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Chemical bonding and the atomic structure of Si_xSe_{1-x} glasses

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The nature of chemical bonding and the atomic structure of Si_xSe_{1-x} glasses is investigated with the use of Raman spectroscopy and neutron-diffraction measurements. In these glasses heteropolar bonds are strongly favored at all compositions (x) and chemically ordered glassy compounds exist having the stoichiometries $SiSe_2$ and Si_2Se_3. There is a one-to-one correspondence in the Raman modes of crystalline and glassy $SiSe_2$. Glassy $SiSe_2$ is composed of randomly oriented chains of edge sharing $Si(Se_{1/2})_4$ tetrahedra. Excess Se $(x<\frac{1}{3})$ and excess Si $(x>\frac{1}{3})$ are accommodated in the glassy structure as Se chains and ethanelike Se_3—Si—Si—Se_3 units. The identifications of the various molecular units are made by comparison with Si-Br compounds and through the use of molecular-cluster calculations. The chemically ordered network model is a good description of the atomic structure of the glasses. A comparison of the present results is made with the previous work on Ge chalcogenide glasses. The differences are discussed in terms of the more covalent nature of Si and the greater molecular character of $SiSe_2$.

I. INTRODUCTION

There is considerable controversy concerning the nature of bonding and degree of chemical order in chalcogenide network glasses. The early work of Lucovsky *et al.*[1] on glasses such as Ge_xSe_{1-x} and As_xSe_{1-x} led to the development of the chemically ordered network model (CONM). In this model heteropolar bonds are favored at all compositions (x) and chemically ordered compounds such as $GeSe_2$ and As_2Se_3 exist. In both the Ge_xS_{1-x} and Ge_xSe_{1-x} glassy systems, Lucovsky *et al.* have proposed that significant molecular ordering occurs and that chemically ordered glasses such as $GeS_2(Se_2)$ and $Ge_2S_3(Se_3)$ exist. In contrast to this, the work of Phillips *et al.*[2] and others[3,4] has suggested that the chemical order is intrinsically broken in $GeSe_2$ and As_2Se_3 glasses. The glasses are proposed to consist of chalcogen-rich and chalcogen-poor clusters. In this model there are some homopolar bonds at all compositions and the presence of these bonds is envisioned to play an important role in glass formation. These ideas have been used to explain anomalous Raman modes in glassy $GeSe_2$ and GeS_2 (Ref. 3) photo-induced atomic structure transformations in glassy $GeSe_2$ (Ref. 5), and glass-forming abilities in binary chalcogenide alloys.[2] At present this subject remains highly controversial with the central focus on the medium-range order and composition of the molecular clusters near the compositions $GeS_2(Se_2)$ and $As_2S_3(Se_3)$. Despite over ten years of intensive work, a definitive description of the degree of chemical order and medium-range in these glasses is lacking.

The present study addresses the question of chemical bonding and the degree chemical order in Si_xSe_{1-x} glasses by Raman spectroscopy. Previous work on SiS_2 and $SiSe_2$ glasses have provided the most compelling evidence for medium-range order and a molecular description of compound amorphous semiconductors.[6] An important advantage of the present study compared to the previous work on Ge- and As-based glasses is the relatively simple atomic structure of both the crystalline and glassy forms of $SiSe_2$. In addition sharp molecularlike modes are observed for all compositions (x) permitting a quantitative analysis of the Raman spectra of the glasses. The results of this study demonstrate that chemically ordered compounds exist at the compositions $SiSe_2$ and Si_2Se_3 and that the CONM is a good description of the Si-based glasses.

II. EXPERIMENTAL PROCEDURE

Bulk glasses (1—2 g) of Si_xSe_{1-x} were prepared by quenching the melts in water. The starting materials (99.999% of pure Si and Se) were vacuum sealed in fused silica tubes and alloyed at 1100 °C for 4—7 d. Water quenching the samples of this study $(0.30 \le x \le 0.40)$ resulted in the formation of defect-free glasses for $0.30 \le x < 0.38$. Beyond $x=0.38$ the samples are visually inhomogeneous containing pieces of undissolved Si. Extended alloying at high temperatures (1150 °C for 6 weeks) failed to remove this inhomogeneity. The as-prepared glasses ranged in color from deep red $(x<\frac{1}{3})$ to yellow $(\frac{1}{3} \le x < 0.36)$ to orange $(0.36 \le x < 0.38)$.

A large glassy sample of $SiSe_2$ (20 g) was prepared for the neutron-diffraction study. The as-prepared sample was crushed and sealed in an air-tight Al sample holder. Neutron-diffraction data were obtained with the use of a step-scan mode on beam port D of the Missouri University Research Reactor. Neutrons of wavelength 1.2877 Å

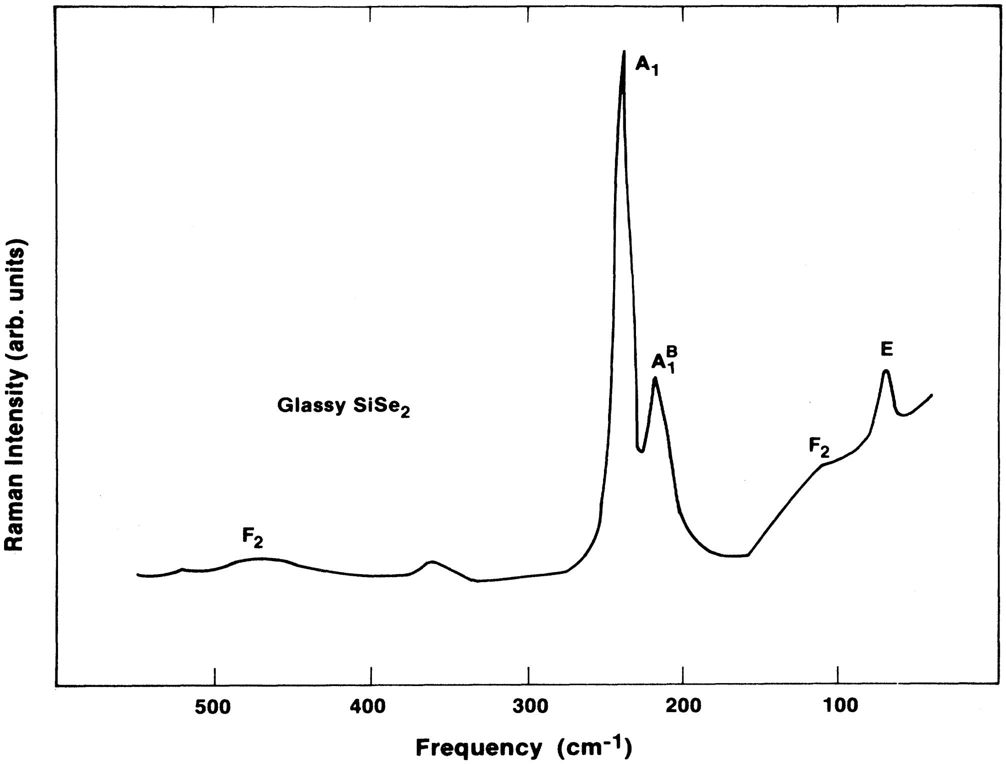

FIG. 1. Room-temperature Raman spectrum of glassy $SiSe_2$. See Table I for the identification of the various lines.

were used with a scan range 5°—40° (2θ). Room-temperature Raman spectra of the glassy Si_xSe_{1-x} samples were taken with a Spex Ramalog model 4-1401 (double monochrometer) equipped with a cooled photomultiplier. Typical spectra were recorded using 20 mW of power at the sample with the 5145-Å line of an Ar-ion laser. The measurements were performed with the samples sealed in fused silica tubes. At these power levels and with the samples sealed in silica tubes, laser-induced sample degradation was avoided. Polarized Raman measurements were made on glassy samples that were found to be homogeneous upon inspection with a polarized optical microscope. Spectral features appeared at the same wave numbers in both polarized and unpolarized spectra. Depolarization spectra are not reported due to the differences in polarization scrambling from spatial variations in the index of refraction of the glasses and from the fused silica tubes. For the purposes of this study, the various modes are simply characterized as strongly polarized (P) or weakly polarized (U).

III. RESULTS AND DISCUSSION

The Raman spectra of several Si_xSe_{1-x} glasses are displayed in Figs. 1 and 2. Sharp molecularlike modes are observed for all compositions. For $x < \frac{1}{3}$ and $x > 0.38$ the glasses are becoming opaque to the laser light. In these samples broad Raman scattering in the region 350—570 cm^{-1} is observed coming from the fused silica tubes. The composition $SiSe_2$ will be examined first, followed by Se-rich and Si-rich glasses.

A. Glassy $SiSe_2$

The Raman spectrum of glassy $SiSe_2$ is shown in Fig. 1. The positions and polarizations of the lines of glassy and crystalline $SiSe_2$ are listed in Table I. Raman investigations of crystalline and glassy $GeSe_2$ have shown that the Raman spectra are dominated by the normal modes of $Ge(Se_{1/2})_4$ tetrahedra.[7] Sen and Thorpe have theoretically analyzed the application of molecular models to such materials.[8] They found that if the B—A—B bond angle in tetrahedral AB_2 glasses is less than some critical value (θ_c), the one-phonon density of states is dominated by the normal modes of the tetrahedral $A(B_{1/2})_4$ units. In other words, a molecular description is valid. This result is independent of the details of the network and applies even to crystalline materials. With the use of the formulation of Sen and Thorpe,[8] no critical angle exists for $SiSe_2$, meaning that a molecular description is always valid for this material. It is therefore not surprising that sharp (~ 14 cm^{-1} wide) molecularlike modes are observed in glassy $SiSe_2$. The starting point for the identification of the Raman modes of glassy $SiSe_2$ is a comparison with the modes of a $Si(Se_{1/2})_4$ tetrahedral unit. There are four Raman-active modes in a tetrahedral unit (symmetry A_1, E, F_2, and F_2) with the most symmetric vibration (A_1) generally having the largest intensity. These modes are identified by a comparison with the experimentally observed modes of $SiBr_4$ (Ref. 9) and a molecular-cluster calculation (see Table I). The molecular-cluster calculation is similar to that of Lucovsky *et al.*[10,11] in which the modes of $Si(Se_{1/2})_4$ are calculated by usage of the modes of $SiBr_4$

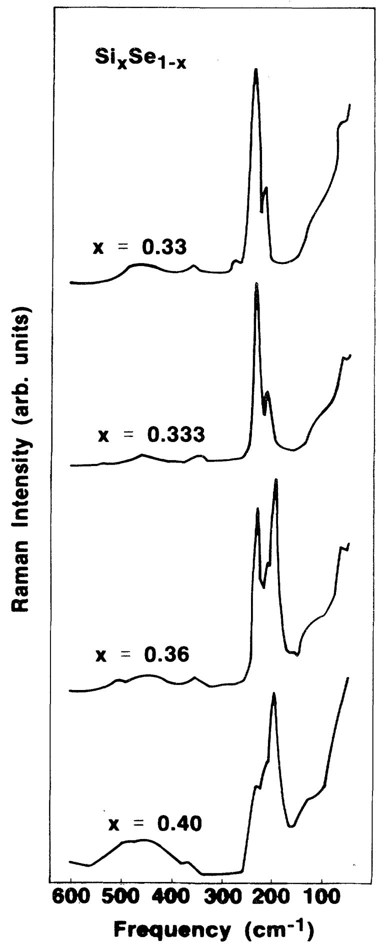

FIG. 2. Room-temperature Raman spectra of the glasses Si_xSe_{1-x}. See Tables I and III for the identification of the various lines. Broad Raman scattering in the region 350—570 cm^{-1} comes from the fused silica tube sample containers.

and correcting for the differences in bond strengths and masses. In Table I, the results of this comparison are shown with the identifications of the four normal modes of the $Si(Se_{1/2})_4$ molecular units.

An additional mode (labeled A_1^B) appears in the spectrum of glassy $SiSe_2$ (at 216 cm^{-1}) not predicted by the use of a $Si(Se_{1/2})_4$ tetrahedral molecular cluster. The presence of this line is a direct indication that the basic unit comprising glassy $SiSe_2$ is larger than a single tetrahedral unit. Table I shows that a similar A_1^B line occurs in crystalline $SiSe_2$. In fact, there is a one-to-one correspondence between the lines observed in the crystalline and glassy forms of $SiSe_2$ (Ref. 6) in both line positions and intensities. This is clear evidence that the short- and medium-range order of the crystalline and glassy forms are similar. The crystal structure of $SiSe_2$ is orthorhombic (*Ibam*, *C*42-type) (Ref. 12) containing chains of edge sharing $SiSe_4$ tetrahedra running parallel to the *c* axis. One such chain is shown in Fig. 3 and it should be noted that the basic repeating unit along the chains is a bitetrahedral unit of composition $Si_2(Se_{1/2})_8$.

In Ref. 6 the microscopic origin of the A_1^B line was deduced from a comparison of the lines of SiS_2 and $SiSe_2$. Since crystalline SiS_2 and $SiSe_2$ are isostructural, it is reasonable to assume that the corresponding glasses have similar structures. In Table II, the A_1 and A_1^B lines of the different forms of SiS_2 and $SiSe_2$ are listed. Expressing the Raman frequencies as $\nu(SiS_2)=\alpha\nu(SiSe_2)$, Table II shows that α is approximately 1.75 for both the A_1 and A_1^B lines. Assuming that the microscopic origin of these modes involves only the motion of chalcogen atoms away from Si atoms, a value of $\alpha=1.77$ is calculated from the differences in S and Se masses and bond strengths with Si. This result combined with the fact that both the A_1 and A_1^B modes are strongly polarized identifies these modes as involving only the symmetric stretching of Se atoms away from fixed Si atoms. The highest cross-section symmetric vibration of the $SiSe_2$ chains that fits the above description is the A_1 mode of the separate $Si(Se_{1/2})_4$ units. The other possible mode of this type involves the symmetric vibration of the outer four Se atoms of the bitetrahedral $Si_2(Se_{1/2})_8$ units (A_1^B mode). The appearance of the A_1^B mode in the glass is direct evidence for chainlike units in the glass. It is important to note here that the key result of this analysis is the discovery that the short- and medium-range order of the crystalline and glassy forms of $SiSe_2$ are very similar. This conclusion is a direct result of the one-to-one correspondence of the lines in the Raman spectra. The argument above concerning the microscopic origin of the A_1^B lines, although compelling, is not conclusive. In any case the A_1^B line is the signature of medium-range order in glassy $SiSe_2$.

The results of the neutron-diffraction study of glassy $SiSe_2$ are shown in Fig. 4. The diffraction pattern is very similar to that of glassy $GeSe_2$ and of special interest is the relatively sharp peak at about 1 $Å^{-1}$. Phillips[2] and

TABLE I. Raman modes of crystalline and glassy $SiSe_2$ and a comparison with $SiBr_4$ and the results of a molecular-cluster calculation (*P*, polarized; *U*, unpolarized).

c-$SiSe_2$ (cm^{-1})	*g*-$SiSe_2$ (cm^{-1})	Molecular cluster [$Si(Se_{1/2})_4$] (cm^{-1})	$SiBr_4$ (cm^{-1})	Mode
82	68(*U*)	68	90(*U*)	E
111, 122	110(*U*)	85	137(*U*)	F_2
204	216(*P*)			A_1^B
248	242(*P*)	224	249(*P*)	A_1
345, 355	350(*U*)			
512	465(*U*)	460	487(*U*)	F_2

others[13] have interpreted this feature in $GeSe_2$ and similar glasses as resulting from quasi-two-dimensional units or fragments of layers in the glasses. Other authors have suggested that this first sharp diffraction peak (FSDP) is simply an indication of the presence of molecular clusters in the glasses. They point out the difficulties in extracting real-space information from a single feature in the diffraction pattern.[14,15]

The formation of layers in glassy $SiSe_2$ seems very unlikely given the crystal structure of $SiSe_2$ and the resemblance of the glassy and crystalline Raman spectra. A more reasonable explanation is that the FSDP is a signature of the presence of molecular clusters, in this case chains of edge sharing $Si(Se_{1/2})_4$ tetrahedra. Both the Raman and neutron results on glassy $SiSe_2$ are consistent with a microstructure consisting of extended bitetrahedral chain molecular clusters. This point will be developed later in the discussion.

B. Role of excess Se

The addition of small amounts of Se to glassy $SiSe_2$ results in the appearance of a line in the Raman spectra at about 270 cm^{-1}. A similar line has been observed in Se-rich Ge-Se glasses[16] and is identified with Se chains (Se-rich glasses) and fragments of Se chains (x near $\frac{1}{3}$). Because the samples rapidly become opaque to the Ar-laser light with increasing Se content, this region was not extensively investigated. The measurements suggest that for x slightly less than $\frac{1}{3}$, the glasses consist of Se chains and fragments of Se chains along with the $SiSe_2$ quasi-one-dimensional tetrahedral chains. As shown in Fig. 2, the intensity of the Se-rich phase goes to zero at $x=\frac{1}{3}$. In contrast to the glassy alloys Ge_xSe_{1-x}, where a rapid change in intensity is observed for the so-called A_1^c companion line with composition, the five Raman modes of the glassy $SiSe_2$ clusters (A_1,A_1^B,F_2,F_2,E) maintain the same relative intensities for $0.30 \leq x \leq \frac{1}{3}$. The microstructure of Se-rich glasses therefore consists of extended $Si_2(Se_{1/2})_8$ tetrahedral chains and Se clusters.

TABLE II. A_1 and A_1^B Raman lines of crystalline and glassy $SiS_2(Se_2)$.

Sample form	A_1 (cm^{-1})		A_1^B (cm^{-1})	
	SiS_2	$SiSe_2$	SiS_2	$SiSe_2$
Glassy	427	242	367, 381[a]	216
Crystalline	430	248	351	204

[a] A_1^B line is split in glassy SiS_2.

C. Role of excess Si

As Fig. 2 illustrates, the addition of Si to glassy $SiSe_2$ results in dramatic changes in the Raman spectra. A smooth growth of modes at 206, 125, and 68 cm^{-1} is observed as the modes of $SiSe_2$ decrease in intensity with increasing Si content. In glassy Ge-Se the first Ge-rich unit to appear beyond $GeSe_2$ is an ethanelike unit Se_3—Ge—Ge—Se_3. Proceeding in a similar manner as in the $SiSe_2$ case, the identification of the Si-rich unit can be made by comparing with a Si-Br compound and by using a molecular-cluster calculation. The halogen compound this time is Br_3—Si—Si—Br_3, and the three most intense modes are listed in Table III along with the modes observed for the Si-rich Si-Se cluster. With the use of the force constants of Si—Se bonds from the tetrahedral $Si(Se_{1/2})_4$ units and making the appropriate corrections for

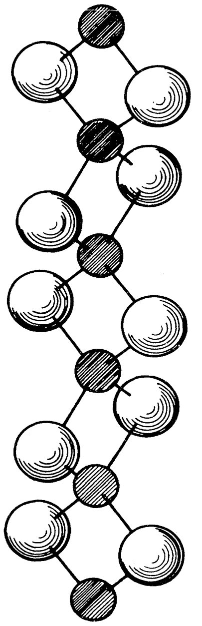

FIG. 3. Bitetrahedral chain of crystalline $SiSe_2$ in which the small closed circles represent Si atoms and the large open circles represent Se atoms. Crystal structure of $SiSe_2$ consists of an array of such units parallel to the c axis.

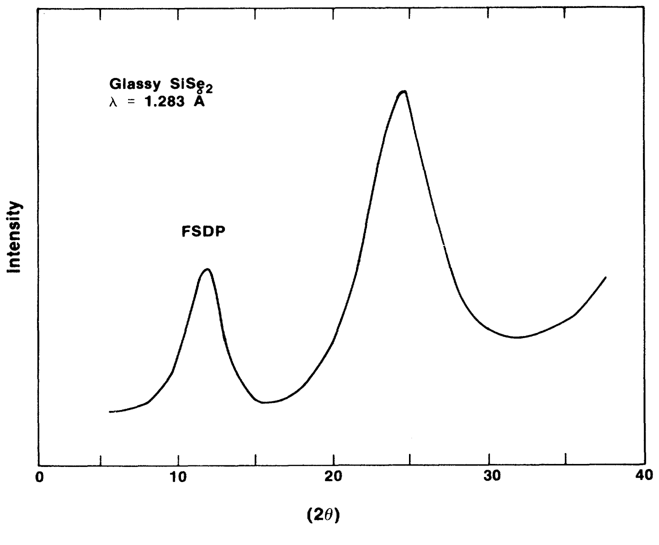

FIG. 4. Neutron-diffraction pattern of glassy $SiSe_2$ taken with $\lambda=1.283$ Å and at room temperature. Data have been corrected for the cell holder and background. FSDP refers to the first sharp diffraction peak in the spectrum at approximately $d=6.35$ Å.

TABLE III. Identifications of the Raman-active modes of Si_2Se_6 and Si_2Br_6 (P, polarized; U, unpolarized).

Se_3—Si—Si—Se_3 (cm^{-1})	Br_3—Si—Si—Br_3[a] (cm^{-1})	Raman-active mode
206(P)	223(P)	$\nu_1(A_{1g});\nu(XY_3)$
125(U)	139(U)	$\nu_{11}(E_g);\nu(XY_3)$
68	80(P)	$\nu_2(A_{1g});\nu(XY_3)$

[a] Three most intense Raman modes.

masses, the $\nu_1(A_{1g})$ frequency for Se_3—Si—Si—Se_3 is computed to be 200 cm^{-1}. The polarizations of the modes of the Si-rich cluster also agree with that of the corresponding modes of Br_3—Si—Si—Br_3. The identification of the Si-rich unit as $Si_2(Se_{1/2})_6$ by the above analysis seems conclusive.

The compositions of the two co-existing clusters in the range of interest ($\frac{1}{3} \leq x \leq \frac{2}{5}$) can be determined by a quantitative analysis of the Raman spectra. The areas under the A_1 and $\nu_1(A_{1g})$ modes are related to the number of Se-rich and Si-rich clusters by their respective Raman cross sections (σ). For the analysis here, only the relative cross section is required. This quantity is determined by least-squares fitting the experimental points ($\frac{1}{3} \leq x \leq 0.37$) to the expected behavior assuming that the two co-existing clusters have compositions $SiSe_2$ and Si_2Se_3. Figure 5 shows the result of this procedure. An especially important point to consider is that a single value of the relative Raman cross section [$\sigma(Si_2Se_3) = 2.33\sigma(SiSe_2)$] is used to bring about the excellent agreement shown in Fig. 3. The lower values for the $x = 0.38$ and 0.40 glasses are related to the inhomogeneity of these glasses mentioned earlier. The relative amount of the $SiSe_2$ and Si_2Se_3 units is described by the equation

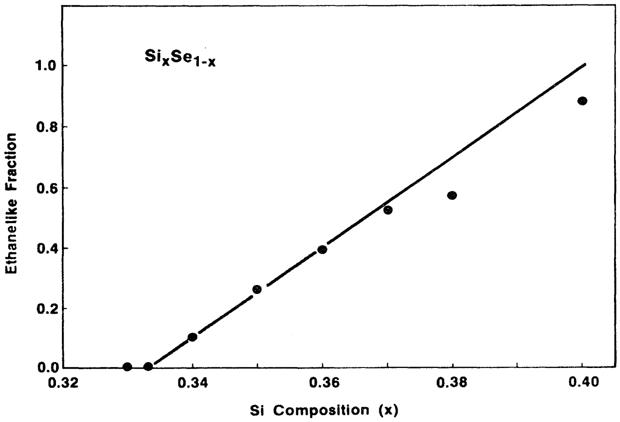

FIG. 5. Compositional dependence of the ethanelike (Se_3—Si—Si—Se_3) fraction for Si_xSe_{1-x} glasses. Solid line is the prediction with the use of the lever rule assuming that the chemically ordered compounds $SiSe_2$ and Si_2Se_3 exist in this system. Points are the actual measurements corrected by the relative Raman cross section (see text). Falloff of the points beyond $x = 0.37$ is the result of the glasses being inhomogeneous at high Si content containing pieces of undissolved Si metal.

$$Si_xSe_{1-x} = 3(2-5x)SiSe_2 + 5(3x-1)Si_2Se_3, \quad \tfrac{1}{3} \leq x \leq \tfrac{2}{5} .$$

This analysis is strong evidence for the existence of chemically ordered molecular clusters of composition $SiSe_2$ and Si_2Se_3 in these glasses. An interesting result of this work is the identification of an unusual valence state of Si. In Si_2Se_3, Si is formally Si^{3+} instead of the much more common Si^{4+}. A similar crystalline compound in the Sn-S system [Sn_2S_3 (Ref. 17)] is observed in which the designation $Sn^{2+}Sn^{4+}S_3$ is appropriate. In this crystalline compound, the different valence states of Sn occupy inequivalent lattice sites. From the Raman measurements, the two Si atoms in the Se_3—Si—Si—Se_3 units appear to be equivalent. Therefore a description such as $Si^{2+}Si^{4+}Se_3$ does not seem reasonable. Instead, a better description is that Si_2Se_3 has more divalent character than $SiSe_2$. The divalent state of Si is very uncommon and there are few examples of divalent Si solid compounds. Of interest here is the work of Zintl and Loosen on the preparation of SiS.[18] They were preparing SiS_2 single-crystals by sublimination and observed a more volatile Si-S compound than SiS_2 that they speculated was crystalline SiS. Attempts to prepare SiSe by the same method have been unsuccessful. At least in the Si-Se system, the more volatile "compound" was found to be a fine mixture of amorphous and polycrystalline $SiSe_2$.[19] The compound SiSe may only exist at high temperatures and perhaps not as a solid.

Although Si_2Se_3 does not exist as a crystalline solid, crystalline compounds such as $Si_2(SR)_6$ (R = Benzene) have been synthesized.[20] The presence of the benzene rings in this compound expands the Si_2S_3 molecule, effectively lowering its density. This kind of negative pressure stabilization is also expected in glasses[21] where the atomic densities are typically 10% lower than the crystalline alloys. Crystalline compounds of composition A_2X_3 (A = Si,Ge; X = S,Se) do not exist. In the Ge glasses (Ge_xS_{1-x}, Ge_xSe_{1-x}) these A_2X_3 units form throughout the composition range $\frac{1}{3} < x < \frac{2}{5}$. As mentioned earlier, the Si_xSe_{1-x} glasses become inhomogeneous beyond $x = 0.37$. Work in progress on the Si_xS_{1-x} system shows that these glasses become inhomogeneous beyond $x = 0.36$. This difference between the Ge and Si glasses results from the fact that divalent Ge is much more stable than divalent Si. The lower density of the glassy state can completely stabilize the Ge_2X_3 units but only partially stabilize the corresponding Si_2X_3 units.

D. Medium-range atomic structure and glass formation of Si_xSe_{1-x} alloys

The extensive Raman spectroscopic measurements and detailed analysis of the present work yields a rather complete description of the atomic structure of Si-Se glasses. At $SiSe_2$, the glassy network consists of randomly oriented chains of edge sharing $Si(Se_{1/2})_4$ tetrahedra. These chains are extended units and have the stoichiometry $SiSe_2$. The major difference between crystalline and glassy $SiSe_2$ appears to be simply the packing of the edge-sharing chains. In crystalline $SiSe_2$ the chains are parallel and slightly distorted to take full advantage of van der Waals bonding and to lower the enthalpy of the solid. In the glass, because it is related to the liquid alloy, entropy considerations become more important, and the chains are randomly packed to increase the entropy of the glassy solid. Another factor that may play a role in the stabilization of the glassy structure is a relaxation of the edge-sharing tetrahedra chains, thereby relieving strain in the alloy. This relaxation is expected to occur in the glassy state because of the removal of long-range order. These randomly oriented, relaxed tetrahedral chains may play a major role in glass formation. In a glass-forming system, as the temperature is lowered through the melting point, the viscosity is expected to increase faster than a material that tends to crystallize. The structure of glassy $SiSe_2$ suggests an interesting mechanism for this process. As the temperature of the melt is decreased, the Si and Se atoms first form tetrahedral units which later aggregate to form the edge-sharing tetrahedral chains. In this process the cluster size increases, leading to a decrease in cluster motion and a rapid increase in viscosity. This rapid increase in viscosity provides a kinetic barrier to crystallization. In addition to this kinetic barrier to crystallization, a topological barrier is also present. The relaxed chains of the glass must become slightly distorted and lower their vibrational entropy before they can be packed together to form the crystalline $SiSe_2$ nuclei.

The addition of excess Se to $SiSe_2$ further enhances the glass-forming ability. The first step in the crystallization of a liquid such as $Si_{0.30}Se_{0.70}$ is the formation of nuclei of $SiSe_2$. In addition to the processes described above for $SiSe_2$, crystallization of a Se-rich liquid involves the mass transport of Se atoms away from the $SiSe_2$ nuclei. With the limited compositional range explored here, the details of how the excess Se is incorporated in the network are not clear. The observation that the intensity ratio of the A_1 and A_1^B lines is a constant in the compositions studied indicates that there are no isolated $Si(Se_{1/2})_4$ tetrahedra and that all the Si atoms are in the $SiSe_2$ chains. The excess Se atoms are probably located between the chains, existing as $(Se)_n$ chains or rings or fragments of Se chains.

Introducing excess Si to $SiSe_2$ has a similar effect on glass formation as the addition of excess Se. The Raman measurements show that the stoichiometry of the Si-rich cluster is Si_2Se_3 and that the local structure is the ethane-like molecule Se_3—Si—Si—Se_3. The nature of the packing of these clusters in the network is not clear. They could play a role in linking the $SiSe_2$ chains or perhaps exist as separate clusters. One very interesting suggestion is that the Si_2Se_3 clusters form quasi-one-dimensional polymer-like units $(Se_3\text{—Si—Si—}Se_3)_n$. This would mean that the microstructure of a glass such as $Si_{0.36}Se_{0.64}$ would contain two quasi-one-dimensional units: $SiSe_2$ chains and Si_2Se_3 chains. However they are incorporated in the network structure, the presence of the Si_2Se_3 clusters will inhibit the formation and growth of crystalline $SiSe_2$ by the same mechanism described above for the Se-rich glasses.

E. Comparison to other glassy systems

The results of the present study provide unusually powerful insight into the structure and formation of covalent glasses. The relatively simple atomic structure and wealth of information obtainable from the Raman spectra make the Si_xSe_{1-x} glasses a model system. The key feature of this work is the direct connection between the glassy and crystalline forms of $SiSe_2$. The edge-sharing tetrahedral chain structure and highly molecular character of crystalline $SiSe_2$ provide a natural starting point for ascertaining the short- and medium-range order of the glass. Furthermore, the molecular cluster for the glass has the same composition as the crystalline compound ($SiSe_2$).

Comparing the Si and Ge chalcogenide glasses, several important differences should be noted. Although the basic unit of the crystalline compounds is a tetrahedral unit (SiX_4 or GeX_4; X=S,Se), the packing of these tetrahedra is considerably different for the two cases. Both a low-temperature three-dimensional and a high-temperature two-dimensional form of $GeS_2(Se_2)$ are known.[22] Ge is considerably less covalent than Si and has a greater tendency to have more than four nearest neighbors and to exist in the divalent state. These factors result in the lower molecular character and more metalliclike nature of the Ge chalcogenide compounds. In addition to the complexity of the crystalline structure of $GeSe_2$, the Raman spectra of crystalline and glassy $GeSe_2$ are qualitatively different. An extra line occurs in the Raman spectrum of the glass at 212 cm^{-1} (the so-called A_1 companion line). The microscopic origin of this line has not been satisfactorily determined.[3,23] A unique feature of the Ge glasses is the anomalously rapid increase with composition of the intensity of the A_1^c line. In the Si_xSe_{1-x} glasses, the modes of the $SiSe_2$ clusters maintain the same relative intensity with composition in the range of composition explored here. Further work on Se-richer glasses is needed to understand the growth mechanisms of the $SiSe_2$ chains.

IV. CONCLUSIONS

Raman studies of Si_xSe_{1-x} glasses have shown that these materials can be described by the chemically ordered network model. There is a strong tendency for forming heteropolar bonds throughout the range of composition studied. Three distinct molecular species have been identified in the Raman spectra. At $x=\frac{1}{3}$ the structure of the glass consists of randomly oriented chains of edge-sharing $Si(Se_{1/2})_4$ tetrahedra. The addition of excess Si results in the formation of Se_3—Si—Si—Se_3 units. Excess Se ($x<\frac{1}{3}$) is accommodated in the glassy structure as isolated Se chains or rings and fragments of Se chains. Quantitative analysis of the Raman spectra show that chemically ordered glassy compounds with the stoichiometrics $SiSe_2$ and Si_2Se_3 exist in the glasses.

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