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$(Si_xGe_{1-x})S_2$ glasses: Networks of separate molecular clusters

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The question of isoelectronic substitution in chalcogenide glasses is explored. Raman measurements on $(Si_xGe_{1-x})S_2$ glasses reveal a microstructure consisting of separate SiS_2 and GeS_2 molecular clusters. The short- and medium-range order of these clusters appears to be unperturbed by alloying. The present results provide strong evidence for the existence of molecular clusters in glasses and illustrate a connection between intramolecular forces and medium-range order of the clusters. The differences between the SiS_2 and GeS_2 clusters are discussed in relation to differences between the corresponding crystalline compounds.

INTRODUCTION

Isoelectronic substitution is a common technique for modifying the optical and electronic properties of amorphous semiconductors for various applications.[1,2] In addition, isoelectronic substitution has been used to probe the atomic structure of network glasses via Raman, infrared, and Mössbauer-effect spectroscopy.[3–6] Implicit in much of this work has been the assumption that isoelectronic substitution [e.g., Sn for Ge in $GeSe_2$ (Refs. 3 and 4)] is possible. At present, although many authors suggest that such substitutions occur, no direct evidence has been obtained to support these claims.

This study addresses the question of isoelectronic substitution in chalcogenide network glasses of the form $(Si_xGe_{1-x})S_2$. Sharp molecularlike Raman lines are observed for all values of x associated with SiS_2 and GeS_2 clusters. The large separation (~ 80 cm^{-1}) between the A_1 modes of $Si(S_{1/2})_4$ and $Ge(S_{1/2})_4$ tetrahedral units permits a quantitative analysis of the Raman spectra of the alloy glasses. A major conclusion of the present work is that isoelectronic substitution does not occur in these glasses within the sensitivity of the measurements and that the alloy glasses consist of separate SiS_2 and GeS_2 molecular clusters. The inability of Si(Ge) to replace Ge(Si) in their respective molecular clusters is discussed in terms of the differences between the crystalline silicon- and germanium-sulfur compounds.

EXPERIMENTAL PROCEDURE AND RESULTS

The starting materials for the preparation of the glasses were 99.999% pure elemental Si, Ge, and S. After sealing in evacuated fused silica tubes, the samples (1—2 g) were alloyed at 1050—1100 °C for 3 d. Defect-free, transparent to slightly yellow glasses were formed upon water quenching. No reaction with the fused silica tubes was observed and the glasses could be easily removed from the walls of the tube.

X-ray diffraction patterns of the as-prepared glasses consisted entirely of smooth broad diffraction peaks characteristic of amorphous materials. Differential scanning calorimetric (DCS) measurements (10 K/min) of the as-prepared samples also confirmed their glassy nature. The glass transition temperatures (T_g) are relatively insensitive to the [Si]/[Ge] ratio and ranged from 453 °C for SiS_2 to 470 °C for GeS_2.

The Raman scattering of the glassy samples was measured using a Spex Ramalog 4-1401 (double monochrometer) equipped with a cooled photomultiplier. The samples were kept in evacuated fused silica tubes during the measurements. Spectra were recorded with the use of 20 mW of power at the sample with the 5145-Å line of an Ar-ion laser and four wave-number resolution. The Raman spectrometer is interfaced to a Nicolet 1180 computer and operated in a multiple sweep mode. Typically 10—20 sweeps were made for each sample.

The Raman spectra of the $(Si_xGe_{1-x})S_2$ glasses are displayed in Fig. 1. Sharp molecularlike modes are observed for all compositions. A relatively large separation exists between the primary Raman features of SiS_2 and GeS_2 due to the greater bond strength of Si—S compared to Ge—S. The spectra appear to be a simple superposition of the Raman spectra of the end-point compounds, with GeS_2 having a noticeably larger Raman cross section than SiS_2. An especially important point to note is that no lines appear in the intermediate compositions that are not observed in the end-point compositions. The Raman scattering in the region 500—600 cm^{-1} of the spectra has been found to come from the fused silica tubes and is not a mode of the glasses.

DISCUSSION

The discussion begins with the end-point compositions GeS_2 and SiS_2. Glassy GeS_2 has been the subject of extensive investigations.[7,8] Although a variety of measurements have provided evidence of medium-range order,[8,9] there is at present no consensus on its detailed nature. A common view is that the medium-range order of glassy GeS_2 has some relation to that of the quasi-two-dimensional high-temperature crystalline phase β-GeS_2.[8] The Raman modes of glassy GeS_2 and their identifications

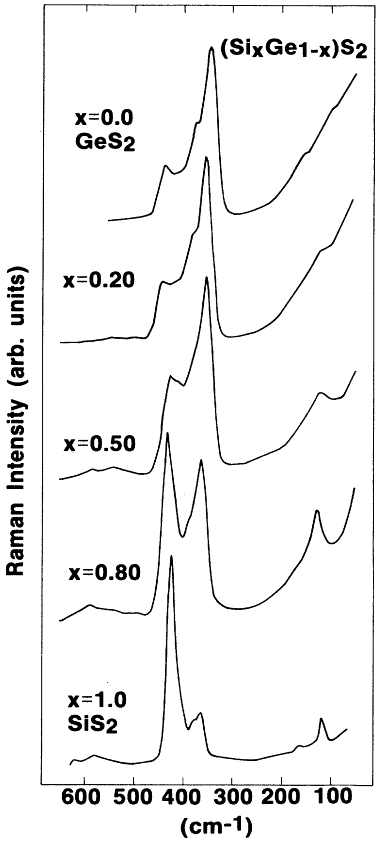

FIG. 1. Room-temperature Raman spectra of the glasses $(Si_xGe_{1-x})S_2$.

are listed in Table I. In addition to the four normal modes of a $Ge(S_{1/2})_4$ tetrahedral unit (A_1,E,F_2,F_2), two additional A_1-like modes (labeled A_1^c) are observed. These modes are believed to be the signatures of medium-range order in glassy GeS_2.[9]

Recent work on Si-based chalcogenide glasses (SiS_2 and $SiSe_2$) has provided dramatic evidence of medium-range order.[10] In glassy SiS_2 for example, the atomic structure consists of randomly oriented chains of edge-sharing tetrahedra. The details of the Raman spectrum of glassy SiS_2 are listed in Table I. In addition to the four normal modes of a $Si(S_{1/2})_4$ tetrahedral unit, an extra line labeled A_1^B is present. In Ref. 10, it was shown that the A_1^B line results from the symmetric stretching of the outer four chalcogen atoms of a bitetrahedral $Si_2(S_{1/2})_8$ unit. The A_1^B line is therefore the signature of medium-range order in glassy SiS_2.

TABLE I. Positions and identifications of the Raman active modes of glassy SiS_2 and GeS_2.

SiS_2 (cm^{-1})	Identification	Comment
121	E	
174	F_2	
367, 381	A_1^B	bitetrahedral mode
430	A_1	
625	F_2	
GeS_2 (cm^{-1})		
110	E	
147	F_2	
345	A_1	
370	A_1^c	companion line
375	F_2	
435	A_1^c	companion line

The indication of whether Si(Ge) replaces Ge(Si) would be the presence of A_1^c lines related to Si substituting for Ge in the GeS_2 clusters or an A_1^B line resulting from Ge substituting for Si in the SiS_2 chains. Fortunately, limits on the positions of these lines can be predicted without a knowledge of the details of the SiS_2 and GeS_2 clusters. As noted in Ref. 10, the A_1^B lines of SiS_2 and $SiSe_2$ scale with the square root of the Si-X force constant divided by the mass of X (S or Se). The A_1^c lines of GeS_2 obey the same kind of scaling. With the use of Si-S and Ge-S stretching force constants from the experimentally observed A_1 modes, the positions of the substitutional lines can be calculated. The A_1^c lines for Si replacing Ge in glassy GeS_2 would be located at 480 and 548 cm^{-1}, while the A_1^B lines for Ge replacing Si in glassy SiS_2 would be at 301 cm^{-1}.

A problem with the above analysis is that it applies to the case of the replacement of all the Si(Ge) atoms responsible for a particular mode by Ge(Si). For example, the value of the Ge-A_1^B line at 301 cm^{-1} corresponds to replacement of two neighboring Si atoms by Ge in the chainlike structure of SiS_2. An additional line would appear for the case of an isolated Ge atom in the SiS_2 chains between the predicted Ge-A_1^B line at 301 cm^{-1} and the Si-A_1^B line at 370 cm^{-1} corresponding to a $SiGe(S_{1/2})_8$ bitetrahedral unit. The number of additional lines that might be expected is therefore dependent on the number of Si(Ge) atoms involved in each particular mode. The calculated values for Ge-A_1^B and Si-A_1^c lines provide limits on the positions of the additional lines. For Ge replacing Si in SiS_2 glassy clusters, additional lines would appear in the region 301—350 cm^{-1}. Likewise, the signature of Si replacing Ge in the GeS_2 clusters would be additional Raman lines in the region 450 to 550 cm^{-1}. As mentioned earlier, no extra Raman lines are observed in the intermediate compositions (x). In addition to this, no changes in the relative intensities of the lines in the various clusters are observed. The intensity of the Raman lines that are associated with medium-range order are expected to be especially sensitive to substitution since it reduces the symmetry of the modes. This fact strongly suggests that only separate SiS_2 and GeS_2 clusters are present.

A test of the above proposal is whether the intermediate compositions can be fit to a superposition of the end-point compositions SiS_2 and GeS_2. The $x=0.80$, 0.50, and 0.20 spectra were least-squares fit in the region from 300 to 500 cm^{-1} to a superposition of the Raman spectra of SiS_2 and GeS_2, allowing the relative amounts of SiS_2 and GeS_2 and the line positions to vary in the fitting procedure. Excellent fits were obtained yielding the relative fraction of SiS_2 and GeS_2 as a function of composition (x) and accounting for all of the modes observed in the glasses. An example of the fitting process is shown in Fig. 2 for the $x=0.50$ spectrum. Polarization measurements of the mixed glasses show that the depolarization ratio of the various lines are the same as in the end-point glasses, providing further evidence for the idea of a separate-cluster network.

To directly compare the relative fraction of $[SiS_2]/[GeS_2]$ obtained from the Raman measurements with the known compositions of the samples, the relative Raman cross section (σ) for SiS_2 and GeS_2 clusters is necessary. Since this quantity is unknown, a constant relative Raman cross section is assumed and its value is determined by fitting to the predicted behavior. Figure 3 shows the result of this process in which the corrected [Si]/[Ge] tetrahedral fraction determined by the Raman measurements is plotted versus composition. A single value of the relative Raman cross section was used to correct the experimental points to bring them into agreement with the expected behavior (solid line). The value of the relative cross section obtained is $\sigma(SiS_2)/\sigma(GeS_2)=0.26$. Figure 3 provides strong evidence for the claim that separate SiS_2 and GeS_2 clusters coexist in the alloy glasses. Since the Raman cross section is determined primarily by the local symmetry of the molecular species, the successful use of a constant Raman cross section illustrates that both the short-range and medium-range order of the SiS_2 and GeS_2 clusters are undisturbed by alloying. Small shifts in the positions of the A_1 modes of SiS_2 and GeS_2 occur with changes in composition. The positions of these lines are listed in Table II and the origin of these shifts will be discussed later.

The existence of separate SiS_2 and GeS_2 clusters in the alloy glasses is at first surprising, given the resemblance of Ge(IV) to Si. The elemental forms, GeI_4 and SiI_4, hexagonal GeO_2 and SiO_2, tetragonal GeO_2 and the rutile form of SiO_2, are all isostructural. In addition to this, the Ge analogs of all the major types of silicates and aluminosilicates have been prepared. In contrast to this, the Si and Ge compounds with S are very different in terms of their medium-range order. The crystalline form of SiS_2 has a simple chain structure, while GeS_2 has a three-dimensional silicalike structure at low temperatures and a two-dimensional layered structure at high temperature.

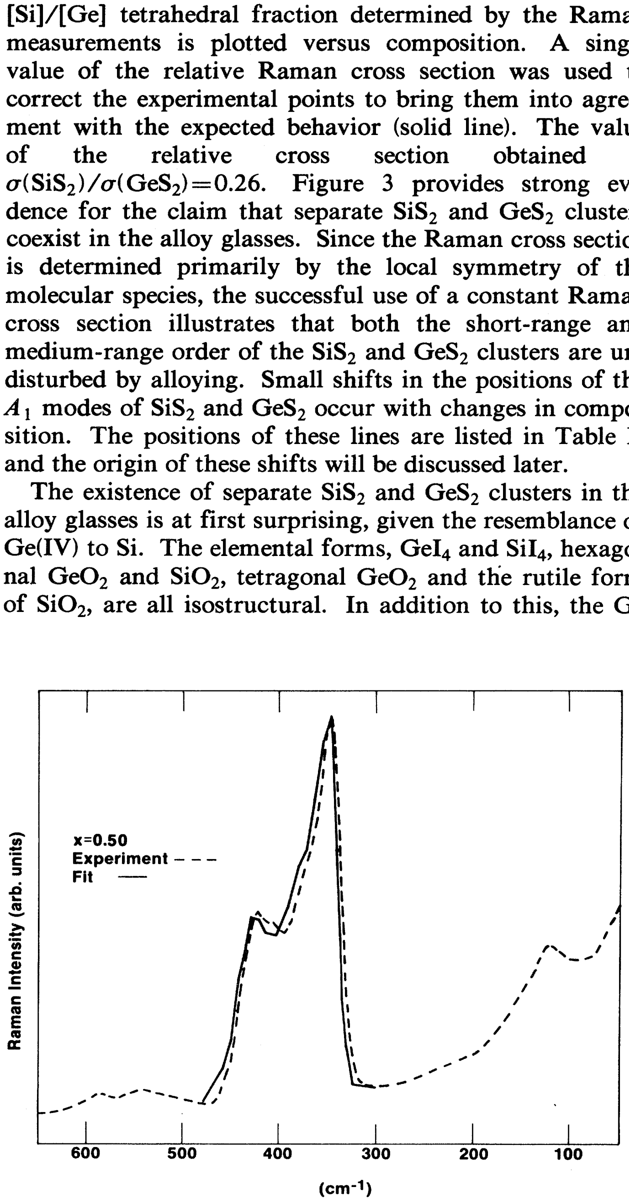

FIG. 2. An illustration of the results of the least-squares fitting procedure for the $x=0.50$ spectrum. The experimental Raman spectrum for the $x=0.50$ glass is shown as a dashed line. The solid line is the fit of the spectrum in the range 300—500 cm^{-1} to a superposition of the Raman spectra of the end-point glasses SiS_2 and GeS_2.

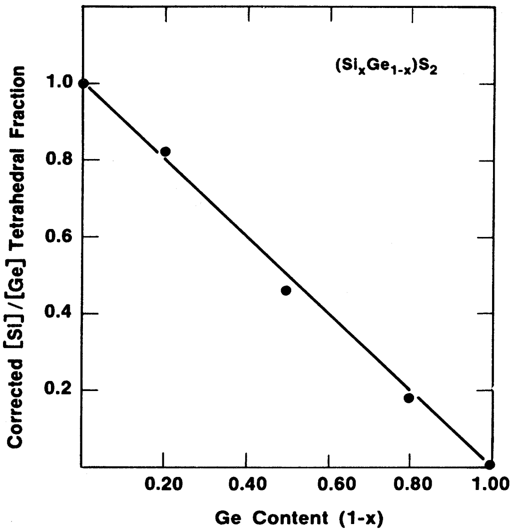

FIG. 3. Corrected [Si]/[Ge] tetrahedral fraction obtained by Raman spectroscopy plotted vs composition (x) of the glasses. The values are corrected by the relative Raman cross sections (see text). The solid line is the predicted behavior for a mixture of SiS_2 and GeS_2 clusters.

As mentioned earlier, the structure of the glassy form of GeS_2 is believed to be related to that of the high-temperature two-dimensional β-GeS_2 crystalline phase. Raman and x-ray studies of crystalline $(Si_xGe_{1-x})S_2$ alloys show that the solubility of Si (Ge) in crystalline GeS_2 (SiS_2) is less than 2%. One obvious difference between Si and Ge is the 10% smaller covalent radius of Si, which implies a strain energy term in the free energy inhibiting isoelectronic substitution. Other important factors include the more covalent character of Si compared to Ge and the greater tendency of Ge(IV) to have six nearest neighbors. In any case, the same factors that lead to phase separation of the crystalline alloys seem to result in the separate cluster networks observed in the glassy alloys.

TABLE II. Positions of the A_1 Raman active lines corresponding to $Si(S_{1/2})_4$ and $Ge(S_{1/2})_4$ tetrahedra in the glasses $(Si_xGe_{1-x})S_2$.

x	$A_1[Si(S_{1/2})_4]$ (cm^{-1})	$A_1[Ge(S_{1/2})_4]$ (cm^{-1})
1.0 (SiS_2)	430(2)	
0.8	430	358(2)
0.5	430	352
0.2	428	346
0.0 (GeS_2)		345

This similarity with the crystalline alloy case is very strong evidence for the existence of molecular clusters in SiS_2 and GeS_2 glasses. The insolubility of Si (Ge) in crystalline GeS_2 (SiS_2) is not surprising, given the differences between the medium-range order of the crystalline compounds. Likewise, the behavior of the glassy alloys indicates the existence of medium-range order and the restrictions it imposes on substitution in the glassy clusters.

A final point concerns the nature of packing of the separate clusters in the alloy glasses. No information is available on how the clusters pack together or the physical extent of the clusters. Low-angle diffraction measurements and possibly high-resolution electron microscopy would be helpful here. The subtle shifts observed in the positions of the A_1 lines with composition (Table II) may be an indication of strain developing between the separate clusters. High-pressure Raman experiments would be useful in investigating this suggestion.

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