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Structural origin of broken chemical order in a $GeSe_2$ glass

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Two clearly defined and chemically inequivalent Sn sites in the alloy glass $(Ge_{0.99}Sn_{0.01})Se_2$ are observed using Mössbauer spectroscopy. These sites are identified with Sn impurity atoms replacing Ge in tetrahedral $Ge(Se_{1/2})_4$ units and ethanelike $Ge_2(Se_{1/2})_6$ units, and provide direct evidence for intrinsically broken Ge chemical order. Compositional variation of site intensities shows that the origin of this broken order derives from the existence of characteristic clusters in the network.

Melts of As and Ge with $X = S$ and Se, As_xX_{1-x} and Ge_xX_{1-x}, are known to form good glasses when cooled rapidly. These glasses when heated above room temperature exhibit a glass transition[1,2] (T_g). The thermodynamic signature of this transition includes abrupt changes in specific heat, compressibility, and thermal expansion. Although a structural relaxation effect in these thermodynamic properties at T_g has been modeled,[3,4] it is only recently that an attempt to describe quantitatively glass phenomenology in these chalcogenides in terms of topology of the network has emerged. The latter approach due to Phillips[5] provides a means to understand the microscopic behavior of glasses. In this respect, $GeSe_2$ glass has received particular attention[5] although the nature of the equilibrium network characterizing this prototypical glass continues to be surrounded by some controversy.[6-8] Convincing evidence that tetrahedral $Ge(Se_{1/2})_4$ units comprise the principal building block of this glass network was originally provided by Raman vibrational spectroscopy[6] and is supported by diffraction method.[9] The more recent spectroscopic observations of photoinduced reversible reconstruction[8] and of chemically inequivalent Se sites[10] indicate, however, that the chemical order of the equilibrium network is partially broken. The degree to which this order is broken and its physical nature remains, however, uncertain. Indeed, broken chemical order may result from the formation at random of some like-atom bonds (wrong bonds) in a chemically ordered network. Alternatively broken chemical order may be an intrinsic feature of the glass network which derives from the existence of characteristic molecular clusters.[5]

To address the important issue surrounding the structure of $GeSe_2$ glass, we have now probed this material using ^{119}Sn Mössbauer spectroscopy. Although this spectroscopy has been applied previously[11,12] to probe short-range order in chalcogenide glasses, conclusions from these earlier works have focused on glass-to-crystal transformation and the role of increasing Sn content as a network modifier in ternary systems of the type Sn–Ge–S, Sn–As–Se, etc. In contrast, we have studied Ge_xSe_{1-x} glasses alloyed with traces ($\cong 0.3$ at.%) of ^{119}Sn impurity atoms systematically as a function of x, to elucidate aspects of the glass network topology. In this Communication we provide the first clear evidence for intrinsically broken Ge chemical order at $x = \frac{1}{3}$ and discuss its structural origin.

Glasses of $(Ge_{0.99}Sn_{0.01})_xSe_{1-x}$ over a wide composition range $0 \leqslant x \leqslant 0.425$ were prepared[10] and the T_g measured by differential scanning calorimetry. The alloy composition x dependence of T_g was found to be in excellent agreement to previous work[13,14] on Ge_xSe_{1-x} glasses. ^{119}Sn Mössbauer spectra of the glasses were studied at 4.2 K in a conventional spectrometer. Figure 1 shows some of the spectra obtained near the composition $x = \frac{1}{3}$.

The most striking result to emerge from these spectra is the presence of two types of Sn sites: a symmetric site A which shows a single line and an asymmetric site B which exhibits a quadrupole doublet (Table I). The site intensity ratio I_B/I, where $I = I_A + I_B$, increases with x in a manner that is sketched in Fig. 2. This figure also shows the T_g of the corresponding glasses for comparison. On crystallizing a $GeSe_2$ glass, we found that site B disappeared and only site A was seen in the spectra. The observed linewidths in the glasses [full width at half maximum $\cong 0.93(3)$ mm/s] are just as narrow as the ones seen in the $SnSe_2$ and SnSe crystal, and this indicates that the sites (A, B) seen in the glasses are chemically well defined. Details of annealing measurements as well as others performed as a function of glass composition will be discussed elsewhere.[15]

We identify site A in our spectra with Sn atoms that have replaced Ge in symmetric tetrahedral $Ge(Se_{1/2})_4$ units. The evidence to support this identification includes (i) the single-line nature of this site which is consistent with a vanishing electric field gradient (EFG) in a local tetrahedral coordination, (ii) the isomer shift of the single line (see Table I) which lies in a range characteristic[16] of tetrahedral Sn, and

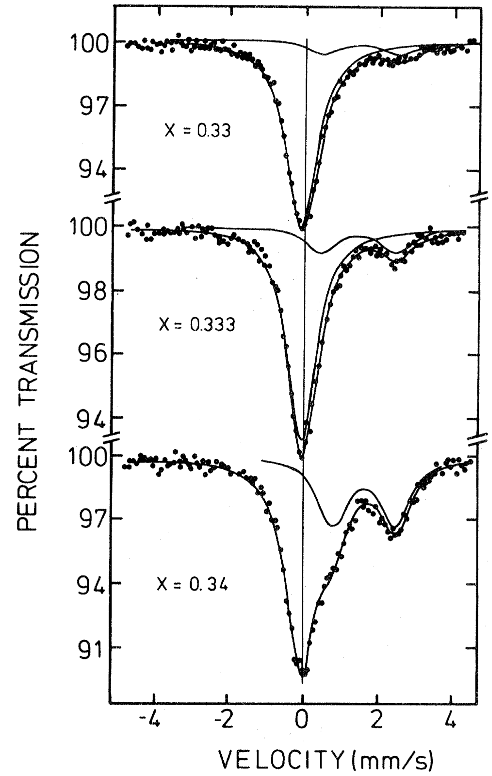


FIG. 1. ^{119}Sn spectra of indicated $(Ge_{0.99}Sn_{0.01})_xSe_{1-x}$ glasses taken with a ^{119m}Sn source in vanadium, showing the presence of two Sn sites: Site A is the intense single line near $v=0$ mm/s, while site B is the quadrupole doublet centered at about +1.5 mm/s.

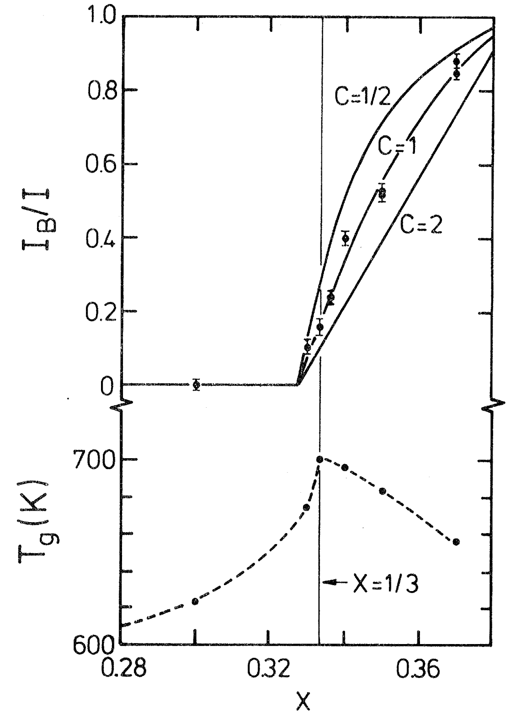
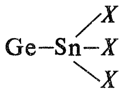


FIG. 2. Observed x dependence of the site intensity ratio I_B/I (top) and glass transition T_g (bottom) in melt-quenched $(Ge_{0.99}Sn_{0.1})_xSe_{1-x}$ glasses. The smooth curves for I_B/I are a plot of Eq. (1) for different C values (see text). The linear variation for the case when $C=2$ also describes the predicted fraction of $Ge_2(Se_{1/2})_6$ units with x and this fraction is amenable to Raman spectroscopy (see text).

(iii) the observation of only site A in c-$GeSe_2$ which consists exclusively of chemically ordered $Ge(Se_{1/2})_4$ units. The dominant nature of site A at $x=\frac{1}{3}$ (shown by $I_B < I$ in Fig. 2) is in accord with results of Raman vibrational spectroscopy which reveal[6-8] that $Ge(Se_{1/2})_4$ units comprise the principal building block of a $GeSe_2$ glass. In our spectra, we identify site B with Sn atoms which have replaced one of the Ge sites in an ethanelike $Ge_2(Se_{1/2})_6$ unit. The evidence in support of this identification includes (i) the doublet nature of this site which we believe results due to the locally asymmetric Sn coordination



$$\mathrm{Ge{-}Sn}\begin{matrix} \diagup X \\ -X \\ \diagdown X \end{matrix}$$

in which the lack of tetrahedral symmetry induces a finite EFG and causes a quadrupole splitting, and (ii) the I_B/I data of Fig. 2 which show that site B dominates ($I_B \approx I$) as $x \rightarrow \frac{2}{5}$, which constitutes strong evidence in favor of the proposed identification since it has been shown by optical[17] and by chemical[14] means that a $Ge_2(Se_{1/2})_6$ ethanelike unit is the building block of a Ge_2Se_3 glass. In our spectra the observation of a finite intensity of site B at $x=\frac{1}{3}$ constitutes, therefore, the first clear evidence for intrinsically broken Ge chemical order in a $GeSe_2$ glass.

TABLE I. ^{119}Sn isomer shift (δ) and quadrupole splitting (Δ) in indicated glass (g) and crystalline (c) samples. The shifts are quoted relative to $BaSnO_3$.

Sample	δ (mm/s)	Δ (mm/s)
g-$GeSe_2$ A	1.55 (3)	. . .
B	3.20 (3)	2.13 (3)
c-$SnSe_2$	1.36 (2)	. . .
c-SnSe	3.31 (2)	0.74 (2)

We have developed a model to relate the populations (N_A and N_B) of $Ge(Se_{1/2})_4$ and $Ge_2(Se_{1/2})_6$ units in the glass network to the measured Sn site occupations (intensities I_A and I_B) of these units. Let us suppose that I_B/I is a smooth function of x and takes on values of 0 and 1 at $x=x_0$ and $x=x_1$. Further, let us suppose that the intensities (I_A, I_B) depend on the populations (N_A, N_B) and on the chemical affinity $C=\exp[(E_B-E_A)/kT_g]$ of Sn atoms to attach themselfes in respective Ge units. E_B-E_A represents the bond energy difference in moving a Sn atom from a site B to a site A. On minimizing the free energy,[15] one can show that

$$\frac{I_B}{I_A+I_B}=\frac{N_B}{CN_A/2+N_B}=\frac{x-x_0}{C(x_1-x)/2+(x-x_0)} \quad . \tag{1}$$

The smooth curve through the data points in Fig. 2 is a fit to Eq. (1), and yields $C \cong 1.0$, $x_0=0.328(1)$, and $x_1=0.385(4)$. The value of $C \cong 1$ indicates that Sn atoms choose randomly the available Ge units, and further that I_B/I equals the fraction of Ge sites in ethanelike units of the network. We define the degree of broken order (DBO) in a $GeSe_2$ glass as the fraction of Ge sites in ethanelike units of the network, i.e., $2N_B/(N_A+2N_B)$ and find its value to be 0.16(1).

The trend of an increase in the site intensity ratio I_B/I with x (Fig. 2), particularly in the composition range $x_0 \leqslant x \leqslant \frac{1}{3}$ where T_g of the glasses increases so rapidly, is a remarkable result. This trend is much too steep to be described by a model in which the chemical order breaking site B is identified with some Ge–Ge bonds formed at random in an ordered bond network. This is seen by comparing the observed slope $d(I_B/I)/dx$ at $x=\frac{1}{3}$ of 32(2) [Fig. 2 and Eq. (1)] with the calculated slope $d(N_{\text{Ge-Ge}}/N)/dx$ of 18 describing the change in the fraction of Ge sites in Ge–Ge bonds at $x=\frac{1}{3}$ in an ordered bond network.[18] Indeed, as the number of Ge–Ge bonds at $x=\frac{1}{3}$ increases (increased disorder), the slope $d(N_{\text{Ge-Ge}}/N)/dx$ decreases from its maximum value of 18 to a minimum value of 0.04 for a completely random covalent network.[18] This trend, on the other hand, is better described as reflecting a rapid growth in the fraction of Ge sites in $Ge_2(Se_{1/2})_6$ units with x. According to our data the fraction $Ge_2(Se_{1/2})_6$ units, i.e., $N_B/(N_A+N_B)$, is predicted to vary linearly with x (straight line corresponding to $C=2$ in Fig. 2). This linear variation is expected to scale with the scattering strength of the 180-cm^{-1} feature [shown by Lucovsky *et al.*[17] to be the bench mark of a $Ge_2(Se_{1/2})_6$ unit] in Raman spectra of Ge_xSe_{1-x} glasses.

The presence of a nonzero fraction of $Ge_2(Se_{1/2})_6$ units at $x=\frac{1}{3}$ requires on grounds of stochiometry that there be a characteristic Se-rich cluster present in a $GeSe_2$ glass. Bridenbaugh *et al.*[7] were the first to propose a specific Se-rich cluster (Ge_6Se_{14}) in this glass which actually consists of a raftlike fragment of the high-temperature (β) crystalline form and which is laterally bordered by Se–Se bonds. This cluster requires[19] that the DBO be 0.40, i.e., a factor of 2.5 higher than the value (0.16) obtained experimentally by us. Inspection of the crystal structure[5] of β-$GeSe_2$ reveals that there are specific lateral dimensions (along b axis) at which broadering by Se–Se bonds can be invoked to produce characteristic clusters of progressively reduced Se richness. One such cluster of $Ge_{22}Se_{46}$ stochiometry, which will yield a DBO of 0.154, provides, according to our data, an excellent candidate to be the characteristic Se-rich cluster of a $GeSe_2$ glass. This cluster, which is more like a ribbon, differs from the outrigger raft[7] cluster in that it consists of six instead of two corner-sharing chains which are bordered by Se–Se bonds.

Direct evidence for the presence of a Se-rich cluster in a $GeSe_2$ was provided recently through measurements[10] of the ^{129}I EFG tensor in $GeSe_{2-x}Te_x$ alloy glasses. In these experiments, composition dependence of the site intensity ratio (see Fig. 2 of Ref. 3) showed a rapid variation as $x \to 0$. In order to quantitatively describe this rapid variation of site intensities, these authors[10] have found it necessary to require the Se-rich cluster to be larger and less Se rich than $Ge_{18}Se_{38}$. It is thus remarkable that two independent experiments lead to the same details of the molecular nature of a $GeSe_2$ glass.

In conclusion, we have presented ^{119}Sn Mössbauer spectra of melt-quenched network glasses that are usually successful in demonstrating the breakdown of short-range chemical order in a $GeSe_2$ glass. The physical nature of this broken topological symmetry is deduced from the compositional variation of site intensities, which relates to the medium-range order of the network, and in particular suggests the existence of a Ge-rich and a large Se-rich cluster.

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$$\frac{2n_{\text{Ge-Ge}}}{0.25n_{\text{Ge-Se}}+2n_{\text{Ge-Ge}}}=\frac{2-3x}{2-2.75x}\ .$$

This yields a slope $d(N_{\text{Ge-Ge}}/N)/dx$ at $x=\frac{2}{3}$ of 18. A similar calculation for a random covalent network yields $d(N_{\text{Ge-Ge}}/N)/dx=0.04$ at $x=\frac{2}{3}$.

[19] Stochiometrically $GeSe_2=2Ge_2Se_3+Ge_6Se_{14}$. There are six $Ge(Se_{1/2})_4$ units ($N_A=6$) for every two $Ge_2(Se_{1/2})_6$ units ($N_B=2$) yielding $2N_B/(N_A+2N_B)=0.4$.