

UNIVERSAL STRUCTURAL PHASE TRANSITION IN NETWORK GLASSES

Mark Stevens,* J. Grothaus† and P. Boolchand

Physics Department, University of Cincinnati, Cincinnati, OH 45221, U.S.A.

and

J. Gonzalez Hernandez

Energy Conversion Devices, Troy, MI 48084, U.S.A.

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Raman and Mössbauer spectroscopy provide evidence for a transition from a molecular cluster network at $x = 0$ to a continuous network at $x = 0.35$ in $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ alloy glasses. The nature of this morphological transition involves a reformation of molecular cluster surfaces in the heterogeneous phase to yield a homogeneous phase. The transition is believed to be a universal property of the easy glass formers and can be effected in one of several ways.

IN RECENT YEARS two distinct and seemingly conflicting descriptions of inorganic covalent glasses have been used as a basis to discuss their structure and physical properties. A description based on a homogeneous microphase morphology pioneered by Zachariasen [1], also known as the continuous random network (CRN) model, has been widely used [2] to understand diffraction and vibrational data on the easy glass formers such as As_2Se_3 and GeSe_2 . In this model, specific local building blocks of known geometry such as pyramidal $\text{As}(\text{Se}_{1/2})_3$ or tetrahedral $\text{Ge}(\text{Se}_{1/2})_4$ units interconnect by bridging chalcogen to form a random network. In contrast, an alternative description has been proposed [3] which regards these glasses as consisting of at least two kinds of morphologically and stoichiometrically distinct large molecular clusters, analogous to donor and acceptor molecules in molecular crystals. In this molecular cluster network (MCN) model proposed by Phillips [3], cluster surfaces play an integral role in determining the glass forming tendency. The existence of these heterogeneous clusters requires that the chemical order of the network be intrinsically broken [4].

In this letter we present evidence from Mössbauer and Raman spectroscopy on $\text{Ge}_{1-x}\text{Sn}_x(\text{S or Se})_2$ glasses that shows that either model may be correct for covalent chalcogenide alloy glasses depending on composition x . The topological principles that govern the selection of a given structure are discussed in an accompanying letter

by Phillips [5]. As he states, extensive measurements of many glasses have led to many inconclusive discussions. We avoid this uncertainty by using our Raman data as an independent check on the structural interpretation of our Mössbauer data.

Although SnSe crystallizes when quenched from the melt with Sn six-fold coordinated, there is a wide range of compositions [6] in which the ternary alloy $\text{Ge}_{1-x}\text{Sn}_x(\text{S or Se})_{2+y}$ does form glasses with Sn four-fold coordinated for $y \geq 0.3$. We have extended this range to $y = 0$ and $0 \leq x \leq 0.6$ by preparing small samples (≤ 0.25 gm) and quenching them rapidly in water [7]. The glass transition temperatures $T_g(x, y)$ for $y = 0$ were measured at a 10 K min^{-1} scan rate by differential calorimetry [4] and are shown in Fig. 1(a). Our Raman data show no evidence for phase-separated $c\text{-SnSe}_N$ or $c\text{-Ge}(\text{S or Se})_N$ with $N = 1$ or 2.

The sensitivity of Mössbauer spectroscopy as a quantitative probe of broken chemical order in a GeSe_2 glass has been discussed earlier [4]. Spectra of $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ glasses at selected compositions x (Fig. 2) in the glass forming range ($0 < x < 0.6$) clearly show that two and only two distinct types of Sn sites are resolved in these glasses. One of these sites (Site A) which exhibits a narrow single line can be uniquely identified [4] from its isomer shift δ_A with tetrahedrally coordinated Sn in a $\text{Sn}(\text{Se}_{1/2})_4$ unit. Moreover δ_A is independent of x , which indicates that the local coordination environment of site A does not change for $y = 0$ and $0 \leq x \leq 0.6$. The second site (Site B), which exhibits significant quadrupole splitting arising from broken tetrahedral symmetry, has been shown earlier [4] to come from Sn replacing Ge in an ethane-like $\text{Ge}_2(\text{Se}_{1/2})_6$ cluster. From the site intensity (I_A, I_B), we have

* Undergraduate, Physics Department, University of Cincinnati, U.S.A.

† Present address: Proctor & Gamble, Miami Valley Lab, Cincinnati, U.S.A.

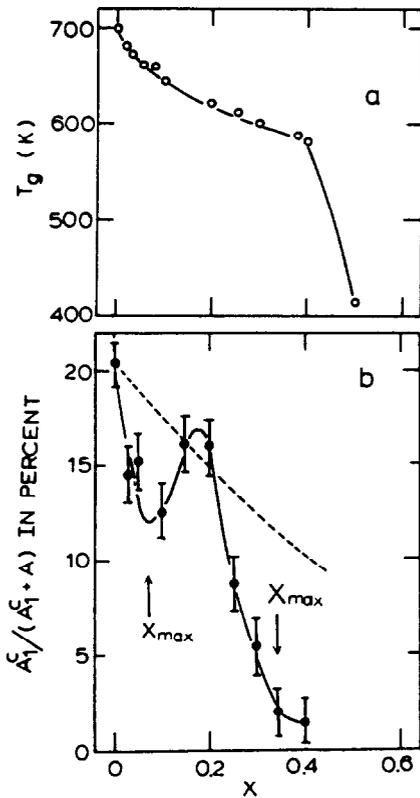


Fig. 1. (a) Glass transitions (T_g) of $\text{Sn}_x\text{Ge}_{1-x}\text{Se}_2$ glasses plotted as a function of x . (b) Normalized $A_1/(A_1 + A)$ scattering strength of the A_1^c companion mode (Ge-Se edge mode) in Raman spectra of $(\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2)$ glasses plotted as a function of x . Here A represents the sum of the $A_1(\text{Ge}(\text{Se}_{1/2})_4)$, $A_1(\text{Sn}(\text{Se}_{1/2})_4)$, and $A_1^c(\text{Sn}-\text{Se})$ mode strengths. The broken line is the expected x -variation of the A_1^c mode strength in a model where Sn randomly replaces Ge in the network. The observed extinction of the A_1^c mode near $x = 0.4$ indicates that a structural transition occurs in these alloy glasses between $x = 0.2$ and $x = 0.4$. The secondary maximum near $x = 0.2$ may arise from an intermediate stage in cluster degradation where the 6-log rafts present at $x = 0$ are replaced by 2-log rafts (for example).

obtained the tetrahedral Sn fraction $T = I_A/(I_A + I_B)$ and have plotted its x dependence in Fig. 3. The microscopic origin of the two peak structure in $T(x)$ will be discussed in connection with network morphology later.

The power of Raman spectroscopy as a sensitive probe of local modes of tetrahedral $\text{Ge}(\text{Se}_{1/2})_4$ units in a GeSe_2 glass has been discussed extensively by a number of previous workers [2, 8–11]. Our low-power (40 mW) Raman spectrum taken with 5145 Å radiation of a $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ alloy glass at $x = 0.03$ is very similar to previously published spectra of a GeSe_2 glass. It reveals the expected Raman active modes of nearly decoupled $\text{Ge}(\text{Se}_{1/2})_4$ units. In addition, it reveals in the bond stretching region, the so-called companion mode (A_1^c) at

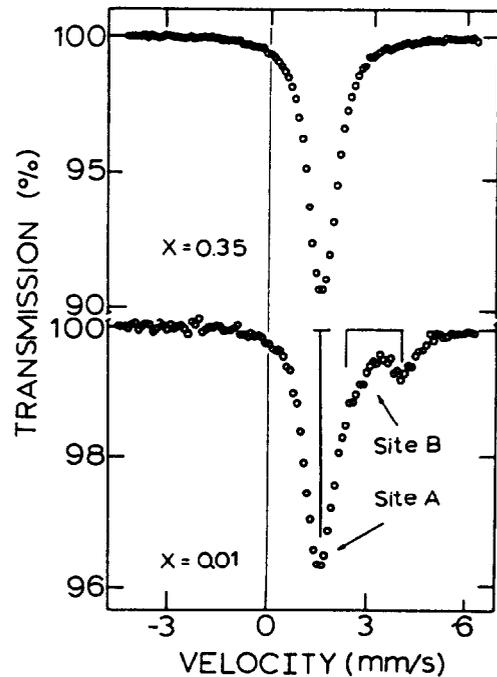


Fig. 2. Mössbauer spectra of indicated $\text{Sn}_x\text{Ge}_{1-x}\text{Se}_2$ alloy glasses showing complete extinction of the asymmetric site B at $x = 0.35$. Only the symmetric site A which represents Sn in a tetrahedral $\text{Sn}(\text{Se}_{1/2})_4$ unit is present at this composition.

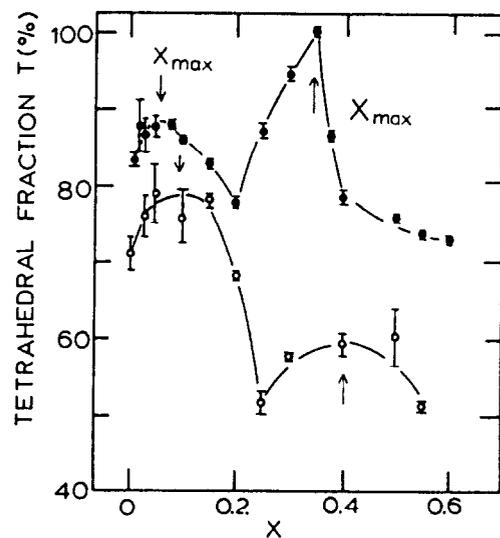


Fig. 3. Mössbauer tetrahedral Sn fraction $T(x) = I_A/(I_A + I_B)$ plotted as a function of x for $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ glasses (●) and $\text{Ge}_{1-x}\text{Sn}_x\text{S}_2$ glasses (○). The two peak structure of $T(x)$ seen in both glasses is discussed in text. Notice that for Se-containing glasses, $T = 1$ at $x = 0.35$ (see Fig. 2).

215 cm^{-1} whose microscopic origin as a cluster edge mode [8] is strongly supported by recent photostructural transformation studies [9]. With increasing x , we find that new modes of tetrahedral $\text{Sn}(\text{Se}_{1/2})_4$ units appear and cause the sharp mode at 202 cm^{-1} to broaden and red shift. Because of the reduced stretching force in $\text{Sn}(\text{Se}_{1/2})_4$ units, one expects a red shift of the A_1 mode of this unit to 185 cm^{-1} as is observed by us. Particularly significant in the spectra of the alloy glasses is the observation that the scattering length of the A_1^c mode extrapolates to nearly 0 as $x \rightarrow 0.35$, as shown in Fig. 1(b). This x -dependence of the $A_1^c(x)$ mode closely complements that of $T(x)$ which is to say that a local minimum in $A_1^c(x)$ corresponds to a local maximum $T(x)$. A qualitatively similar result has been recently found by Murase *et al.* [10] in $\text{Ge}_{1-x}\text{Sn}_x\text{S}_3$ glasses as $x \rightarrow 0.4$. This is a result we will return to later.

The two maxima in $T(x)$ at $x = x_{\text{max}} = 0.07$ and at $x = X_{\text{max}} = 0.35$ in Fig. 3 provide strong support for the existence of large molecular clusters in the alloy glasses for $x < 0.2$. For $x > 0.2$ these clusters being to coalesce. We believe that the polymerization is completed by the formation of a CRN at $x = X_{\text{max}} = 0.35$. The rapid growth in $T(x)$ as x increases in the range $0 < x < x_{\text{max}} = 0.07$ can be qualitatively described in terms of a specific Se-rich cluster of $\text{Ge}_{22}\text{Se}_{46}$ stoichiometry [4] in which Sn atoms selectively replace Ge sites (A_1 sites) on the two outermost logs of the 6 log containing $\text{Ge}_{22}\text{Se}_{46}$ raft structure. This is the case because the attendant stress that has accumulated on the surface of this cluster where Se–Se bonds occur can now be relieved by substituting an atom of a larger covalent radius than Ge. Apparently this process rapidly saturates even when only half of the available A_1 sites in the raft structure are occupied. For $x_{\text{max}} < x < 0.20$ the reduction in $T(x)$ and increase in A_1^c mode strength (Fig. 1(b)) signifies that the fraction of Sn atoms present in polymerized ethane-like units [12] increases at the expense of those in the Se-rich rafts even though this replacement does not maximize the ionic or charge-transfer contribution to the nearest neighbour covalent bonding energies. These Mössbauer and Raman data highlight the delicate interplay between strain fields and valence-force-fields that determines the equilibrium state of a network glass.

Further justification for the correctness of these ideas derives from our results on $\text{Ge}_{1-x}\text{Sn}_x\text{S}_2$ alloy glasses which are also shown in Fig. 3. These exhibit a similar two peak structure for $T(x)$ in which $x_{\text{max}} = 0.10$ i.e., it is shifted towards higher x in relation to the selenide glasses. This trend of a shift in x_{max} to higher x is precisely what one expects to get if a higher degree of broken chemical order prevails in the S-rich cluster in

relation to the Se-rich cluster, as discussed by Phillips [5].

The most profound result to emerge from our experiments is that $T = 1$ at $x = X_{\text{max}} = 0.35$ in $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ glasses. The spectacularly complete restoration of chemical order accompanied by the coincident extinction of the A_1^c mode as $x \rightarrow 0.35$ (Fig. 1(b)), constitutes strong evidence of a change in the micro-phase morphology of the network. We interpret this as a transition of the glass network from a MCN \rightarrow CRN. Specifically, the increase of $T(x)$ in the composition range $0.20 < x < X_{\text{max}} = 0.35$ is visualized as a process in which pure and mixed polymerized ethane-like clusters [12] i.e., $\text{Ge}_2(\text{Se}_{1/2})_6$ and $\text{SnGe}(\text{Se}_{1/2})_6$ reconstruct with the surface of the Se-rich raft clusters to restore the broken chemical order. This reformation process involves a breakdown of bonds between nearly homopolar pairs such as Sn–Sn, Sn–Ge and Se–Se to form the stronger heteropolar Ge–Se and Sn–Se bonds. The extinction of the A_1^c mode is a natural consequence [8] of this bond reformation process. This then leads to the first realization of a Phillips CRN glass [3, 5] consisting only of tetrahedral units of $\text{Sn}(\text{Se}_{1/2})_4$ and $\text{Ge}(\text{Se}_{1/2})_4$ in the approximate ratio of 1 : 2. In contrast, the partial restoration of chemical order ($T = 0.60$) at $x = X_{\text{max}} = 0.40$ in $\text{Ge}_{1-x}\text{Sn}_x\text{S}_2$ glasses indicates that the MCN \rightarrow CRN transition is incomplete and that some degree of molecular clustering prevails both above and below this transition.

In the $\text{Ge}_{1-x}\text{Sn}_x(\text{S or Se})_2$ cation ternary glasses we have selected a system with strong chemical order and a very stable building block (the $\text{Ge}(\text{S}_{1/2})_4$ or $\text{Se}_{1/2})_4$ tetrahedron). We have tuned the number of constraints by replacing Ge with Sn, i.e., erasing some of the bond-bending constraints associated with four-fold coordinated sites. In earlier work [13] on anion ternary glasses $\text{Ge}(\text{Te}_x\text{Se}_{1-x})_2$ more severe tuning was occurring because the chemical order is much weaker. However, similar behavior to that reported here was observed as $x \rightarrow 1$, i.e., the NQR parameters tended to a common value. Unfortunately this value cannot actually be attained in a bulk glass because for $x > 0.6$ devitrification occurs through the disproportionation reaction $\text{GeTe}_2 \rightarrow \text{GeTe} + \text{Te}$. Nevertheless, we believe that other examples of continuous glassy networks can exist. There is some evidence that $g\text{-As}_2\text{Te}_3$ is such a system [14, 15].

In conclusion, we have presented new spectroscopic evidence that points to the existence of a universal transition from a heterogeneous to a homogeneous network morphology for the case of the easy glass forming chalcogenides. These and other recent experiments highlight the central role of internal surfaces in stabilizing the glass network against crystallization that J.C. Phillips

has extensively discussed using a topological theory [3, 5]. It is the existence of this transition that most likely is responsible for the profound photostructural effects native to this class of disordered materials [9].

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