

ds 44,

86).
Rev.

s'
.273.

77)

ys.

47

. B25,

Solid

ys.

STRUCTURAL ORDERING As_2S_3 BULK GLASS: ROLE OF QUENCH TEMPERATURE

I. Zitkovsky and P. Boolchand

Physics Department University of Cincinnati
Cincinnati, Ohio 45221-0011

Direct microscopic evidence for a precipitous drop in the concentration of homopolar S-S bonds in melt-quenched As_2S_3 glass as a function of quench temperature is observed at $T > 700^\circ C$. This may be related to the breaking up of S_8 rings present in the glass below the indicated temperature.

INTRODUCTION

There is growing evidence that the molecular structure of S-bearing glasses differs from their Se-bearing counterparts in significant ways. For example, the Ge tetrahedral fraction of 0.71(2) found¹ in GeS_2 glass may be compared to a higher value of this fraction of 0.84(1) found in $GeSe_2$ glass. It has been suggested¹ that, chemically, this result is signature of a higher degree of network polymerization of $GeSe_2$ glass in relation to GeS_2 glass. S-bearing glassy networks appear in general to phase separate more pronouncedly into characteristic molecular clusters than their Se counterparts. Chemically, this tendency may be the consequence of the higher stability of the S-S bond in relation to the Se-Se bond. It appears that for this reason S_8 rings proliferate in S-rich glassy networks of binary Si-S, Ge-S and As-S alloys for which Raman spectroscopic evidence^{2,3} is available. It is possible that a small but finite concentration of S_8 rings persists even in stoichiometric glasses such as GeS_2 and As_2S_3 .

The molecular structure of melt-quenched As_2S_3 and As_2Se_3 glasses has been the subject of several previous investigations using scanning calorimetry⁴, Raman scattering⁵, X-ray diffuse scattering⁶ and Mossbauer spectroscopy⁷. In the present work we have used Mossbauer spectroscopy to probe the chalcogen chemical order in these prototypical glasses as a function of fixative or quench temperature (T_q). The details of this technique to probe the molecular structure of glasses has been described in several articles^{8,9}. The present results show qualitative differences between the two pnictide glasses. Specifically, the T_q variation of Mossbauer site intensity ratios unambiguously demonstrates that the concentration of homopolar S-S bonds in As_2S_3 glass decreases strikingly above a threshold quench temperature ($T_q > 700^\circ\text{C}$) although no such effect is observed in As_2Se_3 glass. We associate this effect with the presence of a small but finite concentration of S_8 rings in stoichiometric As_2S_3 glasses quenched from $T_q < 700^\circ\text{C}$. At $T_q > 700^\circ\text{C}$, apparently, the S_8 rings are systematically cut or broken in a thermally reversible fashion. Consequences of these results on the optical absorption edge and Raman scattering studies are briefly commented upon.

EXPERIMENTAL

99.999% pure As_2Se_3 and 98% pure As_2S_3 samples were purchased from Aesar and alloyed with traces of the Mossbauer active elements (^{125}Te and ^{128}Te) and elemental As to maintain the stoichiometry. Prior to alloying, both the As_2S_3 starting material and enriched ^{125}Te metal (or ^{128}Te metal) were purified to remove traces of HCl and oxygen, respectively, by procedures described elsewhere^{10,11}. A master alloy glass was prepared by heating the starting materials in evacuated fused quartz ampules held vertical in a furnace at 600°C for a five-day period. The temperature was then lowered to 350°C and the melt equilibrated at this temperature for 24 hours prior to a water quench. The master alloy was then split in several parts and each part quenched from a pre-selected T_q in the temperature range $350^\circ\text{C} < T_q < 1000^\circ\text{C}$, and examined by both ^{125}Te absorption and ^{129}I emission Mossbauer spectroscopy. Details of the experimental procedure appear elsewhere^{8,9}.

^{125}Te spectra of the glasses are characterized by a quadrupole doublet¹² (Figure 1). The separation between the doublet (i.e., the quadrupole splitting) is found to remain constant as a function of T_q for As_2Se_3 glass (Figure 2). On the other hand the quadrupole splitting is found to display a profound, precipitous drop at $T_q > 700^\circ\text{C}$ for As_2S_3 glass, and this is also illustrated in Figure 2.

^{129}I emission spectra of As_2S_3 glass display evidence of two types of sites (Figure 3) whose microscopic nature was discussed previously^{7,12}.

has been
ry⁴,
7. In
ogen
or
lecular
esent

lguously
ss de-
ugh no
the
ric
ings are
ences of
s are

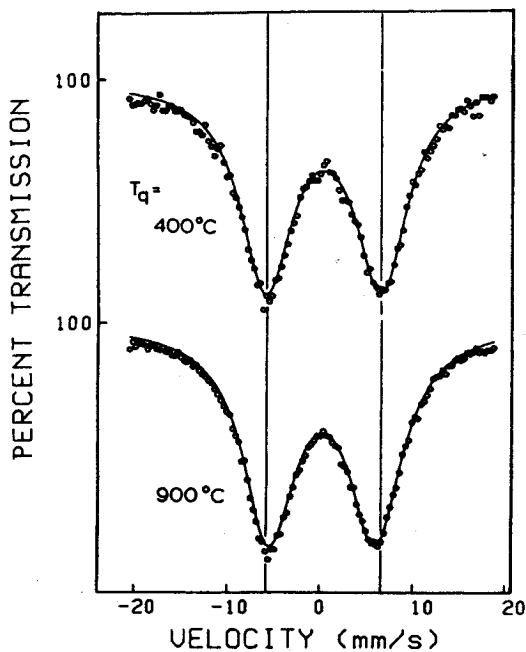


Figure 1

^{125}Te Mossbauer spectra of $\text{As}_2\text{S}_{2.98}\text{Te}_{0.02}$ glass samples quenched from indicated temperatures. Note that the quadrupole splitting decreases with T_q . Spectra were recorded at 4.2K^q using a source of $^{125}\text{Te}^m$ in GeTe .

Aesar
(e) and
 As_2S_3
d to
lse-

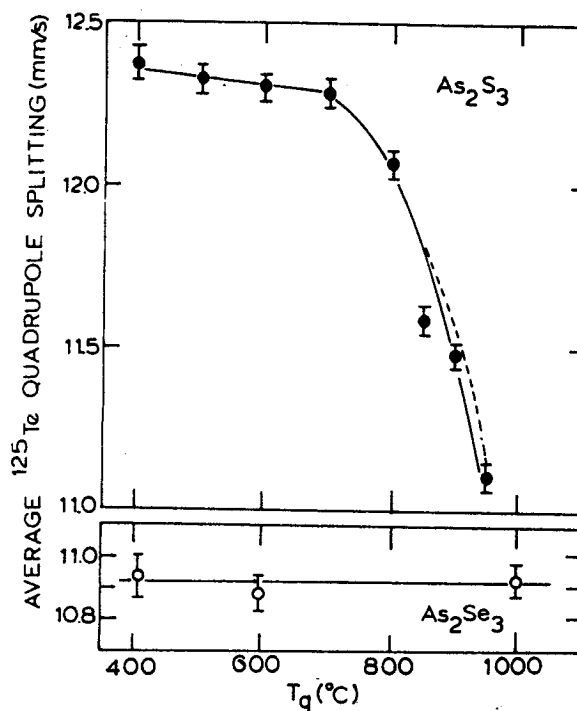
t 600°C
e melt
The
a pre-
th
he

let¹²

ass
lay a

Figure 2

T_q dependence of average quadrupole splitting in As_2S_3 (top) and As_2Se_3 (bottom) glass. Note the precipitous drop in $\langle\Delta(T_q)\rangle$ at $T_q > 700^\circ\text{C}$ for As_2S_3 glass.



of

Briefly, the A site represents a chemically ordered As-Te-As site which results when a Te atom replaces a S site two-fold coordinated to As, while the B site represents a chemically disordered S-Te-As site which results when Te replaces S in an As-S-S string or a S-S-S string or both. The B site consequently is signature of S-S homopolar bonds in the network. The T_q variation of the Mossbauer site intensity ratio I_B/I_A deduced from a standard deconvolution of the spectra is plotted in Figure 4. We note that the $I_B/I_A(T_q)$ trend displayed in Figure 4 mimics that of the average ^{125}Te quadrupole splitting $\langle\Delta(T_q)\rangle$ shown in Figure 3. In fact, given the measured I_B/I_A site intensity ratio of Figure 4, we can calculate the expected $\langle\Delta(T_q)\rangle$ variation using the relation

$$\langle\Delta\rangle = I_A \Delta_A + I_B \Delta_B \quad (1)$$

where Δ_A and Δ_B represent the respective Te quadrupole splittings at the A and B site. The dashed curve displayed in Figure 2 is the expected variation of $\langle\Delta(T_q)\rangle$ for fixed values of $\Delta_A = 7.1$ mm/s and $\Delta_B = 14.7$ mm/s. These quadrupole splitting values are fully compatible with the microscopic

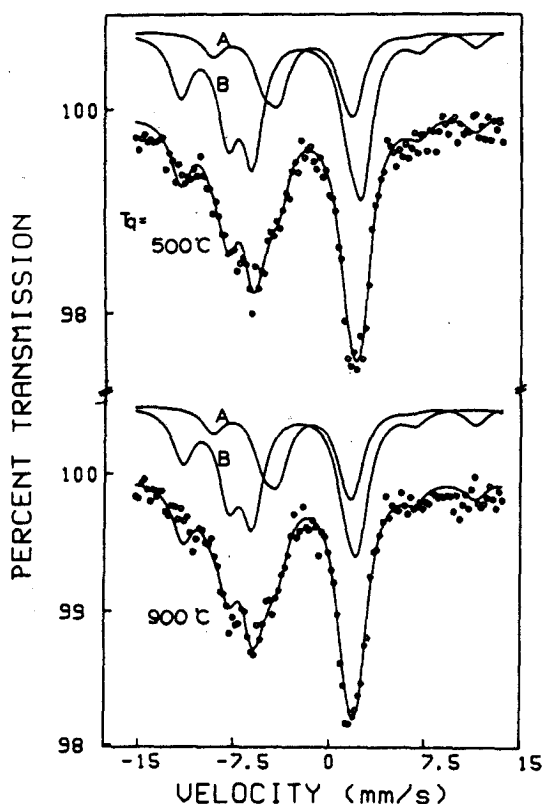


Figure 3

Selected ^{129}I emission spectra of $\text{As}_2\text{S}_{2.98}\text{Te}_{0.02}$ glasses quenched from indicated temperature. The two sites A and B are partially resolved because of the narrower line-width of this resonance. Spectra were recorded at 4.2K using a NaI^{129} absorber.

$\frac{I_B}{I_A}$

identi
comple
DISCUS

Th
drop i
(Figur
Tanaka
glass.
the op
in the
with a
quench
Figure

Th
scatte
band (
increa
could
remain
ectly
strate
mode
terize
even
change
normal

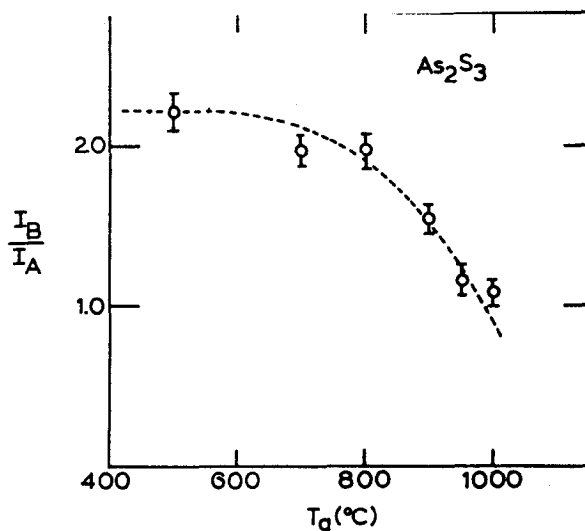


Figure 4

T_q dependence of the ^{129}I Mossbauer site intensity I_B/I_A deduced from the spectra of Figure 3. The B site represents signature of S-S bonds.

identification of the Te A and B sites and the reader is referred to a more complete discussion of this point in reference 12.

DISCUSSION

The principal result to emerge from the present work is the precipitous drop in the concentration of S-S bonds in As_2S_3 glass quenched from $T_q > 700^\circ\text{C}$ (Figure 4). We note that quite a similar trend was reported independently by Tanaka, Gohda and Odajima¹³ in the T_q variation of the optical band gap of this glass. Given that in binary $\text{As}_x\text{S}_{1-x}$ glasses there exists a local minimum¹⁴ in the optical band gap near the stoichiometric composition of $x \approx 0.4$, the reduction in the optical band gap of As_2S_3 glass quenched at $T_q > 700^\circ\text{C}$ is fully compatible with a reduction in the concentration of homopolar S-S bonds present in glasses quenched above 700°C . The present experiments also show that the trend of Figure 4 is thermally reversible and this is a point of interest in itself.

The Raman scattering results of reference 13 display an increase in the scattering strength of the 200cm^{-1} mode (As-As bond) normalized to the 344cm^{-1} band (As-S bond) with increasing T_q . These results do not necessarily imply an increase in the concentration of S-S bonds as suggested by the authors. This could have been the case provided the scattering strength of the 344cm^{-1} band remained independent of T_q . Finkman, DeFonzo and Tauc¹⁵ several years ago directly studied the T-dependence of Raman scattering from liquid As_2S_3 and demonstrated that the scattering strength of both the 344cm^{-1} band and the 220cm^{-1} mode decreases sharply with T, with the activation energy for each band characterized respectively by values of 190meV and 70meV. These results suggest that even if the concentration of wrong bonds in As_2S_3 melts were to remain unchanged with T, one may expect the scattering strength of the 200cm^{-1} mode normalized to the 344cm^{-1} band to actually increase with T.

In As_2Se_3 glass melt-quenching from various temperatures does not alter I_B/I_A ratio. In As_2S_3 glass on the other hand a drastic reduction in I_B/I_A takes place at $T_q \approx 700^\circ\text{C}$ suggesting that a new type of cluster must be populated in the S-bearing glass which is not intrinsic to the Se-bearing glass. S_8 rings are stable species in S-vapor as shown from optical absorption edge studies¹⁶, although this is not the case for Se_8 rings. Furthermore because S_8 rings are known to be present in sizable concentrations to be detected in Raman spectra of S-rich ($y > 0$) $\text{As}_2\text{S}_{3+y}$ glasses, it appears plausible to propose that a small concentration ($\approx 2\%$) of S-S bonds in the form of S_8 rings persists in the stoichiometric ($y=0$) glass. Evidence for As-As bonds in As_2S_3 glass has already been documented¹⁷ by previous Raman scattering experiments.

We acknowledge stimulating discussions with Dr. J.C. Phillips and the assistance of Dr. Gary Ehrhart in neutron irradiations. This work was supported by NSF grant DMR-85-21005.

REFERENCES

1. P. Boolchand, J. Grothaus, M. Tenhover, M.A. Hazle and Robert K. Grasselli, *Phys. Rev.* **B33**, 5421 (1986); P. Boolchand in *Comments Condensed Matter Phys.* **12**, 163 (1986).
2. G. Lucovsky, J.P. deNeufville and F.L. Galeener, *Phys. Rev.* **B9**, 1591 (1974).
3. J.E. Griffiths, M. Malyj, G.P. Espinosa and J.P. Remeika, *Phys. Rev.* **B30**, 6978 (1984); M. Tenhover, M.A. Hazle and R.K. Grasselli, *Phys. Rev.* **B29**, 6732 (1984).
4. M.B. Meyers and E.J. Felty, *Mater. Res. Bull.* **2**, 535 (1967).
5. R.J. Kobliska and S.A. Solin, *Phys. Rev.* **B8**, 756 (1973); also see M. Malyj and J.E. Griffiths, *Solid State Commun.* **62**, 671 (1987); **62**, 667 (1987).
6. L.E. Busse, *Phys. Rev.* **B29**, 3639 (1984).
7. P. Boolchand, W.J. Bresser and P. Suranyi, *Hyperfine Interactions* **27**, 385 (1985).
8. P. Boolchand in *Physical properties of Amorphous Materials*, Ed. by David Adler, Brian B. Schwartz and Martin C. Steele (Plenum, N.Y. 1985) p. 221.
9. W.J. Bresser, P. Boolchand, P. Suranyi and J.P. deNeufville, *Phys. Rev. Lett.* **46**, 1689 (1981).
10. J.E. Griffiths (private communication).
11. P. Boolchand, W.J. Bresser and Gary J. Ehrhart, *Phys. Rev.* **B23**, 3669 (1981).
12. Jack Wells and P. Boolchand, *J. Non Cryst. Solids* **89**, 31 (1987).
13. K. Tanaka, S. Gohda and A. Odajima, *Solid State Commun.* **56**, 899 (1985).
14. R.A. Street, R.J. Nemanich and G.A.N. Connell, *Phys. Rev.* **B18**, 6915 (1978).
15. E. Finkman, A.P. deFonzo and J. Tauc in *Amorphous and Liquid Semiconductors*, Ed. by J. Stuke and W. Brening (Taylor and Francis, London 1974), p. 1275.
16. G. Weser, F. Hensel and W.W. Warren, Jr., *Ber Bunsenges Phys. Chem.* **82**, 588 (1978).
17. F. Kosek, J. Chlebuy, Z. Cimpl, J. Masek *Phil. Mag* **B47**, 627 (1983).

Meas
fere
glas
orde
of s
by t
tion

INTRODU

Silica
consist
hedrons
"X-amor
/1/. Nu
of the
deviati
to be i
consist
sion, w
the con
more ar
tions /
experin