and will be discussed elsewhere.

Particularly noteworthy in our scans is the existence of two crystallization temperatures $T_{c1}$ and $T_{c2}$ at $x \leq 0.21$ but only one crystallization exotherm at $x > 0.21$. Similar homogeneous behavior in crystallization temperatures of these glasses above the threshold composition $x_c$ is also observed by Asokan et al. on their samples. We have also carried out these calorimetric experiments at a much smaller scan rate of 5 K/min and find that the threshold composition $x_c \approx 0.20$ is not altered although the absolute values of $T_{c1}$ and $T_{c2}$ are systematically lowered. Clearly the existence of the threshold composition $x_c = 0.20$ is not a

![FIG. 1. Differential scanning calorimetry results on Si$_x$Te$_{1-x}$ glasses plotted as a function of $x$. A scan rate of 20 K/min, a range setting of 5, and ~20 mg mass of the glass sample were used to obtain these scans on a Perkin-Elmer model 2C instrument.](image1)

![FIG. 2. Glass transition temperatures $T_g(x)$, first crystallization temperatures $T_{c1}(x)$, and second crystallization temperatures $T_{c2}(x)$ in binary Si$_x$Te$_{1-x}$ glasses plotted as a function of $x$. Note that at $x = x_c \approx 0.21$ $T_{c1}$ and $T_{c2}$ coalesce and at $x \geq 0.21$ only one crystallization temperature is observed. The linear variation of $T_g(x)$ is signature of molecular phase separation of the glassy networks as discussed in text.](image2)
kinetic phenomenon associated with the crystallization process but must have a structural origin.

We identify the temperature $T_{c1}$ with crystallization of the “floppy part” of the glass network, i.e., amorphous Te, to form c-Te, while the temperature $T_{c2}$ is associated with crystallization of the rigid Si-containing cross links to form c-Si$_2$Te$_3$. The floppiness of the amorphous Te network derives from both chemical as well as topological considerations. The former is due to the large mass of the Te atoms ($m_{Te} = 127$) relative to silicon ($m_{Si} = 28$) producing very soft Te—Te covalent bonds and, therefore, a low melting point. The low coordination number of Te ($m = 2$) on the other hand represents the topological factor contributing to the floppiness of the amorphous Te network. The first step toward crystallization of Te-rich binary Te$_{1-x}$Z$_x$ glasses ($Z = Si, Ge, Al, Ga, \ldots$) is the splitting off$^{7,10}$ of trigonal Te$_3$ chains leaving a glass residue that is enriched in Z and understandably is characterized$^{10}$ by a higher $T_c$ than the virgin glass. Above the threshold, i.e., $x \geq 0.20$, the occurrence of a unique crystallization temperature may be explained by the coalescing of the Si(Te$_{1/2}$)$_4$ units with the excess Te (in the chain fragments) to nucleate a new rigid molecular fragment based on close-packed layers of Te in which Si$_2$ units are inserted. The linear variation of $T_c(x)$ observed in the present glasses is quite similar to a variation reported earlier in As-S (Ref. 11) and Ge-Sn-S glasses.$^{12}$ These results are consistent with the idea that phase separation of these glassy networks intrinsically occurs on a scale characteristic of large molecules.

FIG. 3. (a) Raman spectra of Si$_{18}$Te$_{32}$ as a function of laser power in mW at 7525 A: A, 21; B, 32; C, 45; D, 64; E, 10. Power was reduced to 10 mW for 30 min after D before scanning to record E. Asterisks indicate laser plasma lines. Spectra are offset for clarity. Experimental parameters are 0.25 cm$^{-1}$/step, 10 sec counting time per step, spectral slit width, 1.2 cm$^{-1}$. The amplitudes of the most intense peaks in A–E vary. They are 3000 counts/sec in E and 18 counts/sec in A. (b) Raman spectra of Si$_{16}$Te$_{17}$ as a function of laser power in mW at 7525 A: A, 64; B, 16; C, 19.3; D, 28.5. Asterisks indicate laser plasma lines. All other parameters are the same as in 3(a).

FIG. 4. $^{125}$Te Mössbauer spectra of indicated glass and crystal recorded at 4.2 K using a source of $^{125}$Te$^{m}$ in c-GeTe. The quadrupole splitting ($\Delta$) of g-Si$_{14}$Te$_{76}$ and c-Si$_2$Te$_3$ are 8.4 and 7.1 mm/s. The lower panel shows the x variation of $\Delta$ in the glasses exhibiting a cusp near $x = 0.20$. See text for details.
Support for such a picture can be found in our spectroscopic results which we discuss next.

B. Raman scattering

Our Raman scattering results on Si$_{18}$Te$_{62}$ glass [Fig. 3(a)] at the lowest power (spectrum A, 21 mW) display three broad peaks at 118, 138, and 173 cm$^{-1}$. The lowest-frequency modes can be attributed to disordered chains of Te which are either phase separated by photoinduced bond cleavage or are connected at one end of each chain to structural elements existing in the glass. Analogous phonon frequencies for ordered chains (Te$_x$) in c-Te are known to occur at 123 and 143 cm$^{-1}$. Dramatic changes begin to evolve at higher powers (B–D). The peak at 173 cm$^{-1}$ rapidly grows in strength in B and almost completely disappears by D. Simultaneously, a very intense peak of complex band shape continues to grow from B through D with peak frequency of about 141 cm$^{-1}$. These changes appear to indicate the existence of SiTe$_3$ face-sharing tetrahedra emerging in the glasses. Such tetrahedra are known to occur in c-Si$_2$Te$_3$. One also notes that the nature of the peak near 120 cm$^{-1}$ changes its position and shape as the bulk glass in the scattering volume evolves toward a Si$_2$Te$_3$ composition.

Several comments can be made on the microscopic origin of the 173-cm$^{-1}$ mode. This mode does not arise from elemental Te nor is it observed in the spectrum of c-Si$_2$Te$_3$. A reasonable candidate is clusters composed of SiTe$_4/2$ tetrahedral units which intrinsically occur in the virgin glass as revealed by the presence of this band in spectrum A. Laser irradiation at a 32-mW power level (spectrum B, Fig. 3) significantly enhances the signal strength of the 173-cm$^{-1}$ band probably because cleaving of Te$_x$ chains blue-shifts the optical-absorption edge and leaves a Si-rich bulk glass in which metastable clusters of tetrahedral SiTe$_4/2$ units predominate. At still higher power levels, these clusters reconstruct with the cleaved Te$_x$ chains to nucleate Si$_2$Te$_3$ crystals which display the narrow but intense band at 145 cm$^{-1}$. These results also show the metastable character of the SiTe$_4/2$ units present in the glass. Such tetrahedral units apparently do not occur in a crystalline form as revealed by the absence of a stable crystalline compound of SiTe$_2$ stoichiometry.

One may estimate the expected peak vibrational frequencies of possible SiTe$_4/2$ structural units by analogy with the frequencies of similar structural entities in Si$_x$S$_{6+x}$ and Si$_x$Se$_{6+x}$ glasses and in Si$_x$S$_{6+x}$ and Si$_x$Se$_{6+x}$ nonstoichiometric glasses. The structural units are face-sharing tetrahedra in silicon-rich nonstoichiometric glasses, and both corner-sharing and edge-sharing tetrahedra in the stoichiometric SiS$_2$ and SiSe$_2$ glasses. To factor out the reduced mass effect on the frequencies on going from the sulfides to the tellurides each observed frequency is scaled to the appropriate $\nu_1$ frequency of SiC$_4$, SiBr$_4$, or SiI$_4$ molecules. For example, the frequency associated with the symmetric $\nu_1$ mode of a face-sharing tetrahedron in SiSe$_2$ glass occurs at 200 cm$^{-1}$. The ratio of this frequency to the $\nu_1$ mode at 247 cm$^{-1}$ in SiBr$_4$ is 0.81. For SiS$_2$, one uses the 333-cm$^{-1}$ peak frequency of the face-sharing mode and the 424-cm$^{-1}$ $\nu_1$ frequency of SiC$_4$ to give 333/424 = 0.79, a value very close to the 0.81 value determined for SiS$_2$. Thus, one might expect a similar value for SiTe$_4/2$ face-sharing tetrahedra. A summary of such considerations is given in Table I. From these calculations, the observed band at 173 cm$^{-1}$ in the Si-Te glasses would appear to arise from a stretching mode localized in edge-sharing tetrahedra. Correspondingly, the band observed at 141 cm$^{-1}$ appears to be associated with vibrational motions in face-sharing tetrahedra.

After spectrum D was recorded at a power level of 64 mW, the incident power was reduced to 10 mW for 30 min before scanning $E$ at that power. This significantly reduces the optical and thermal energy input to the sample and allows cooling and crystallization to occur with the formation of c-Si$_2$Te$_3$ as is evident in $E$. The scattering cross section of Si$_2$Te$_3$ is so large compared to other species that it dominates the observed spectrum. In the dark, over a period of 17 h at room temperature, crystallization is partially reversed but the spectrum of c-Si$_2$Te$_3$ can still be observed. Its intensity relative to $E$ is reduced by a factor of about 50. The surface of the sample, however, has suffered observable damage. Melting is indicated and is consistent with the observations in spectra D and $E$.

Samples with $x > 0.20$ behave under the influence of laser irradiation in much the same way as those with $x < 0.20$ with one main exception. The amplitude of the 173-cm$^{-1}$ band is much diminished and as the Si to Te ratio increases, it plays a lesser and lesser role in the convoluted pathway toward crystallization [Fig. 3(b)]. This supports our previous inference that the molecular structure responsible for this band has a composition $x < 0.4$. It is striking that this transitional band appears most strongly for $x$ close to $x = 0.18$ which is close to $x_i = 0.20$. Samples with $x = 0.18 \pm 0.02$ show this band more strongly than for samples with $x = 0.23$. The structure responsible for this band forms just before $x$ increases to $x_i$, and may be a precursor to defective Si$_2$Te$_3$.

C. Mössbauer spectroscopy

$^{125}$Te Mössbauer spectra of the binary glasses display a partially resolved doublet (upper panel of Fig. 4) whose origin is traced to a nuclear quadrupole splitting ($\Delta$) in the $3^+$ first excited state. The quadrupole splitting measures the electric field gradient, which in these covalent materials is determined principally by the distribution of electrons in the $5p$ bonding and nonbonding lone pairs of Te at various sites in the network. Since the natural linewidth of the $^{125}$Te resonance of $5.20$ mm/s is comparable to the quadrupole splittings (~8 mm/s) of the Te sites, it is not possible to unambiguously deconvolute contributions of the chemically inequivalent Te sites from the spectra. However, we have succeeded in deconvoluting contributions of at least two types of Te sites in these glasses using $^{129}$I emission spec-
TABLE I. Structure-element frequency calculations.

<table>
<thead>
<tr>
<th>Structural elements</th>
<th>( v_1 ) (cm(^{-1}))(^{a})</th>
<th>( v_1 ) (SiSe(_3)) / ( v_1 ) (SiCl(_4))</th>
<th>( v_1 ) (cm(^{-1}))(^{b})</th>
<th>( v_1 ) (SiSe(_2)) / ( v_1 ) (SiBr(_4))</th>
<th>( v_1 ) (cm(^{-1}))(^{c})</th>
<th>( v_1 ) (SiTe(_2)) / ( v_1 ) (SiI(_2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Face sharing</td>
<td>333(^d)</td>
<td>0.79</td>
<td>200</td>
<td>0.81</td>
<td>141</td>
<td>0.85</td>
</tr>
<tr>
<td>Corner sharing</td>
<td>381</td>
<td>0.90</td>
<td>227</td>
<td>0.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Edge sharing</td>
<td>427</td>
<td>1.01</td>
<td>245</td>
<td>0.99</td>
<td>173</td>
<td>1.04</td>
</tr>
</tbody>
</table>

\(^{a}\)Reference 16.
\(^{b}\)Reference 17.
\(^{c}\)This work.
\(^{d}\)Data from (a) are interpreted in terms of the recent structural model of (b).

In summary, our scanning-calorimetry results and Raman and Mössbauer spectroscopic observations on Si\(_x\)Te\(_{1-x}\) glasses provide evidence of a major structural reorganization taking place at the vector percolation threshold. The proposed structural reorganization provides a natural explanation for several of our observations which include (a) the sharp decline in \(\langle \Delta \rangle\) marked by a cusp at \(x = 0.20\) (1), (b) the absence of \(T_{1g}\) crystallization exotherm associated with Te chains at \(x \geq 0.20\), (c) the formation of c-Si\(_2\)Te\(_3\) as the final crystalline product upon crystallization of the Si-rich \((x > 0.20)\) glasses, and (d) rapid growth in scattering strength of vibrational modes characteristic of microcrystalline-Si\(_2\)Te\(_3\) at \(x \geq 0.20\). Our structural model could provide a basis to understand the cusp near \(x = 0.20\) in the composition dependence of the semiconductor-metal transition pressure observed elsewhere.\(^{21}\) The structural consequences of rigidity percolation in glassy networks appear to have a common theme. The present results on Si-Te glasses and those reported recently on Ge-Se (Ref. 3) and As-Se glasses\(^{22}\) suggest that at or above the mechanical threshold, the elastically rigid domains largely derive from crystal-like molecular fragments.

Previous observations of mechanical threshold anomalies in Ge\(_x\)S\(_{1-x}\) alloy glasses have generally shown weak power-law behavior proportional to \((x - x_c)^\alpha\) with \(\alpha\) of order 2 or 3. This is quite different from the kink shown in Fig. 2, or the cusp in the metal-semiconductor transition pressure \(P_c(x)\) reported by Asokan et al.,\(^{21}\) both of which correspond to \(\alpha < 1\). Why are the threshold anomalies so much stronger in Si\(_x\)Te\(_{1-x}\)? We believe that the answer to this question is contained in the respective crystal structures of Si\(_x\)Te\(_{1-x}\) and GeSe\(_2\). It seems likely to us that the defect compound Si\(_{1-x}\)Te\(_x\) is stabilized by internal pressure, and that at the mechanical threshold \(x = x_c\) there is a kink in the internal pressure \(P_c(x)\) which stabilizes SiTe\(_2\)-type defect submicrocrystallites. For stable crystals like GeSe\(_2\) a glassy alloy Ge\(_x\)Se\(_{1-x}\) may be a partially phase-separated mixture of submicrocrystalline clusters of Ge\(_2\)Se\(_4\) and Se chain segments near...
$x = x_c = 0.2$. This produces threshold effects almost as weak as those predicted theoretically for an idealized (defect-free) continuous random-network model.\textsuperscript{2}

It is striking that cluster stability (stoichiometrically stable crystals compared to stoichiometrically unstable defect crystals) has a drastic effect on $\alpha$ but very little effect on $x_c$. Moreover, that small effect is such as to bring $x_c$ (within experimental resolution) exactly to the ideal theoretical value $x_c = 0.20$ for the defect case. It appears that nonequilibrium effects could be responsible for $x_c = 0.23$ (2) in Ge$_x$Se$_{1-x}$ alloys.\textsuperscript{3} These nonequilibrium effects on global mechanical equilibrium may be minimized by a nonequilibrium concentration of point defects which locally relieves global mechanical stresses generated by quenching.

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