Origin of Glass Formation

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Close parallels exist in Mössbauer-site signatures of $Ge_{2-2x}Sn_{2x}S_3$ glasses and crystalline alloys. The drastic loss of glass-forming tendency in this ternary for $x \geq 0.62$ correlates exactly with a change in molecular structure of corresponding crystals, thus favoring a microcrystalline origin of glass formation.

Most inorganic solids can be made amorphous by vapor deposition onto cold substrates. However, only a handful of inorganic melts can be readily supercooled by an air or water quench to yield bulk glasses which solidify at the glass transition temperature. Oxides and chalcogenides of Si, Ge, and As represent some of the best-known glass formers in nature. The fascination of glass formation thus derives from the truly selective nature of this physical property.

The origin of the glass-forming tendency (GFT) is a subject of great interest. For more than fifty years two opposed explanations have attracted wide support: the microcrystalline model,[1] or the random-network[2] and random-packing models.[3] Recently, Landau theory has supported random models for elemental amorphous metals and metallic glasses ($Pd_{0.8}Si_{0.2}$) as well as covalent (GaAs) glasses based on icosahedral (noncrystalline) bond order.[4] In this Letter we present new Mössbauer results on the molecular structure and GFT of ternary $Ge_{2-2x}Sn_{2x}S_3$ alloys. We find very close parallels between the glass (g-) and crystalline (c-) site signatures. We also find that the GFT changes drastically over a narrow composition range associated with a change in molecular structure of corresponding crystalline alloys. Our data provide direct support for the microcrystalline model.

Our choice of the present ternary, with cation/anion ratio $\frac{2}{3}$ rather than the more common ratio of $\frac{1}{2}$ or less, was based on several factors. (a) Homogeneous glasses can be made in this ternary by water quenching over a wide range of composition $0 < x < 0.62$. The glass transition temperatures T_g, and crystallization temperatures T_x, are found to decrease as a function of x as sketched in Fig. 1. Experiments also show that for $x > 0.62$, the GFT declines so rapidly that at $x = 0.70$, water quenching results in crystalline samples that exhibit neither a T_g nor a T_x. (b) Stoichiometric compounds of well-established crystal structure[5] exist at the compositions $x = \frac{1}{2}$ and 1. The molecular fragments of these crystalline compounds play a crucial role in determining the GFT and microstructure of glasses, an idea that will emerge centrally from the present experiments. (c) Finally, the presence of Sn in the present ternary makes feasible the use of Mössbauer spectroscopy to probe[6] directly the

chemical structure of *both* the glasses and crystals. In Mössbauer spectroscopy, the physical structure of the glasses evolves from the chemical one, with the crystalline alloys providing an unambiguous connection between the two types of structures. Selective spectra of glasses and crystals at $x \geq \frac{1}{2}$ appear in Figs. 2 and 3. We note that two principal features dominate these spectra: a partially resolved doublet whose centroid (δ isomer shift) is displaced to large positive velocities of ca. 3 mm/s (characteristic of Sn^{2+}), and/or a narrow single line residing at ca. 1 mm/s, due either to Sn^{4+} or tetrahedral covalent Sn.[6]

Our spectra of the stochiometric crystals ($x = \frac{1}{2}$ and 1 in Fig. 2) are in excellent accord with those reported[7,8] previously. The structural interpretation of these spectra is straightforward. c-$SnGeS_3$ (Fig. 4) consists of zig-zag polymeric chains of corner-sharing GeS_4 tetrahedra that couple laterally through weaker Sn-S bonds. This molecular structure permits one type of a Sn site only, a Sn^{2+} site that is asymmetrically coordinated, accounting for the presence of a quadrupole doublet having a large positive δ in the spectrum (at $x = 0.5$ in Fig. 2). c-Sn_2S_3 is made of infinitely long, thin, and narrow molecular ribbons [Fig. 4(b)] that
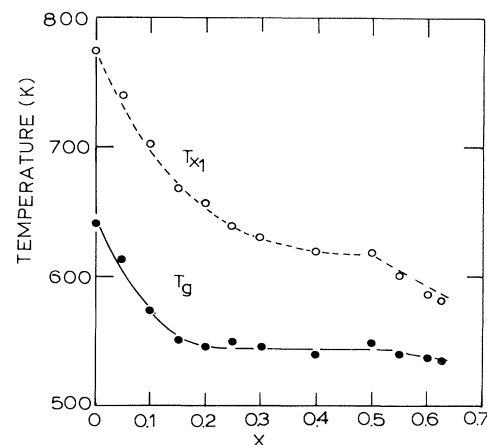

FIG. 1. Glass transition T_g and first crystallization temperature T_{x1} in $Ge_{2-2x}Sn_{2x}S_3$ glasses (obtained from scanning calorimetry at a 20-K/min scan rate) as functions of glass composition x.
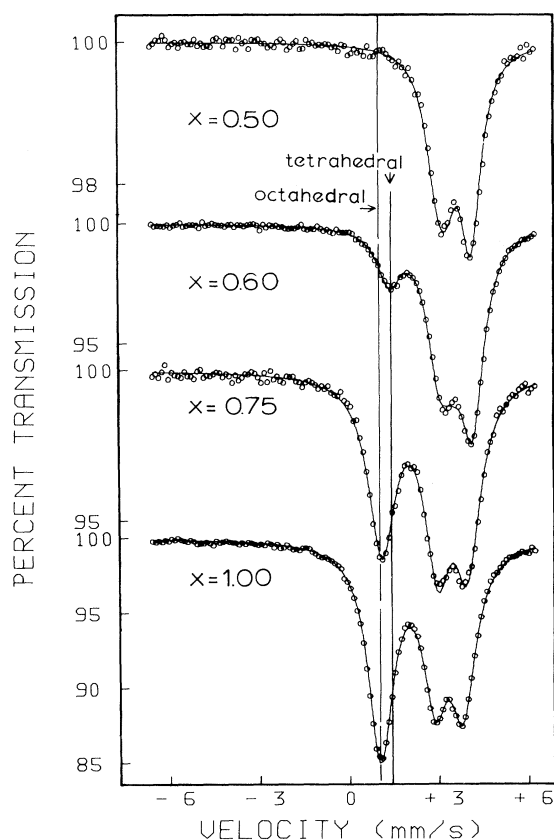
FIG. 2. Mössbauer spectra of crystalline $Ge_{2-2x}Sn_{2x}S_3$ alloys show a decrease in the singlet isomer shift in going from the composition $x=0.60$ to 0.75. See Fig. 5 for additional details. This is due to a change in the Sn site character from tetrahedral (at $x=0.6$) to octahedral (at $x=0.75$) on account of a crystallographic phase change.

couple through weaker van der Waals forces. A given ribbon [Fig. 4(c)] provides for two types of cation sites which occur with equal frequency: symmetrically coordinated (octahedral) Sn^{4+} sites in the ribbon interior and asymmetrically coordinated (threefold) Sn^{2+} sites at the ribbon edges. In the spectrum (at $x=1.0$ in Fig. 2), the singlet near $+1$ mm/s represents Sn^{4+} sites, while the doublet displaced to $+3$ mm/s represents Sn^{2+} sites.

An important result of the present work is that spectra of crystalline alloys at intermediate compositions ($\frac{1}{2} < x < 1$) are not mere superpositions of the end-member spectra for all x. Close examination of the singlet isomer shift reveals an almost steplike change near $x=0.70$, a behavior that is more vividly displayed in Fig. 5. We note that the shift $\delta(x)$ at $x < 0.62$ virtually coincides[9] with that of a tetrahedrally coordinated $Sn(S_{1/2})_4$ species as found in c- or g-GeS_2, while the shifts at $x > 0.8$ acquire a lower value characteristic of the octahedrally coordinated Sn^{4+} species as found in
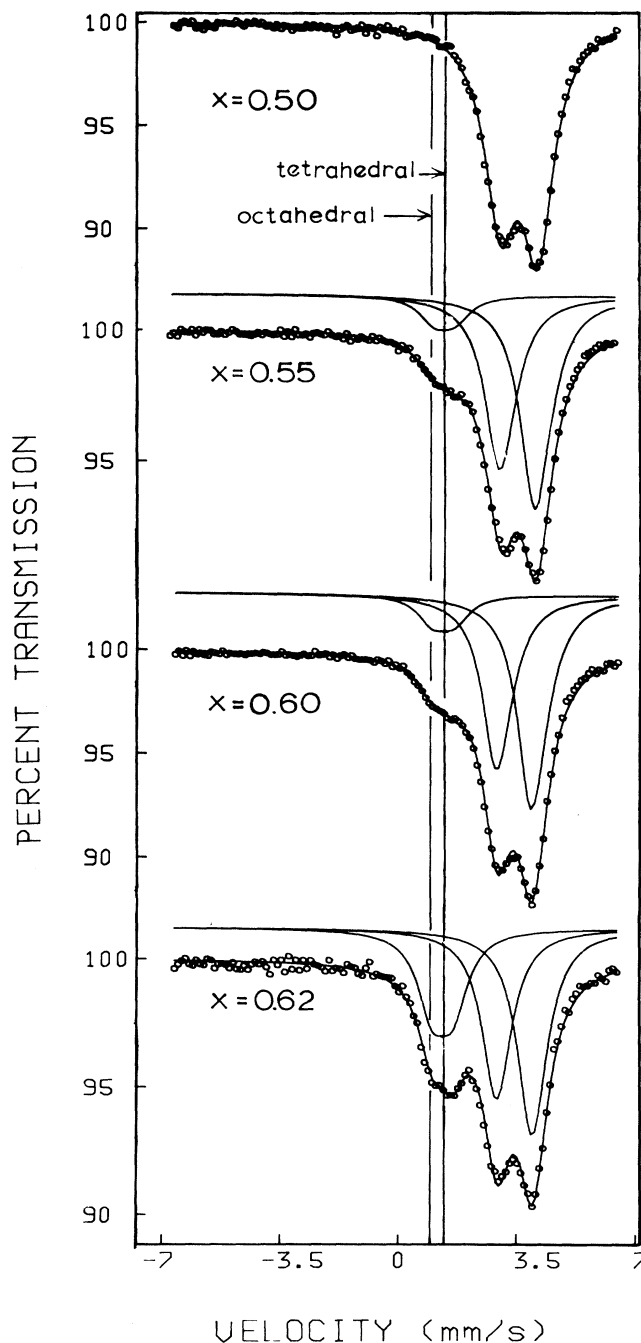

FIG. 3. Spectra of $Ge_{2-2x}Sn_{2x}S_3$ glasses shown near the limit ($x \leq 0.62$) of glass formation. The spectra were least-squares fitted in terms of an asymmetric doublet and a broad singlet (composed of a symmetric doublet). In all these spectra, the broad singlet centroid of 1.31(3) mm/s and quadrupole splitting 0.62(3) mm/s was found to be glass-composition independent in the range $0.5 < x \leq 0.62$. The centroid of the broad singlet is characteristic of a tetrahedral Sn site as in $Sn(S_{1/2})_4$. All spectra were taken at 78 K with a $^{119}Ca^m SnO_3$ source.
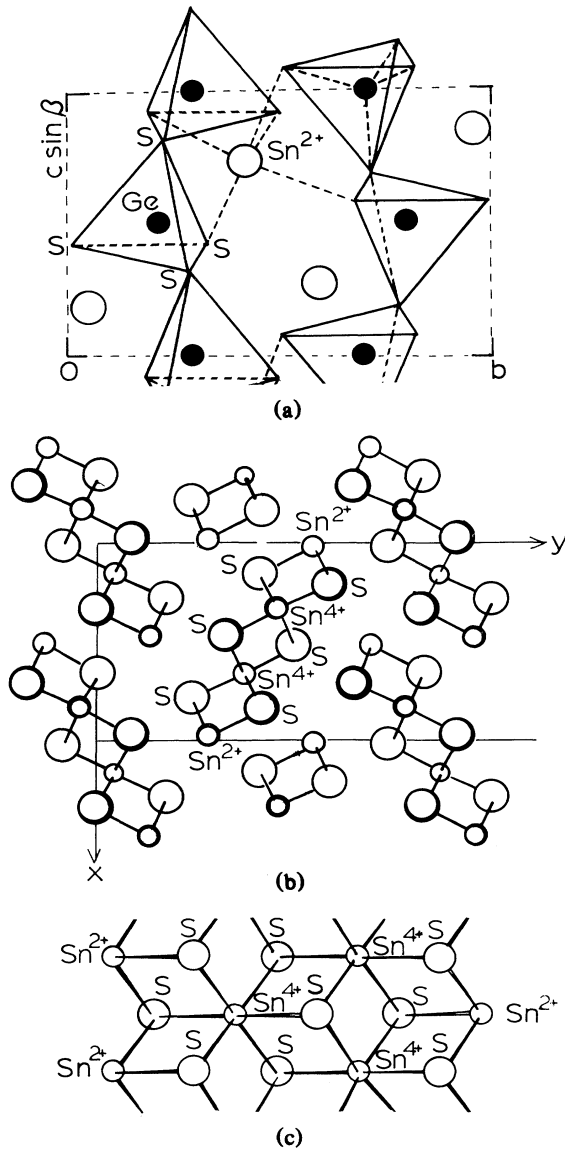
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(a)

(b)

(c)

FIG. 4. (a) Crystal structure of $SnGeS_3$ showing zig-zag chains of corner-sharing GeS_4 tetrahedra that couple laterally (along the b axis) by weaker Sn-S bonds. (b) c-Sn_2S_3 structure which consists of infinitely long, thin, and narrow molecular ribbons having their planes along the z axis. (c) A lateral view of the ribbons showing Sn^{2+} and Sn^{4+} edge and interior cation sites.

FIG. 5. Singlet $\delta(x)$ in c-$Ge_{2-2x}Sn_{2x}S_3$ alloys showing a steplike behavior as a function of x. Shifts characteristic of octahedral (o) and tetrahedral (t) Sn bonded to S near neighbors (taken from Ref. 9) appear on the right-hand side of the plot. X_c designates the limiting glass-forming composition. All shifts are quoted relative to $CaSnO_3$ at 78 K.

c-Sn_2S_3.[9] As discussed in Ref. 9, the shifts of both tetrahedrally and octahedrally coordinated Sn sites in general scale with ligand electronegativity with the octahedral shifts being always lower than the tetrahedral shifts. On this basis, we suggest that the steplike change in $\delta(x)$ is the signature of an increase in Sn coordination number from 4 to 6 that is driven by a crystallographic phase change. Specifically, crystalline
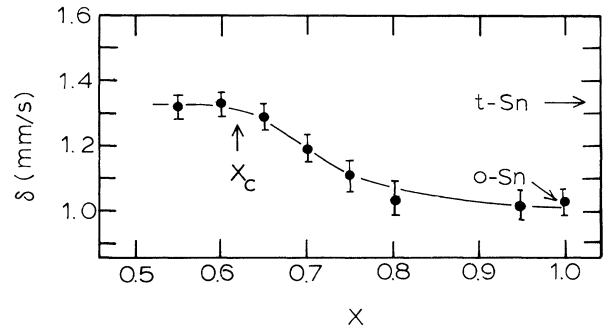
alloys in the composition range $0.5 < x < 0.62$ retain the $SnGeS_3$ structure with the excess Sn atoms replacing Ge sites in the corner-sharing chains to yield $Sn(S_{1/2})_4$ signatures.[10] At compositions $x > 0.80$, the crystalline alloys undergo linear phase separation into c-$SnGeS_3$ and c-Sn_2S_3 with the singlet in the spectra deriving from Sn^{4+} sites of the c-Sn_2S_3 phase. This interpretation of the Mössbauer spectra is confirmed[10] by Raman-scattering results and will be discussed elsewhere.

Spectra of crystalline and glassy alloys in the range $0.5 < x < 0.62$ show that site signatures are quite similar. Specifically, the singlet shifts in both crystalline and glassy alloys coincide with the shift of a Sn site present in a $Sn(S_{1/2})_4$ tetrahedron. Furthermore, in both crystalline and glassy alloys, the singlet-to-doublet site intensity ratio is found to increase with x as ca. $2x - 1$, i.e., fully compatible with the excess Sn's replacing Ge sites in the $SnGeS_3$ structure. In the spectra, the singlet width (FWHM) in glasses is found to be noticeably broader than in crystals. This indicates that the $Sn(S_{1/2})_4$ units display some bond-angle distributions which probably originate from the zig-zag chains' bending or twisting and inducing local strains in the glass network.

The central discovery of the present work is that the drastic loss of GFT at $x > 0.62$ correlates exactly with a change in molecular structure of the corresponding crystalline alloys as discussed above. This correlation implies that the polymeric zig-zag chains, in which both the cations and anions conform to the $8 - N$ coordination rule, promote glass formation. One may understand this result because morphologically, the polymeric chains can easily bend or twist to give rise to a floppy network lacking the periodicity of a crystal. In the planar ribbons of c-Sn_2S_3, both the cations and anions do not conform to the $8 - N$ coordination rule, and one has a more rigid and constrained molecular

unit that suppresses glass formation because it is less amenable to surface or edge reconstruction. Bond reconstruction to promote network formation is in general facilitated when bonding electrons are locally available, as in the polymeric chains, when the $8 - N$ coordination rule is satisfied.

The results obtained here appear surprising in view of the claim[4] that the molecular structure of many glasses is locally noncrystalline. We note, however, that the easy glass-forming composition range in $Pd_{1-x}Si_x$ alloys extends only from $x = 0.16$ to 0.20, close to the eutectic composition[11] $x_e = 0.18$, and that microcrystalline models based on trigonal prismatic clusters explain many detailed features of radial distribution functions in metallic glasses.[12] Elemental transition metals and tetrahedrally coordinated semiconductors do not form bulk (melt-quenched) glasses, but can be made amorphous only when vapor deposited on substrates at low temperatures.

The present results are more easily understood by regarding alloy glassy networks as consisting of elastically rigid and floppy regions[13] which may percolate through the solid. A bulk glass is obtained when floppy $SnGeS_3$ regions dominate the elastic (vector) percolation process,[14] whereas a polycrystalline powder is produced when the rigid Sn_2S_3 regions dominate. Similar behavior (but less dramatic because of greater complexity in the phase diagrams) has been observed in the GFT in As-(S, Se, Te) and Sn-Ge-(S, Se, or TE) chalcogenide glasses.[6]

In conclusion, our Mössbauer data show that the composition dependence of the GFT in chalcogenide alloys parallels the equilibrium phase diagram.[6] Similar parallels are observable in other network glasses and even in many metallic glasses. Reversible microcrystallization of chalcogenide glasses has been observed.[15] Idealized models of glass structure[2-4] are not incorrect, but they describe glass formation only in rare cases where first-order equilibrium effects are small. More realistic models[6,13,14] focus on percolative microcrystalline internal-strain energies, and these explain the composition dependence of glass formation in almost all conventional glasses.

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[10]Independent confirmation of the present model is available from Raman scattering where the A_1 band strength of $Sn(S_{1/2})_4$ units (at 320 cm^{-1}) normalized to the A_1 band strength of $Ge(S_{1/2})_4$ units (at 340 cm^{-1}) is found to increase with glass composition x in the range $0.5 < x < 0.62$.

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