

Dual Chemical Role of Ag as an Additive in Chalcogenide Glasses

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Ternary $(\text{Ge}_x\text{Se}_{1-x})_{1-y}\text{Ag}_y$ bulk glasses in the Se-rich region ($x < \frac{1}{3}$) are shown to be intrinsically *phase separated* into an Ag_2Se -rich glass and a residual $\text{Ge}_t\text{Se}_{1-t}$ backbone ($t > x$ at $y \neq 0$) with Ag acting as a *network modifier*. The existence of an Ag_2Se glass with a $T_g = 230^\circ\text{C}$ is explained quantitatively in terms of constraint counting algorithms. In contrast, Ge-rich glasses ($x \geq \frac{2}{3}$) are homogeneous, wherein Ag acts as a *network former*, replacing available Ge sites of the backbone to be 3-fold coordinated to Se.

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Ag as an additive in chalcogenide glasses (CGs), and particularly thin films of such glasses, has attracted widespread interest in glass science [1–3]. The interest stems in part from light-induced effects relevant to optical recording and information processing [3]. It also stems from the drastically increased electrical conductivity [4] of Ag-CGs, some of which are solid electrolytes [4]. The structure of glasses containing group IB (Cu, Ag) additives in CGs, as for the celebrated cases of group IV (Si, Ge) and group V (P, As) additives in CGs, has been generally modeled [5], and diffraction results analyzed [6–8], in the spirit of *homogeneous random networks*. In Ag-CGs, Ag-centered local structures apparently *phase separate* from the host network, and one observes *bimodal glass transition temperatures* (T_g). These new structure results provide an attractive starting point to model electrical transport and light-induced effects in Ag-CGs.

Glass forming compositions [9], and particularly the composition variation [10] of T_g in network glasses, contain vital clues on the *connectivity* of the backbone. Ideas on constraint counting [11] have provided the *tools* to decode these clues and to gain insights into the structure of glasses. Binary $\text{Ge}_x\text{Se}_{1-x}$ glasses are rather well studied [12], and it thus appeared attractive to closely examine the chemical role of Ag as an additive in such glasses. Ternary $(\text{Ge}_x\text{Se}_{1-x})_{1-y}\text{Ag}_y$ glasses form in two distinct compositional regions [7,13,14], a Se-rich region ($0 < x < \frac{1}{3}$), labeled I, and a Ge-rich region ($0.38 < x < 0.42$), labeled II (Fig. 1). These regions are separated by a corridor along the GeSe_2 -Ag tie line. Remarkably, no bulk glass formation occurs along this corridor ($x = \frac{1}{3}, y \neq 0$) until the Ag concentration exceeds $y \geq 0.20$ and the two regions I and II coalesce. We have now examined these bulk glasses in modulated differential scanning calorimetry (MDSC), Raman scattering, and ^{119}Sn Mössbauer spectroscopy measurements. In this Letter, we show for the first time that, in Se-rich compositions ($x < \frac{1}{3}$), Ag acts as a *network modifier* and phase separates into an Ag_2Se -rich glass, leaving the $\text{Ge}_t\text{Se}_{1-t}$ backbone Se deficient ($t > x$ at $y \neq 0$), while in Ge-rich compositions ($x \geq \frac{2}{3}$) Ag becomes a *network former*. The *dual* chemical behavior of Ag in the

present CG can be expected to extend *generally* to other Ag-CG systems.

Bulk glasses were synthesized starting from 99.999% pure elements and reacting them at 1000°C for at least 24 h in evacuated (10^{-7} Torr) fused silica ampules. Glass transitions were established using a T -modulated DSC (model 2920 MDSC from TA Instruments, Inc). The intrinsically *heterogeneous* character of Se-rich glasses is seen from the MDSC scans of Fig. 2(a), which reveal two glass transitions, a low T_g (T_g^l) between 180°C and 200°C and a high T_g (T_g^h) at 230°C for a series of glasses at $x = 0.20$ with increasing Ag content. For this case, T_g^l represents the glass transition of the host $\text{Ge}_{0.20}\text{Se}_{0.80}$ backbone. The specific heat jump associated with T_g^h increases in proportion to the Ag content of the glasses, and we identify T_g^h as the glass transition of an Ag-rich phase which crystallizes at $T_x = 300^\circ\text{C}$. Figure 2(b) provides a summary of the $T_g(x, y)$ variation in the present ternary. On this plot, only T_g^l values are plotted in the Se-rich

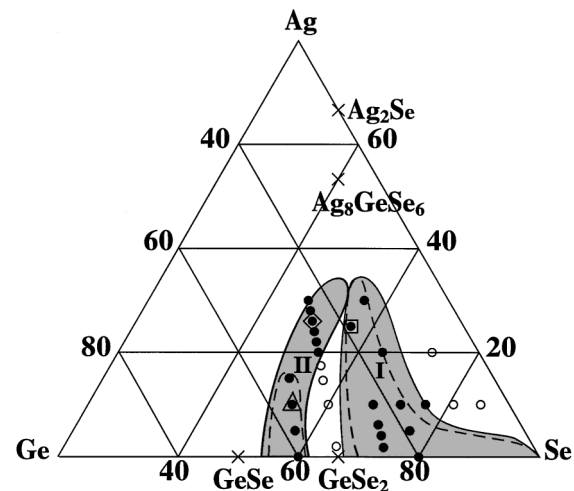


FIG. 1. Glass forming regions I and II in $(\text{Ge}_x\text{Se}_{1-x})_{1-y}\text{Ag}_y$ ternary. The dashed lines give the results of Ref. [4] and the solid lines are from the present work. (○) crystalline samples, (●) glassy samples, and (△) glass samples at $x = 0.4; y = 0.1$ Ref. [5], and (◇) glass sample at $x = \frac{1}{3}; y = 0.28$ Ref. [7], (□) glass sample at $x = 0.25; y = 0.25$ Ref. [8].

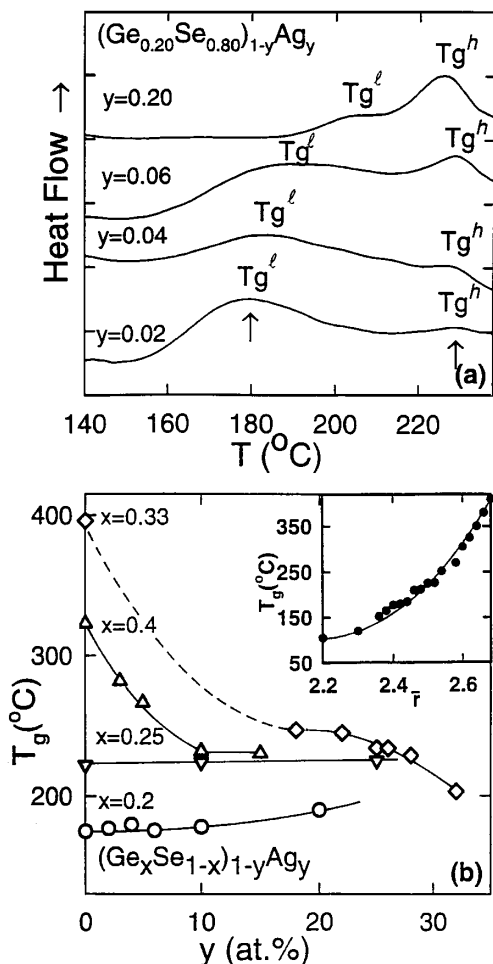


FIG. 2. (a) MDSC scans of indicated glasses taken at a $3^\circ\text{C}/\text{min}$ scan rate with $10^{-2}^\circ\text{C}/\text{s}$ modulation, and 6×10^{-4} (cal/s)/g resolution (distance between hash marks on vertical) showing bimodal glass transitions in Se-rich glasses. (b) $T_g(x, y)$ variation in $(\text{Ge}_x\text{Se}_{1-x})_{1-y}\text{Ag}_y$ ternary glasses showing T_g results from the present work. Only T_g^l values are plotted at $x < \frac{1}{3}$. Inset shows $T_g(\bar{r})$ trend in Ge-Se glasses, Ref. [12].

glasses. One finds $T_g^l(y)$ to mildly increase with y because the $\text{Ge}_t\text{Se}_{1-t}$ backbone becomes progressively Se deficient as the Ag phase separates into an Ag_2Se glass. In contrast, Ge-rich glasses display one T_g which rapidly shifts to lower values upon Ag alloying. Such a $T_g(y)$ dependence at $x = \frac{2}{5}$; $y \neq 0$ suggests that the additive now forms part of the backbone and reduces the connectivity of the alloyed network, as will be discussed later.

Se-rich glasses.—One can describe the phase separation of Se-rich glasses into Ag_2Se glass phase and a Se-deficient backbone by the following:

$$(\text{Ge}_x\text{Se}_{1-x})_{1-y}\text{Ag}_y = (3y/2)(\text{Ag}_{2/3}\text{Se}_{1/3}) + (1 - 3y/2)(\text{Ge}_t\text{Se}_{1-t}). \quad (1)$$

with $0 < x < \frac{1}{3}$, and $t = x(1 - y)/(1 - 3y/2)$. The observed T_g of 230°C for the Ag_2Se glass phase suggests a mean coordination $\bar{r} = 2.5$ based on the general $T_g(\bar{r})$ correlation observed [10,12] [inset of Fig. 2(b)] in CGs.

$\alpha\text{-Ag}_2\text{Se}$ crystallizes [15] in a body-centered cubic lattice of Se atoms in which four Ag^+ ions rapidly diffuse through tetrahedral interstitial sites. Rapid diffusion occurs because of a delicate balance [16] between ionic and covalent interactions that drive the free energy difference ($E_6 - E_4$) between Ag coordination numbers (CN) of 6 and 4 to vanish. Topologically, the structure of $\alpha\text{-Ag}_2\text{Se}$ bears a similarity to that of its melt, as revealed by neutron structure factors [15], and may be used to model the glass as well. The consequence of $E_6 \rightarrow E_4$ is that the *bond-bending force* for the mobile Ag^+ cations *weakens and promotes glass formation* because the underlying *bond-bending* (β) constraint is *broken*. Enumeration of both α (bond-stretching) and β constraints for Se^{2-} anions (CN = 4), but only α constraints for Ag^+ cations (CN = 4) in cubic Ag_2Se , yields the mean constraints/atom of $6\bar{n}_c = 22$, or $\bar{n}_c = 3.66$. The mechanically effective connectivity (\bar{r}_m) of such a network is related to \bar{n}_c as follows:

$$\bar{n}_c = \frac{5}{2}\bar{r}_m - 3 \quad (2)$$

and yields $\bar{r}_m = 2.66$. It may be compared to the thermally (T_g) inferred connectivity of $\bar{r} = 2.50$. Both reside close to the critical connectivity $\bar{r}_c = 2.40$ to optimize the glass forming tendency (GFT) within the constrain counting theory [11].

Figure 3(a) displays the evolution of the Raman line shapes with Ag content in ternary glasses at $x = \frac{1}{4}$. The modes at 200 , 215 , and 250 cm^{-1} have been previously identified [12] with corner-sharing (CS) [and edge-sharing (ES)] $\text{Ge}(\text{Se}_{1/2})_4$ tetrahedra and Se_n chains, respectively. Noteworthy in these scans is the systematic reduction in the scattering strength of the Se-chain mode (CM) with Ag alloying. Although Ag_2Se glass phase appears Raman silent, one can infer its presence by depletion of the Se_n CM. Figure 3(b) provides a plot of the observed scattering strength of the CM (A^{cm}) normalized to that of the CS mode (A^{cs}) as a function of y . For comparison, we also plot the corresponding mode scattering strength ratio, $A^{\text{cm}}/A^{\text{cs}}(z)$, observed in binary $\text{Ge}_{0.2+z}\text{Se}_{0.8-z}$ glasses in Fig. 3(b). The results show that the depletion rate $d(A^{\text{cm}}/A^{\text{cs}})/dy = 2.9 \pm 0.2$ in the ternary glass, while $d(A^{\text{cm}}/A^{\text{cs}})/dz = 3.9 \pm 0.2$ in the binary glass. The depletion rates [17] directly give the Ag-CN's and Ge-CN's. These Raman results suggest that Ag, present at *triangular interstitial sites* with a CN = 3 in $\alpha\text{-Ag}_2\text{Se}$, may be a good representation of the glass structure. Such a network will possess $\bar{n}_c = 3.33$ and, from Eq. (2), yield $\bar{r}_m = 2.53$, much closer to the thermally (T_g) inferred connectivity of 2.50 of the glass.

The Raman line shape in a ternary glass at $x = y = \frac{1}{4}$ [Fig. 3(a)] reveals modes of CS and ES tetrahedra but, as expected, little or no scattering from the Se_n CM. At high Ag content all of the excess Se present in Se_n chains is depleted to form the glassy Ag_2Se phase that separates from the $\text{Ge}_t\text{Se}_{1-t}$ backbone [Eq. (1)]. At $y = \frac{1}{4}$, Eq. (1) shows that the backbone acquires a stoichiometry of $\text{Ge}_{0.3}\text{Se}_{0.7}$, a prediction that is confirmed by the T_g^h of 290°C found for the residual network (with $\bar{r} = 2.60$).

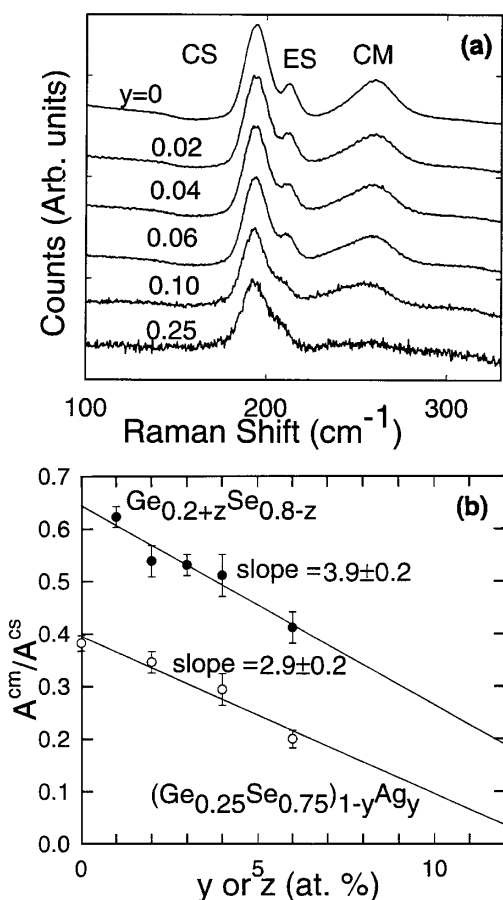


FIG. 3. (a) Raman scattering in $(\text{Ge}_{0.25}\text{Se}_{0.75})_{1-y}\text{Ag}_y$ ternary glasses excited by 647.1 nm line showing depletion of the Se_n -chain mode with Ag content. (b) Se_n -chain-mode scattering strength variation normalized to CS mode, $d(A^{\text{cm}}/A^{\text{cs}})/dy$ in ternary glasses and $d(A^{\text{cm}}/A^{\text{cs}})/dz$ in binary glasses. See Ref. [12] for details.

In contrast, a homogeneous structural model of the $x = y = \frac{1}{4}$ bulk glass, consisting of a specific 19-atom cluster, was proposed [8] from neutron scattering results. The connectivity of the cluster is found to be $\bar{r} = 3$. The bimodal T_g 's do not support a homogeneous structure, and, furthermore, the observed magnitude of T_g^l (230 °C) and T_g^h (290 °C) are too low to be compatible [10,12] with a network possessing $\bar{r} = 3.00$.

Ge-rich glasses.—Molecular structure of the pristine stoichiometric ($x = \frac{1}{3}, y = 0$) and Ge-rich ($x = \frac{2}{5}, y = 0$) glasses was *quantitatively decoded* [18] using ^{119}Sn Mössbauer spectroscopy, and showed the presence of distorted rocksalt GeSe (henceforth labeled *C*) and ethanelike Ge_2Se_3 (henceforth labeled *B*) nanophases. The relative concentrations (I_n/I) of these nanophases (Fig. 4) reveal that the *C* phase ($n = C$) is the majority phase once $x > \frac{2}{5}$. In the *C* phase, cations possess three short and three long Ge-Se bonds.

The ^{119}Sn Mössbauer spectrum of a ternary $(\text{Ge}_{0.4}\text{Se}_{0.6})_{1-y}\text{Ag}_y$ glass at $y = 0.15$ is compared to that of the pristine glass ($y = 0$) in Figs. 5(a) and 5(b). The observed line shapes reveal a partially resolved

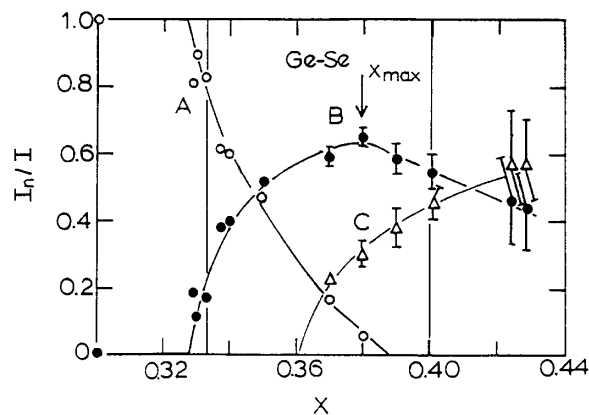


FIG. 4. Mössbauer site intensity ratio, $I_n/I(x)$, reflecting the concentration variation of *A*, *B*, and *C* molecular phases in $\text{Ge}_x\text{Se}_{1-x}$ glasses in the Ge concentration range $0.32 < x < 0.40$ taken from Ref. [18].

doublet. A deconvolution of the resonance line shape in terms of two quadrupole doublets (*B* and *C*) shows that the site-intensity ratio I_B/I_C increases from a value of 1.08 at $y = 0$ to 1.44 at $y = 0.15$. Investigations at intermediate Ag compositions confirm the trend of an $I_B/I_C(y)$ increase with y . These observations suggest that Ag preferentially replaces Ge in the *C*-molecular phase, thereby precluding Sn occupancy of it, and resulting in the Mössbauer site intensity ratio I_B/I_C to increase with y . Ag also replaces Ge sites (quasitetrahedral) in the *B*-molecular phase; however, such a replacement must lead to a severing of the Ge-Ag contacts because of the Coulomb repulsion between the two electropositive cations. Such chemical changes are thought to provide for a reduced connectivity of the backbone as reflected by the decreasing $T_g(\frac{2}{5}, y)$ shown in Fig. 2(b).

Stoichiometric glasses.—The absence of bulk glass formation at low Ag concentrations ($y < 0.20$) is due to the lack of *excess* Se, and results in Ag segregating in its *elemental form*. It is for this reason that Ag photodoping in $\text{Ge}_x\text{Se}_{1-x}$ and $\text{Ge}_x\text{Se}_{1-x}$ films display a maximum [14] at $x = \frac{1}{3}$, as Ag can freely migrate in the free volume [12] of the open GeSe_2 and GeS_2 glass structure. Bulk glasses form when $y > y_c = 0.20$, as ternary melts become unstable against disproportionation into Ag_2Se and marginally rigid Ge_2Se_3 nanophases, with Mössbauer spectroscopy providing evidence for the Ge-rich phase. In the pristine GeSe_2 glass, two Ge(Sn) local environments appear [Fig. 5(d)], and these were identified earlier [18] as Ge(Sn) in CS $\text{Ge}(\text{Se}_{1/2})_4$ tetrahedra (narrow line—*A*) and Ge(Sn) in ethanelike $\text{Ge}_2(\text{Se}_{1/2})_6$ units (doublet feature—*B*). The *qualitative changes* in the line shape [Fig. 5(c)], observed upon alloying Ag in GeSe_2 once $y > y_c = 0.20$, constitute direct evidence for the incipient disproportionation of melts (glasses) which was alluded to above. Specifically, we note that, at $x = \frac{1}{3}$ and $y = \frac{1}{4}$, Eq. (1) yields $t = \frac{2}{5}$, i.e., Ge_2Se_3 . It is for this reason that the spectrum of Ag alloyed GeSe_2 glass [Fig. 5(c)] looks quite similar to that of Ge_2Se_3 glass [Fig. 5(b)].

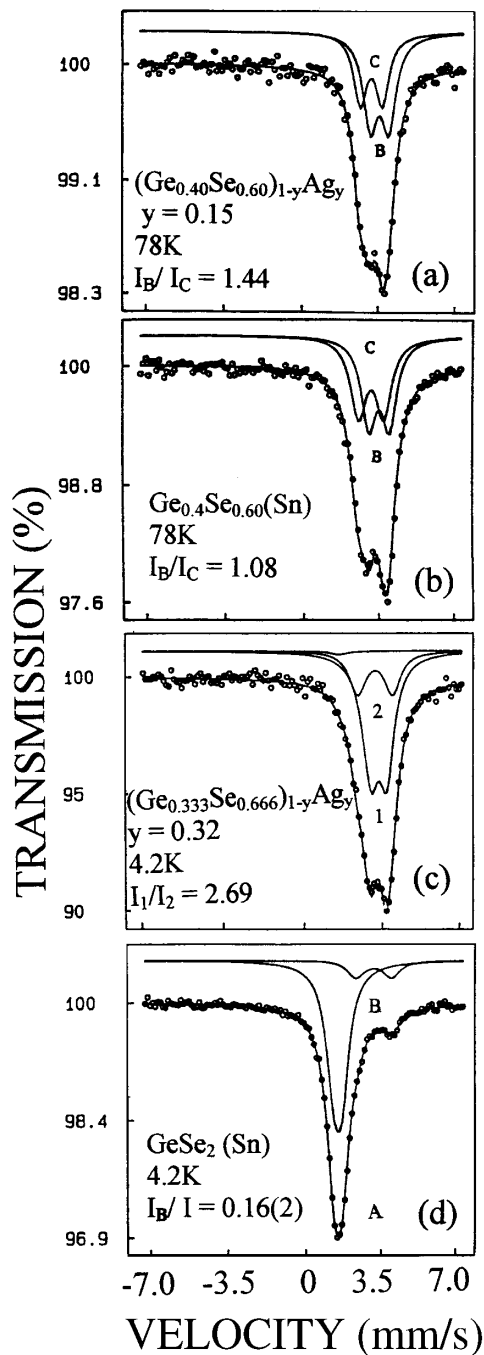


FIG. 5. Mössbauer spectra of indicated glass samples taken using an emitter of ^{119m}Sn in CaSnO_3 .

These new structure results also provide a basis for understanding the electrical conductivity of the present glasses. It has been shown [4] that Se-rich glasses in the present ternary are superionic conductors with conductivity increasing with Ag content and then saturating. In the present model, such behavior is traced to the existence of the superionic Ag_2Se glass phase that should percolate as Ag content increases. On the other hand, Ge-rich glasses ($x = \frac{2}{3}, y$) are found [4] to be semiconductors with the activation energy decreasing progressively with y . Such contrasting electrical behavior is consistent with

the network forming character of Ag as an additive in the Ge-rich glasses to produce states in the gap and narrow it, and thereby increase conduction by the hopping of carriers.

Existence of Ag_2Se glass phase in ternary Ge-Ag-Se glasses is established, and its T_g is quantitatively explained in terms of constraint counting algorithms with no adjustable parameters. The dual role of Ag as a network modifier in Se-rich glasses and as a network former in Ge-rich glasses of the present ternary is demonstrated. Such a role can be expected to extend to other CGs.

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