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Nanoscale phase separation of GeS_2 glass

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Abstract

Molecular structure of Ge_xS_{100-x} glasses in the $30 < x < 34$ atomic percentage range is examined by Raman scattering, ^{119}Sn Mössbauer spectroscopy, and temperature-modulated differential scanning calorimetry. The results show that the stoichiometric glass with $x = 33.33$ ($T_g = 508°C$) is chemically disordered. Raman scattering places mode strengths of corner-sharing $Ge(S_{1/2})_4$ tetrahedra (A), ethane-like $Ge_2(S_{1/2})_6$ units (B), and the distorted rocksalt $Ge(S_{1/6})_6$ units (C) at approximately 93.4 : 3.6 : 3.0 not normalized for mode cross-sections. Mössbauer spectroscopy places the concentration of these units as A : B : C = 76.2 : 8.8 : 15. The drastic reduction in the slope of the glass transition temperature T_g with Ge content x coincides with first appearance of these units once x exceeds 32.50, suggesting that these units are demixed and form separate nanophases to lower the global connectivity of the glass network.

§ 1. Introduction

The nature of chemical order in stoichiometric chalcogenide glasses, such as Ge(Se or S)$_2$ and As$_2$(S or Se)$_3$ has enjoyed special attention in glass science. Here one can directly compare the structure of the glass with corresponding crystals. Furthermore, such studies provide a convenient testing ground of theory based on molecular dynamic simulations (Cobb and Drabold 1997, Massobrio *et al.* 2001) to account for observed neutron structure factors (Susman *et al.* 1990, Petri *et al.* 2000). Closely relevant are aspects of glass structure deduced from spectroscopic (Boolchand *et al.* 1982, Boolchand and Bresser 2000) and thermal analysis experiments (Boolchand 2000a) that are in many cases more sensitive probes of local structures such as units and/or sites and their connectivity than diffraction experiments. In $GeSe_2$, diffraction, spectroscopic and thermal measurements have now converged to show (Boolchand and Bresser 2000) that the glass is neither *completely* chemically ordered nor *completely* polymerized (Boolchand 2000a). The result is consistent with presence of homopolar bonds (Penfold and Salmon 1991) in liquid $GeSe_2$, and also with the non-Arrhenius temperature variation in viscosity (Angell 2000) characteristic of the fragile liquid.

For GeS_2 glass, the situation is less clear. In 1986, from Mössbauer spectroscopy, the degree of broken chemical order was found (Boolchand *et al.* 1986, Boolchand 2000b) to be 0.29, nearly twice that in $GeSe_2$ glass. Here the degree of broken order is defined as the fractional concentration of non-tetrahedral Ge sites. These aspects of

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broken chemical order were less clear in Raman scattering (Boolchand *et al.* 1986, Boolchand 2000b) at the time. Furthermore, a recent neutron diffraction study (Petri and Salmon 2001) of GeS_2 glass found no compelling evidence for homopolar bonding. Given the diversity of these results it appeared appropriate to re-examine the issue, particularly since substantial advances in characterization of glasses by thermal analysis have now become possible using temperature-modulated differential scanning calorimetry (MDSC). The method permits a measurement of T_g independent of scan rates and sample history, and thus fix glass compositions (Georgiev *et al.* 2000). Furthermore, in conjunction with micro-Raman scattering, the method permits one to establish structural homogeneity of glasses.

In this work, we elucidate the molecular structure of the stoichiometric ($x = 33.33$) glass by examining the Ge_xS_{100-x} binary in the $25 < x < 34$ interval. There are two significant results to emerge from the present work. Firstly, we identify the heat treatment conditions necessary to obtain homogeneous Ge–S glasses. These conditions differ significantly from those of corresponding selenides. Secondly, GeS_2 glass is found to be chemically disordered; in addition to *majority* tetrahedral $Ge(S_{1/2})_4$ (A) units, there are two distinct *minority* local structures, ethane-like $Ge_2(S_{1/2})_6$ units (B) and distorted rocksalt $Ge(S_{1/6})_6$ units (C). The degree of broken chemical order inferred from ^{119}Sn Mössbauer spectroscopy measurements is in harmony with the Raman results. The global maximum in T_g near $x = 33.33$ suggests (Boolchand 2000a) that the B and C units are demixed from the A units and form separate nanophases.

§2. EXPERIMENTAL DETAILS

2.1. *Sample synthesis and thermal characterization*

Binary Ge_xS_{100-x} glasses in the $25 < x < 34$ interval were synthesized by reacting 99.999% Ge and S pieces from Cerac, Inc. in evacuated (5×10^{-7} Torr) fused quartz tubings of 5 mm inner diameter and 1 mm wall thickness with a typical sample mass of 2 g. The temperature was slowly (over 2 days) increased to 1000°C and melts homogenized at that temperature for at least $t_h = 72$ h before lowering temperatures to a suitable quench temperature $T_q = T_l + 30$°C and equilibrating melts for $t_e = 24$ h before a quench in cold water. Samples homogenized at 1000°C for a shorter period such as $t_h = 24$ h were found to display fluctuations in T_g of up to 25°C from one part of the sample to the other that correlate well with micro-Raman estimates of sample stoichiometry. These T_g fluctuations examined at $x = 31.6$ translate into compositional fluctuations in x of typically about 1.0 at.%. Upon increasing t_h to 72 h or more, fluctuations in T_g decreased to 2°C as glass samples became homogeneous. Care was taken to ensure that T_q did not exceed T_l (liquidus) by more than 30°C; otherwise inner walls of sample tubes develop a yellow flashing suggestive of a S-rich deposit.

Glass transition temperatures were measured from the inflection point of the reversing heat flow using a TA Instruments model 2920 temperature-modulated differential scanning calorimeter. Figure 1 (*a*) displays a MDSC trace of the stoichiometric glass at a scan rate of 3°C min^{-1} and a modulation rate of 1°C per 100 s and yields a $T_g = 508$°C. Here T_g is defined as the *mean value* of the inflection point for scans up and then down in temperature. Defined as such, the T_g values become independent not only of scan rate but also of sample thermal history. Figure 1 (*b*) gives a DSC trace of the same GeS_2 glass sample at a scan rate of 10°C min^{-1} and yields an *apparent* T_g (midpoint) of 502°C. Figure 2 provides a summary of the $T_g(x)$

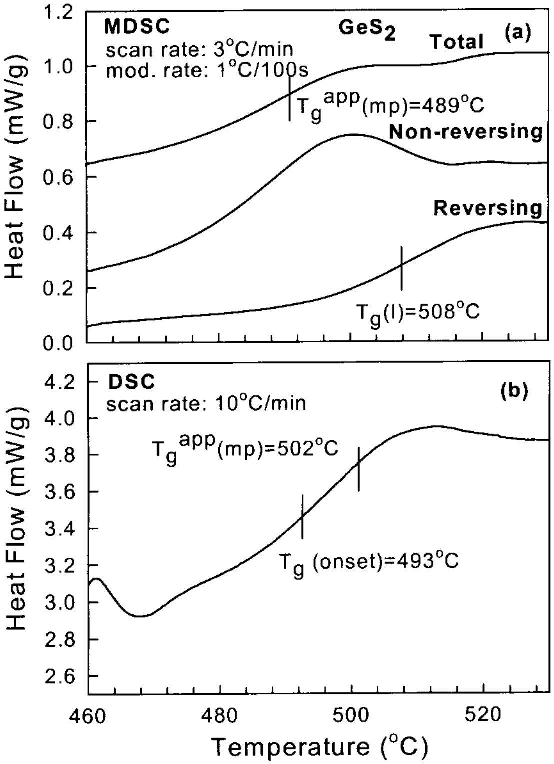

Figure 1. (*a*) MDSC scan of GeS$_2$ glass showing a T_g of 508°C, independent of scan rate. (*b*) Differential scanning calorimetry (DSC) scan of the same GeS$_2$ glass showing an apparent T_g of 502°C obtained at a scan rate of 10°C min^{-1}.

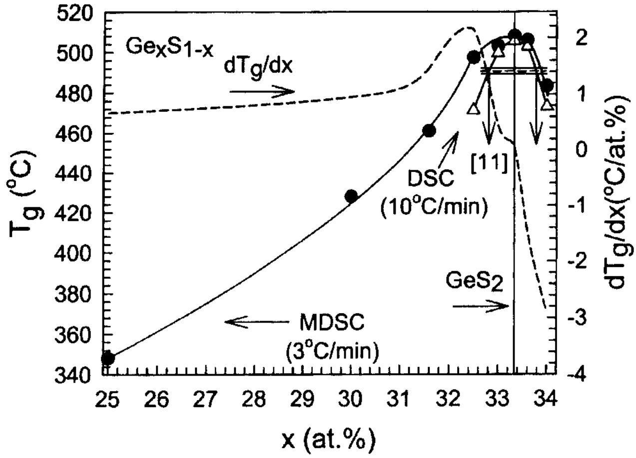

Figure 2. Compositional trend in the T_g values of Ge$_x$S$_{1-x}$ glasses obtained by MDSC (●) and DSC scans (△), showing a threshold behaviour near $x = 33.33$. The horizontal strip projects the DSC measured apparent T_g of the GeS$_2$ glass sample used by Petri and Salmon (2001): (– – –), curve giving the slope dT_g/dx of MDSC measured T_g values.

trends with full circles representing the temperature-modulated DSC results, and the open triangles the DSC results. Also projected in figure 2 is the DSC measured T_g (midpoint) = 491(5)°C of the GeS_2 sample used by Petri and Salmon (2001) which may be compared with a value of 502°C for our GeS_2 sample (figure 1 (*b*)) measured under identical DSC scanning conditions.

2.2. *Raman scattering results*

Figure 3 (*a*) displays Raman line shapes of Ge–S glasses recorded at room temperature using a model T-64000 triple-monochromator system (Boolchand and Bresser 2000) from Instruments SA, Inc. The back-scattered radiation was excited using 6 mW at 514.5 nm in a conventional macro-Raman set-up with glass samples contained in the quartz tubes used for synthesis. The principal modes at 340 cm^{-1}, 360 cm^{-1}, and 440 cm^{-1} are assigned (Feng *et al.* 1997) to the CS, ES and F_2 modes respectively of $Ge(S_{1/2})_4$ tetrahedra. We have also obtained the longitudinal optical (LO) and transverse optical (TO) infrared (IR) response of our GeS_2 glass sample

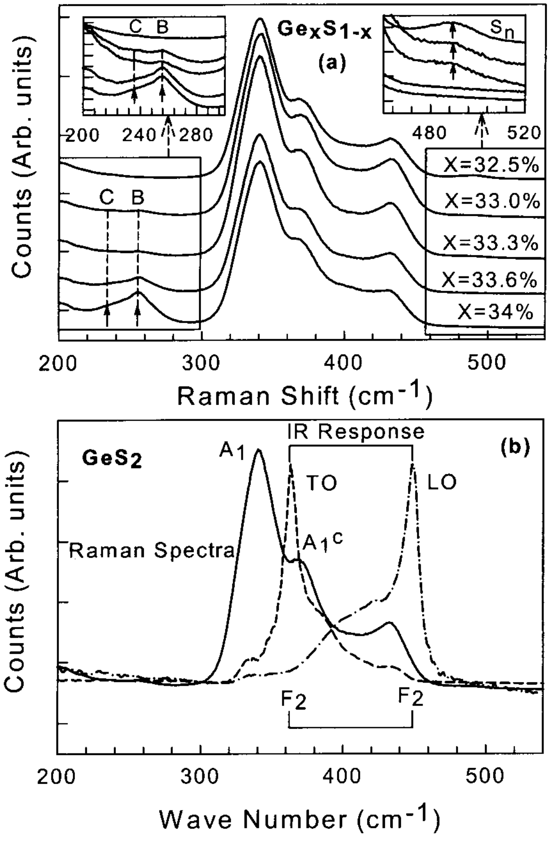

Figure 3. (*a*) Raman scattering in indicated glass samples obtained using 514.5 nm excitation in a macro-configuration. Note the presence of modes near the 250 and 500 cm^{-1} regions in the stoichiometric glass, providing evidence of homopolar bonds. (*b*) Raman and IR response in GeS_2 glass, showing the contributions of A_1, A_1^c and F_2 modes.

using a Nicolet model 870 Fourier transform IR spectrometer, and the results appear as the broken curves in figure 3(*b*). The sharp features at 362 and 449 cm^{-1} are ascribed to the strongly IR-active F_2 modes of $Ge(S_{1/2})_4$ tetrahedra. Of special interest here are Raman modes observed in the 500 and 250 cm^{-1} regions that are enlarged in the right and left insets of figure 3(*a*). One can discern the S_n-chain mode at 494 cm^{-1} in the right inset for samples with $x = 32.5$, 33.0 and 33.33, but not those with $x = 33.6$ and 34.0. In the left inset, one observes a pair of modes labelled B at 255 cm^{-1} and labelled C at 236 cm^{-1}, which progressively grow in scattering strength with increasing x, starting at a threshold Ge concentration $x = 32.5$. Compositional trends in the scattering strength of the B and C modes normalized to the A_1 mode (340 cm^{-1}) strength appear in figure 4(*a*). At the stoichiometric composition with $x = 33.33$, the mode scattering strength ratio of $A_B(255)$ to A_1 is 0.036(5) and that of $A_C(236)$ to A_1 is 0.029(5). We assign the B mode to ethane-like $Ge_2(S_{1/2})_6$ nanophase, and the C mode to distorted rocksalt $Ge(S_{1/6})_6$ nanophase as discussed later. The presence of the S_n-chain, B and C modes shows that the stoichiometric glass is chemically disordered.

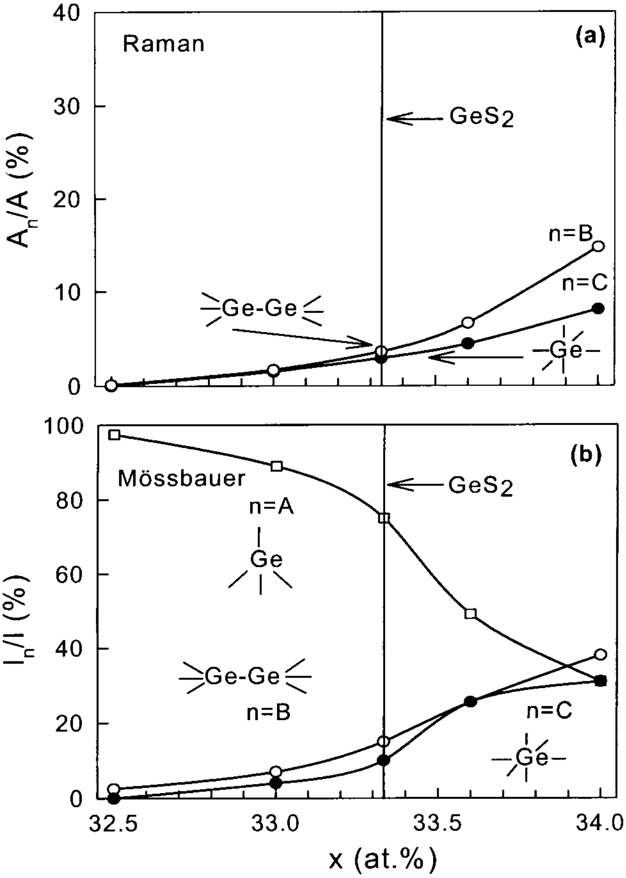

Figure 4. Compositional trends in (*a*) the normalized Raman scattering strengths of the B and C nanophase associated modes at 255 and 236 cm^{-1} and (*b*) the integrated intensity of the B-site and C-site doublets from ^{119}Sn Mössbauer spectroscopy.

2.3. *Mössbauer spectroscopy results*

$(Ge_{0.995}Sn_{0.005})_xS_{100-x}$ glasses doped with traces of enriched ^{119}Sn were independently synthesized and examined in Mössbauer spectroscopy measurements (Boolchand *et al.* 1986, Boolchand 2000b) at 78 and at 4.2 K using an emitter of ^{119m}Sn in $CaSnO_3$. Figure 5 (*a*) displays the observed line shape for a glass sample with $x = 33.33$. The line shape is dominated by a strong absorption centred near $1.6\,mm\,s^{-1}$ and a weak satellite feature at $4.5\,mm\,s^{-1}$, as also noted earlier (Boolchand *et al.* 1986, Boolchand 2000b). Figures 5 (*b*) and (*c*) show deconvolutions of the observed line shape in terms of three doublets (A, B and C) and also two doublets (Boolchand *et al.* 1986, Boolchand 2000b) (A and B) respectively. The three-site fit is better and it also conforms to the Raman results. Table 1 summarizes the quadrupole splittings Δ, isomer shifts δ and intensities I. Figure 4 (*b*) provides a summary of the compositional variation in the integrated area I_n/I under the A, B and C doublets normalized to the total area. The B- and C-site integrated intensities systematically grow at the expense of the A-site intensity, once $x > 32.5$. In particular at 4.2 K, we obtain $I_B/I = 0.17(2)$ and $I_C/I = 0.15(1)$ for GeS_2 glass,

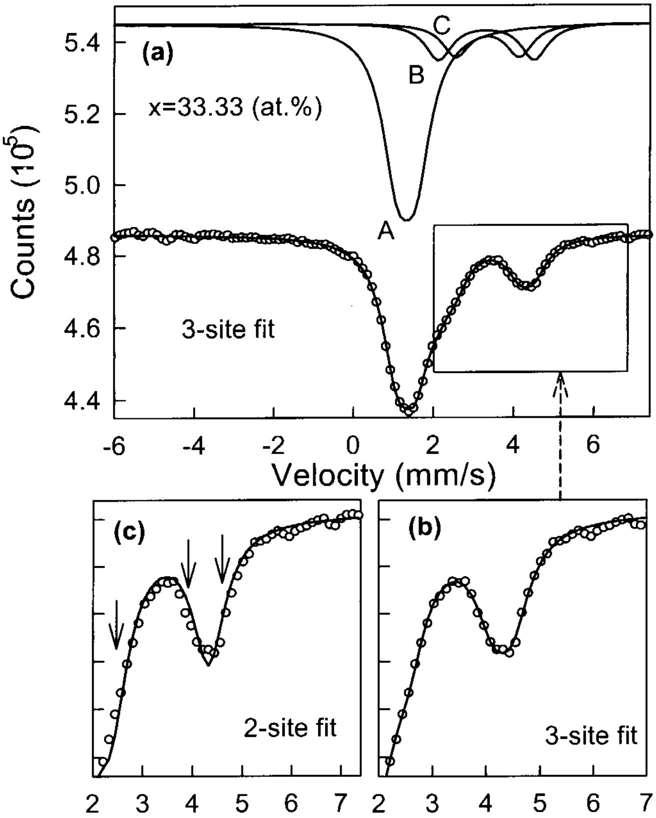

Figure 5. (*a*) ^{119}Sn Spectrum of a $Ge_{0.995}Sn_{0.005}S_2$ glass sample taken at 4.2 K. (*b*), (*c*) Deconvolution of the line shape into three sites (A, B and C) and two sites (A and B) respectively. Systematic misfits appear at the locations of the arrows when two sites are used.

Table 1. Mössbauer isomer shifts δ, quadrupole splittings Δ and integrated intensities of sites A, B and C observed in the indicated $(Ge_{0.995}Sn_{0.005})_xS_{100-x}$ glasses at the indicated temperatures. The typical errors in the δ and Δ parameters are $\pm 0.02\,\mathrm{mm\,s^{-1}}$.

		Site parameters ($\mathrm{mm\ s^{-1}}$)						
		A		B		C		
x (at.%)	T (K)	δ	Δ	δ	Δ	δ	Δ	Site intensities (A : B : C)
32.5	78	1.33	0.45	3.26	2.18			97.5 : 2.5 : 0
33.0	78	1.33	0.45	3.35	2.42	3.32	1.52	89 : 7 : 4
33.33	78	1.32	0.43	3.30	2.28	3.33	1.56	75 : 15 : 10
33.33	4.2	1.32	0.47	3.30	2.27	3.33	1.57	68 : 17 : 15
33.6	78	1.32	0.44	3.31	2.36	3.37	1.48	49.0 : 25.5 : 25.5
34.0	78	1.33	0.45	3.35	2.20	3.34	1.36	31 : 38 : 31

reinforcing the conclusion from Raman scattering that the stoichiometric glass is *chemically disordered.*

§3. DISCUSSION

A first-principles density functional calculation of vibrational modes on selective GeS_n clusters has shown (Jackson *et al.* 1999) that ethane-like $Ge_2(S_{1/2})_6$ units possess two strongly active Raman modes: one at $254\,\mathrm{cm^{-1}}$ and the other at $366\,\mathrm{cm^{-1}}$. These calculations (Jackson *et al.* 1999) provide justification to assign the mode at $255\,\mathrm{cm^{-1}}$ to the presence of ethane-like units (Lucovsky *et al.* 1977). Our Raman spectra also reveal a mode at $236\,\mathrm{cm^{-1}}$, and it is assigned to the presence of distorted rocksalt $Ge(S_{1/6})_6$ units in analogy to the A_g mode observed (Chandrasekhar *et al.* 1977, Boolchand *et al.* 1986, Boolchand 2000b) in c-GeS at $238\,\mathrm{cm^{-1}}$. The cluster calculations (Jackson *et al.* 1999) also show the Raman cross-section of the $254\,\mathrm{cm^{-1}}$ mode to be nearly half that of the $340\,\mathrm{cm^{-1}}$ mode, suggesting that the concentration of ethane-like units to CS tetrahedral units is 7.2%. Since there are two Ge sites per ethane-like unit, we must conclude that the concentration ratio of ethane-like Ge sites to CS tetrahedral Ge sites is 14.4%. At this stage we must pause and reiterate that, in Mössbauer spectroscopy, one utilizes SnS_2 dopant to probe the structure of the GeS_2 glass. The simplest assumption is to say that Sn dopant randomly selects available Ge sites of the base glass. In Mössbauer spectroscopy, one is unable to distinguish CS from ES tetrahedra. Fortunately, in Raman scattering, the ratio of A_1 to A_1^c mode strength of 0.40(4) shows that there are four ES for every ten CS tetrahedra in the structure. At 4.2 K, the Mössbauer I_B/I result of 17% or $I_B/I_A = 25\%$ translates into a ratio of ethane-like units to CS units of $25 \times (10/14) = 17.9\%$, which is in reasonable agreement with the matrix element corrected Raman scattering strength ratio of 14.4%.

For the C nanophase, I_C/I (Mössbauer) = 15%, or $I_C/I_A = 22\%$, translates into a ratio of rocksalt units to CS units of $22 \times (10/14) = 15.7\%$, and this ratio may be compared with the Raman mode scattering strength ratio of A_c to A_1, which is 2.90(5)%. These two results would be compatible if the Raman cross-section of the A_1 mode were fivefold larger than that of the $236\,\mathrm{cm^{-1}}$ mode. Unfortunately the cross-section of the $236\,\mathrm{cm^{-1}}$ Raman mode is currently unavailable. The quantitative aspects of chemical order are better addressed by Mössbauer spectroscopy than Raman scattering because these matrix element effects are not easily decoded.

The Mössbauer spectroscopy result obtained at 4.2 K corrects for the recoil-free fraction changes between these sites (Boolchand *et al.* 1986, Boolchand 2000b) and provides a good representation of the concentration ratio of the octahedral to CS tetrahedral sites of 15.7% in GeS_2. The Raman results are generally consistent not only with the ^{119}Sn Mössbauer effect results presented here but also with earlier ^{129}I Mössbauer effect results (Bresser *et al.* 1981) that show evidence of S—S bonds in GeS_2 glass. The latter contribute to S_n mode at 494 cm^{-1} (figure 3(*a*)) and compensate for the presence of Ge—Ge bonds in the stoichiometric glass.

The absence of compelling evidence for homopolar bonds in GeS_2 glass from neutron structure factors (Petri and Salmon 2001) can be understood. Given the concentration of ethane-like units and rocksalt units above, one arrives† at a concentration ratio of Ge—Ge to Ge—S bonds of 1.2% for GeS_2. The concentration of homopolar bonds anticipated for the stoichiometric glass is at the limit of sensitivity of a diffraction measurement. These results highlight the much higher sensitivity of local probes to ascertain the broken chemical order of a network by accessing sites or units of a network rather than by counting the number of heteropolar versus homopolar bonds.

In recent years, compositional trends in T_g in network glasses have been analysed with remarkable success by stochastic agglomeration theory (Kerner and Micoulaut 1997, Micoulant and Naumis 1999). The theory shows that within 5–10% latitude of bond strengths, changes in T_g intimately reflect those in network global connectivity. In our case the rapid increase in T_g in S-rich glasses, particularly near $x = 30.0$, shows that all the Ge additive serves to cross-link S_n chains. The maximum in the slope dT_g/dx near $x = 32.5$, which *precedes* the maximum of T_g near $x = 33.33$ (figure 2), emphasizes (Boolchand 2000) that, for $x > 32.5$, the additive preferentially nucleates structures (B and C units) that do *not* form part of the tetrahedral network and lowers the global connectivity. In glass systems where T_g continues to increase with increasing cation concentration (Griffiths *et al.* 1984, Selvanathan *et al.* 2000), such as the Si_xSe_{1-x} binary, the Si—Si bonds formed for $x > 33.33$ are part of the backbone and melt viscosities increase astronomically. Taken together the Raman scattering, Mössbauer effect results and trends in T_g provide a rather complete picture of structure in the present glasses. They show that the stoichiometric glass is composed of a majority tetrahedral phase (A) in which minority nanophases (B and C) grow and break the chemical order and reduce the global connectivity of the network.

§4. CONCLUSIONS

We have presented new Raman scattering and Mössbauer spectroscopy results that show the chemical order of GeS_2 glass to be intrinsically broken. The GeS_2 glass structure differs from that of $GeSe_2$ in one significant respect; the distorted rocksalt units are an intrinsic feature of the former glass but not of the latter, a result that probably derives from the higher Pauling (1960) electronegativity of S (2.5) in relation to Se (2.4), which promotes growth of this ionically bonded structure.

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† In a GeS_2 network, for every 100 CS units, we have 40 ES units, 15 distorted rocksalt units and 8.8 ethane-like units. The bond fraction $N_{\mathrm{Ge\ GE}}/N_{\mathrm{Ge-S}} = 8.8/(100 \times 4 + 40 \times 4 + 15x \times 6 + 8.8 \times 6) = 1.2\%$.

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