

Molecular Origin of Glass Forming Tendency in Ternary Te–Se–Br(Cl) Chalcogenide Glasses*

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Z. Naturforsch. **51 a**, 373–380 (1996); received January 5, 1996

Bulk glasses of $\text{Te}_{3-z}\text{Se}_z(\text{Cl or Br})_{2+y}$, the composition spanning the glass forming range, were characterized by differential scanning calorimetry, ^{125}Te absorption, and ^{129}I emission Mössbauer spectroscopy. The results reveal that the stoichiometric glasses $\text{Te}_3(\text{Cl or Br})_2$ consists of c- Te_3Cl_2 -like chain fragments about 1.5 nm long and terminated by one-fold coordinated halogen atoms. The ^{125}Te electric hyperfine structure results reveal that Te replacement by Se ($z \neq 0$) leads to preferential occupancy at those Te sites in the chains that are two-fold coordinated, and in a rather striking fashion demonstrate that the average length of the chain fragments remains independent of Se concentration. Halogen atoms in the glasses act as chain terminators, and also bond to Te-sites in the chains to produce four-fold coordinated sites. The low glass transition temperatures ($T_g \sim 70 - 90^\circ\text{C}$), the low average coordination number of the proposed chain-fragments, along with the hyperfine structure results, suggest that the extensive glass forming tendency in the chalcogenides derives from the floppiness of the chain-fragments.

Key words: ^{125}Te Absorption Mössbauer Spectroscopy, ^{129}I Emission Mössbauer Spectroscopy, Chalcogenide Glasses, Molecular Structure, Glass Formation.

Introduction

Elemental Te is not a glass former, although its subhalides readily form bulk glasses [1]. In fact in the Te–Se–X ternary (Fig. 1), where X = Cl, Br and I, extensive bulk glass formation is known to occur, although the microscopic origin of this unusual behavior has remained largely unknown. These chalcogenide glasses are also transparent [1] to optical radiation in the mid IR region ($\lambda \sim 20\mu$) and have therefore attracted interest as prospective IR transmitting optical fiber materials.

To understand these materials at a basic level, we have recently examined [2] the molecular structure of the stoichiometric glasses $\text{Te}_3(\text{Cl or Br})_2$ in the present ternary corresponding to $z = 0$. In the Te–Cl binary phase diagram, crystalline compounds are known to

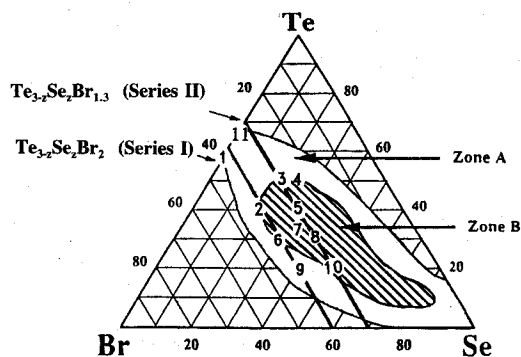


Fig. 1. Phase diagram of the Te–Se–Br ternary. Glass forming domain in this system is represented by zone A. The glasses in zone B do not exhibit a crystallization peak. Series I and II show different cuts through the glass forming region. glass sample identification is as follows: 1 - Te_3Br_2 , 2 - $\text{Te}_2\text{Se}_1\text{Br}_2$, 3 - $\text{Te}_5\text{Se}_2\text{Br}_3$, 4 - $\text{Te}_2\text{Se}_1\text{Br}_1$, 5 - $\text{Te}_4\text{Se}_3\text{Br}_3$, 6 - $\text{Te}_{1.5}\text{Se}_{1.5}\text{Br}_2$, 7 - $\text{Te}_1\text{Se}_1\text{Br}_1$, 8 - $\text{Te}_3\text{Se}_4\text{Br}_3$, 9 - $\text{Te}_1\text{Se}_2\text{Br}_2$, 10 - $\text{Te}_2\text{Se}_3\text{Br}_3$, 11 - Te_2Br_1 (11 is from [9]).

* Presented at the XIIIth International Symposium on Nuclear Quadrupole Interactions, Providence, Rhode Island, USA, July 23–28, 1995.

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occur at the compositions Te_3Cl_2 and TeCl_4 . The composition of Te_3Cl_2 is of special interest, since melts of this composition can be easily supercooled to form glasses. c- Te_3Cl_2 consists of quasi one-dimensional

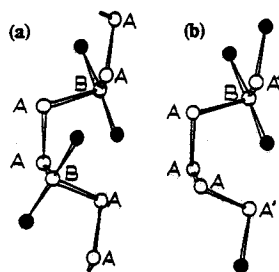


Fig. 2. (a) Polymeric chain structure of $c\text{-Te}_3\text{Cl}_2$ following the work of Kniep, *et al.* [4]. (b) Proposed molecular structure of $g\text{-Te}_3\text{Cl}_2$ and $g\text{-Te}_3\text{Br}_2$. It consists of Te (open circles) chain-fragments based on $c\text{-Te}_3\text{Cl}_2$ which are terminated by halogens (filled circles).

polymeric chains [3]. In a chain two types of Te cation sites are known to occur; a Te site (site A) two-fold coordinated to Te nearest neighbors (nn) and a Te site (site B) four-fold coordinated to a pair of Te and a pair of Cl nn, as illustrated in Figure 2a.

We recently reported [2] on the microscopic nature of Te sites in Te_3Cl_2 glass, using ^{125}Te absorption and ^{129}I emission Mössbauer spectroscopies. Because of the higher resolution in ^{129}I emission Mössbauer spectroscopy measurements, we could clearly discern a trimodal distribution of parent Te-sites and establish their microscopic structure from the measured isomer shift and Electric Field Gradient (EFG) parameters. Two of these Te sites (site A and site B) could be readily identified as the intrachain sites characteristic of $c\text{-Te}_3\text{Cl}_2$. The third site (site A'), peculiar to the glassy state, was identified as a chain-terminating Te-site having a Cl and a Te nearest neighbor (nn). Since the nuclear resonant absorption signal provides a direct measure of site-concentrations in the network, from the observed Mössbauer-site-intensity ratios $I_{A'}/I_A$ and $I_{A'}/I_B$, we could deduce the average chain-length in the glasses. The average length was found [2] to be 1.5 nm, and it corresponds to two formula units of $c\text{-Te}_3\text{Cl}_2$ as illustrated in Figure 2b.

In the present work we have now extended these measurements to a finite Se content in the $\text{Te}_{3-z}\text{Se}_z(\text{Cl}$ or $\text{Br})_2$ ternary starting from sample 1 (corresponding to $z = 0$), to samples 2, 6, and 9 (possessing progressively increasing z values) henceforth designated as series I as illustrated in Figure 1. Furthermore, to elucidate the role of halogen atoms in the glass structure, we have also prepared a second series of samples labelled 3, 5, 8, and 10 corresponding to a smaller Br content than series I. The samples in series II inter-

ested us because of yet another reason. These permit a scan through the middle of zone B of the phase diagram. In zone B, the glass forming tendency is so high that on a time scale of minutes, characteristic of scanning calorimetry measurements, crystallization exotherms are not observed.

In the next section we present details on sample preparation and glass characterization results by DSC and Mössbauer spectroscopy. A discussion of these results in context of glass structure is presented in the third section. The principal conclusions of this work are then summarized in the last section.

Experimental Procedure and Results

Sample Preparation and Characterization by DSC

Bulk glass samples were produced using 99.999% pure Te and Se and 99.9% pure TeBr_4 or TeCl_4 as starting materials. The TeBr_4 powder was weighed in a N_2 filled glove bag. The starting materials were sealed in evacuated fused quartz tubes (12mm diameter, 3mm walls) and slowly heated (30 hours) to about 540°C for 3 days in a vertical electric furnace. The alloy melts were then quenched in an ice-salt-water bath. The use of thick wall quartz tubes and a slow heating rate is necessary because of the high vapor pressure of the halogens. A total of eight glass samples (series I (1, 2, 6, 9) and series II (3, 5, 8, 10)) spanning two cuts of the glass forming region (Fig. 1) were made in the Te–Se–Br ternary.

A Perkin-Elmer differential scanning calorimeter (Model 2C) was used to measure the glass (T_g) and crystallization (T_x) temperatures of all the glasses. A scan rate of 10 K/min was used for all scans. Typical scans of our glasses are displayed in Figure 3. The T_g 's of all our glasses reside in a narrow temperature window $70^\circ\text{C} < T_g < 90^\circ\text{C}$, in agreement with previous work by Lucas *et al.* [1]. This is a broad consequence of the low average coordination number of ~ 2 of the present glasses and is in general agreement with the universal correlation of T_g as a function of average coordination number $\langle \text{CN} \rangle$ noted earlier [4] for the chalcogenide glasses.

We have plotted T_g 's as a function of the Se: Te ratio ' R ' = $z/(3-z)$ in the present ternary (Fig. 4) and find a clear correlation. In the sequence 1, 2, 6 and 9, and also the sequence 3, 5, 8 and 10, as Se systematically replaces Te (see Fig. 1) in the glasses, we find T_g 's to systematically increase by about 15 K. This result

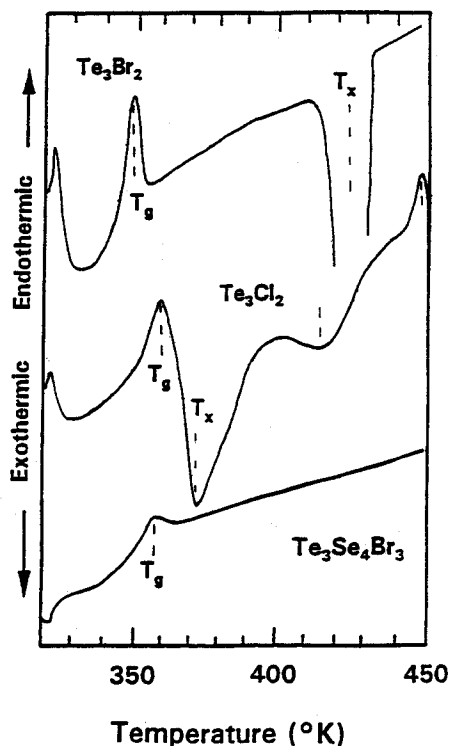


Fig. 3. Differential calorimetric scans of g- Te_3Br_2 and g- Te_3Cl_2 and a typical ternary glass showing a glass transition (T_g) and crystallization (T_x) temperature.

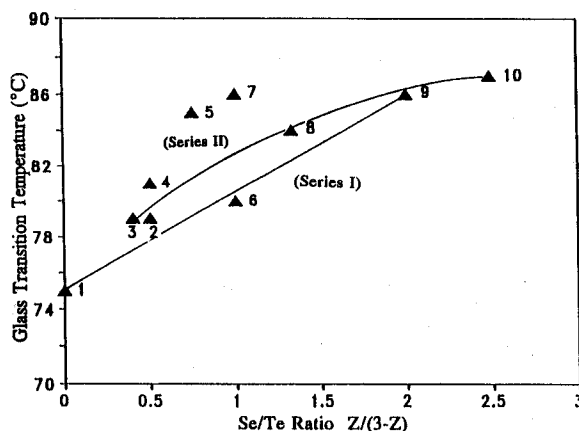


Fig. 4. Plot of the T_g 's as a function of the Se to Te ratio $z/(3-z)$ in the present ternary.

is most likely due to the chemically more stable Se-Te and Se-Se bonds emerging at the expense of the weaker Te-Te bonds in the polymeric chain-structure of the glasses. We shall return to discuss these results in context of glass structure latter.

^{125}Te Mössbauer Absorption Spectroscopy

^{125}Te Mössbauer spectra of the glass samples were studied at 4.2 K in an exchange gas liquid He dewar using a constant acceleration drive. Fifty-eight day ^{125m}Te in Mg_3TeO_6 matrix was used as a source of the 35.5 KeV γ -rays. The high f -factor, narrow linewidth and ease of producing such sources by neutron irradiation has attracted widespread interest [5] in this matrix. A Xe-proportional counter was used to detect the 5.8 keV escape peak of the 35.5 keV γ -ray. In our system both the source and absorber were cooled to 4.2 K. Thus, the isomer-shift of the glasses was measured relative to Mg_3TeO_6 source at 4.2 K. Nevertheless, as discussed in [5], since the second order Doppler shift of the source matrix changes little between 4 K and 300 K because of the high Debye temperature of this matrix, the quoted isomer shift can also be taken to represent shifts relative to the Mg_3TeO_6 matrix at 300 K.

Figure 5 represents selective spectra of the Te-subhalide glasses and c- Te_3Br_2 obtained in the present work. In general the observed lineshapes in the glasses and crystal reveal a partially resolved doublet. Deconvolution of the observed lineshape in terms of one quadrupole doublet requires an observed linewidth (Γ_{obs}) of 7.9 mm/s.

This Γ_{obs} is significantly larger than the characteristic linewidths observed ($\Gamma_{\text{obs}} = 6.1$ mm/s) in Te compounds like Te-metal, α - TeO_2 and β - TeO_2 hosts which possess one type of a non-cubic Te site. Excellent fits to the spectra of the present Te-compounds could be obtained by deconvoluting the observed lineshape in terms of two pairs of quadrupole doublets, keeping the observed linewidth fixed to a physically acceptable value of 6.1 mm/s. Our choice of this particular value of Γ_{obs} is based on our recent experience with a variety of Te compounds studied using this source. We take these linewidth considerations to indicate the presence of at least two chemically inequivalent Te-sites possessing different quadrupole splittings in the present glasses and crystals. In this bimodal distribution, we then define the site characterized by a larger (smaller) quadrupole splitting as the 1(2) site. Typical computer fits of observed spectra in terms of two quadrupole doublets are displayed in Fig. 5 as the continuous lines. The site (1, 2) parameters such as quadrupole splittings (Δ_1 , Δ_2) and isomer shifts (δ_1 , δ_2) as a function of Br content are displayed in Figure 6.

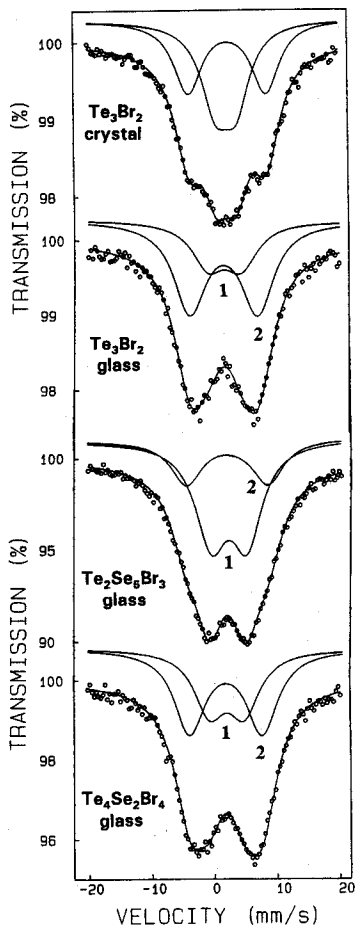


Fig. 5. ^{125}Te Mössbauer spectra of c- and g- Te_3Br_2 and selected Te-Se-Br glasses reveal a partially resolved doublet which is deconvoluted in terms of two quadrupole doublets (1 and 2).

We are struck by the near constancy of quadrupole splittings for site-2 (Δ_2) but a substantial variation of the quadrupole splittings for site-1 (Δ_1) in the glasses. To more clearly bring out the compositional variation of Δ_1 , we plot in Fig. 7, Δ_1 as a function of the Se/Te ratio $R = z/(3-z)$ in the glasses, and can clearly observe a linear correlation. This correlation is reminiscent of a parallel correlation noted earlier in binary Se-Te glasses [6] over two decades ago. These experimental trends already provide important clues on site identification. The Δ_1 and Δ_2 results suggest that the site-1 represent a Te-site that is two-fold coordinated to chalcogen (Se, Te) near-neighbors, while the site-2 represents a 4-fold coordinate Te-site that is associated with a pair of Te and a pair of halogen nn.

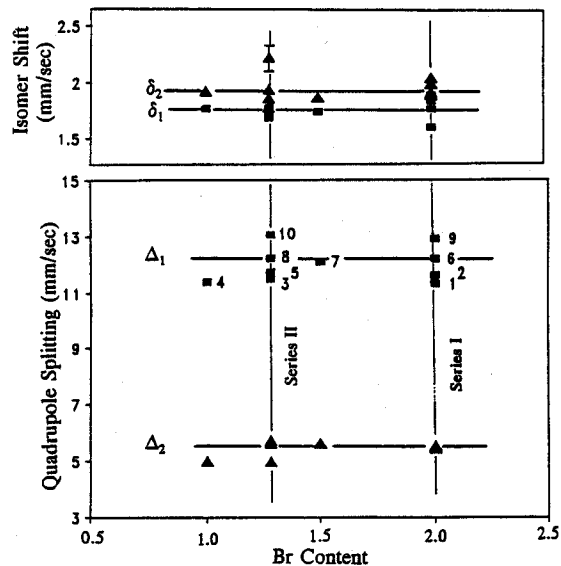


Fig. 6. Isomer shifts (δ_1 and δ_2) and quadrupole splittings (Δ_1 and Δ_2) as a function of Br content for Series I (1, 2, 6, 9) and Series II (3, 5, 8, 10) glasses.

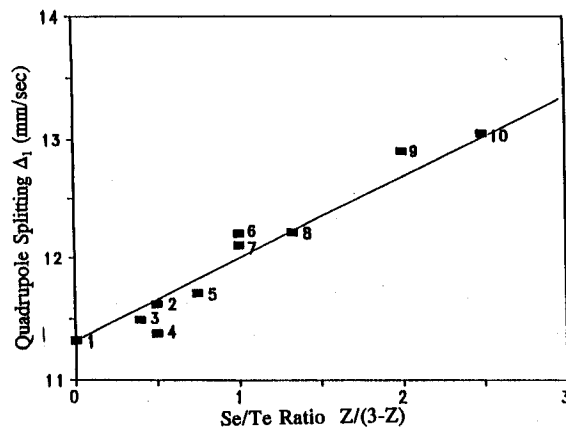


Fig. 7. Plot of quadrupole splitting (Δ_1) versus Se/Te ratio $z/(3-z)$ showing a linear increase in the parameter Δ_1 with the addition of Se.

Perhaps the most revealing results to emerge from these Mössbauer spectroscopy measurements pertain to the site-intensity ratio I_1 / I_2 as a function of Se-content $3-z$ (see Fig. 8) for both series I and II. The circles represent results obtained by deconvoluting the Mössbauer spectra in terms of two quadrupole doublets. Starting from the stoichiometric Te_3Br_2 glass ($y = 0$), we find that the effect of Se-alloying is to linearly lower the site intensity ratio I_1 / I_2 for samples in series I. A parallel result is found for the glass samples

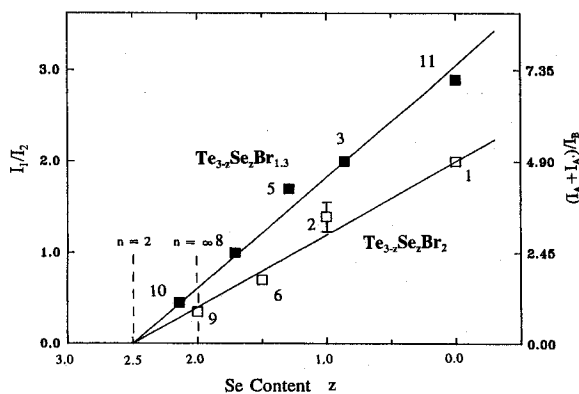


Fig. 8. Plot of site-intensity ratio I_1/I_2 as a function of Se content z for Series I (open squares) and Series II (filled squares). The effect of alloying Se in Series I or II is to systematically lower the site intensity ratio. The effect of increasing the Br content (going from Series II to Series I) is to increase I_2 thus lowering the site intensity ratio. Note that the result on sample 11 is from Takeda *et al.* [9].

in series II, but with a slightly higher slope. Remarkably, we find that for both series of samples the linear variation of I_1/I_2 extrapolates to zero near $z = z_c = 5/2$ corresponding to a stoichiometry $\text{Te}_{1/2}\text{Se}_{5/2}\text{Br}_{2+y}$. z_c thus represents the critical Se concentration at which $I_1/I_2 \rightarrow 0$.

^{129}I Emission Mössbauer Spectroscopy

The Mössbauer effect of the 27.8 keV γ -ray in ^{129}I , using $^{129}\text{Te}^m$ sources provides a complementary method to tag various Te environments in a host. The much narrower linewidth $\Gamma_n = 0.69$ mm/s and the $5/2^+ \rightarrow 7/2^+$ spin sequence of the 27.8 keV gamma-transition permits a unique measurement of the sign and asymmetry parameter of the EFG in glasses. Often the results of ^{129}I experiments provide a check on the interpretation of ^{125}Te Mössbauer spectroscopy results in Te-bearing compounds.

Sources of ^{129m}Te in Te-metal were prepared by neutron irradiation of enriched ^{128}Te metal. Traces of ^{129m}Te labelled Te-metal were reacted with Te-chalcogenide glass used as a starting material. The starting materials were encapsulated in evacuated quartz ampules and slowly heated to 550 °C, i. e. past the melting temperature of c-Te at 450 °C, and reacted for 48 hours with periodic mixing. The melts were quenched in ice water to realize the glass. ^{129}I Mössbauer emission spectra of the Te_3Cl_2 glass were

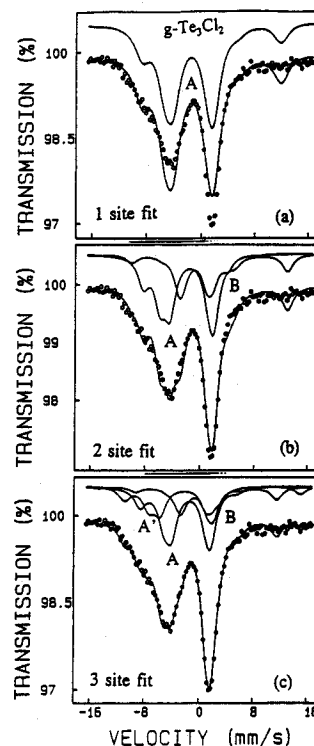


Fig. 9. ^{129}I Mössbauer emission spectra of $g\text{-Te}_3\text{Cl}_2$ deconvoluted in terms of (a) one, (b) two, and (c) three sites. See text for details.

recorded using a Cu ^{129}I absorber, with both the source and absorber cooled to 4.2 K using a liquid helium dewar. The 27.8 keV γ -ray was detected using an intrinsic Ge-detector.

Figure 9 reproduces ^{129}I emission spectra of glassy Te_3Cl_2 taken from [2]. To deconvolute the observed lineshape we found it necessary and sufficient to require 3 chemically inequivalent sites, henceforth labelled A, B and A'. Table 1 provides a summary of the Mössbauer effect parameters of the various sites observed in Te_3Cl_2 and Te_3Br_2 glass. For comparison, Mössbauer effect parameters of several crystalline reference compounds are also included in Table 1.

^{129}I spectra of glasses at other compositions in series I and series II are in the process of being studied. Nevertheless, the available ^{125}Te and ^{129}I Mössbauer spectroscopy results presented here in the present ternary already provide important clues on the molecular structure of these glasses and in particular, on the role played by Se and Br atoms in altering the chain-structure which we discuss next.

Table 1. Mössbauer effect parameters.

Host		e^2qQ (MHz)	η	δ^\dagger (mm/s)	Γ_{obs} (mm/s)
g-Te ₃ Cl ₂	A	-1005(20)	0.41(3)	1.28(7)	2.0(1)
	A'	-1352(50)	0.23(3)	1.80(8)	
	B	+ 652(20)	0.01	1.34(12)	
g-Te ₃ Br ₂	A	- 974(17)	0.36(3)	1.37(7)	1.9(1)
	A'	-1339(50)	0.21(3)	1.75(8)	
	B	+ 623(10)	0.01	1.37(12)	
α -TeO ₂ ^(a)		+ 826(3)	0.56(2)	2.98(5)	1.10(10)
c-Te ^(b)		- 397(2)	0.70	1.08	1.13(2)

[†] shifts quoted relative to I⁻(δ_0): A shift of 0.13 mm/s is assumed for Cu¹²⁹I absorber relative to I⁻;

^(a) see [7]; ^(b) see [8].

Discussion

Molecular Structure of Te₃Cl₂ and Te₃Br₂ glass

The fairly complete ¹²⁵Te and ¹²⁹I Mössbauer spectroscopy results on the Te₃Cl₂ and Te₃Br₂ stoichiometric glasses permitted a clear determination of the local as well as the medium-range structure of these chalcogenide glasses. As discussed in [2], the observed ¹²⁹I Mössbauer site intensity ratios $I_{A'}/I_A$ and $I_{A'}/I_B$ indicate that the length of the chains in the glass is on an average two formula units long (Fig. 2), and this corresponds to 1.5 nm.

Our experience with the ¹²⁵Te lineshape analysis in the stoichiometric glasses also tells us that the limited resolution of this nuclear resonance permits deconvolution of the lineshape *uniquely* only in terms of two quadrupole doublets (see Figures 5, 6). This is, of course, not to say that the observed ¹²⁵Te lineshape in these glasses cannot be fit to three quadrupole doublets as suggested by the narrower ¹²⁹I nuclear resonance results on the glasses. But in order to do so, ¹²⁵Te site parameters need to be constrained corresponding ¹²⁹I site parameters (δ and e^2qQ) in the 3-site fit as discussed in [2].

Thus although we have analyzed ¹²⁵Te Mössbauer spectra in the present ternary glass system in terms of two sites (see Figs. 5 and 6) labeled '1' and '2', these fits are actually an approximation to three or more sites that we believe are populated in the glasses. It is also transparent that the site-1 quadrupole splitting $\Delta_1 \sim 12$ mm/s (see Fig. 6) actually represents a weighted average of the 2-fold coordinated Te sites A and A' quadrupole splittings, while site-2 quadrupole

splitting $\Delta_2 \sim 6$ mm/s is characteristic of the 4-fold coordinated Te site B quadrupole splitting. With these caveats, we can discuss the consequences of the present ¹²⁵Te Mössbauer effect results on the molecular structure of the ternary glasses.

Role of Se addition for Te in the Ternary Glasses

The central result of the present work is the linear reduction in the site intensity ratio I_1/I_2 as a function of increasing Se content in the two series of ternary glasses displayed in Figure 8. The natural explanation of this trend is that Te replacement by Se in the chains occurs principally at the A-sites, i. e. the two-fold coordinated Te sites having two Te nns in a chain fragment. A parallel behavior was observed [6] in binary Se-Te alloys. Such replacement progressively removes Te-A sites in the chains keeping the Te-B sites intact. Remarkably, I_1/I_2 extrapolates to zero near $z = z_c = 5/2$, corresponding to a composition Te₁Se₅Br₄ in series I. This has the obvious interpretation that at z_c , Se has completely replaced available A and A' sites of the $n = 2$ chain fragments with the result that $I_1 = I_A + I_{A'} \rightarrow 0$.

The Δ_1 variation as a function of the $z/(3-z)$ ratio displayed in Fig. 7 provides us yet another clue on the way Se replaces Te in the chains. In series I, we note that Δ_1 increases monotonically in the sequence 1, 2, 6 and 9 with large jumps occurring between glass samples 2 and 6 and then between 6 and 9. Given that Δ_1 is a weighted average of Δ_A and $\Delta_{A'}$ with $\Delta_{A'} > \Delta_A$, the trend displayed in Fig. 7 strongly suggests that Se first replaces Te A-sites and then the Te A'-sites in the chain fragments. Specifically for glass sample 6, corresponding to $z = 3/2$, on an average only Te A' site contributes to the site integrated intensity I_1 . Not surprisingly, Δ_1 increases sharply, since $\Delta_{A'} > \Delta_A$. At $z = 5/2$ then $I_1 \rightarrow 0$ since the only Te site present in the chain fragment at this point is a Te-B site which contributes to I_2 . We shall identify the critical value of z when $I_1 \rightarrow 0$ as z_c .

Role of Br content

The observed variation of I_1/I_2 as a function of Se content for glass samples in series II is quite similar to the one in series I. In the samples of series II, we note that the Br-content is smaller in relation to series I samples. A direct consequence is that comparatively more A-sites than B-sites are populated in the chains, since there are not as many halogen atoms available to form B-sites. It is for this reason that the starting

value of I_1/I_2 in sample 11 (corresponding to Te_2Br composition) is larger than in sample 1 (Te_3Br_2). The ^{125}Te Mössbauer results on sample II are taken from the work of Takeda and Greenwood [9]. Remarkably for samples in series II as well, we note that I_1/I_2 extrapolates to 0 at $z = 5/2 = z_c$. The essential difference between the two series of samples is that the initial population of A- and B- sites in the chains are different. In both series of samples halogen atoms serve a dual role. They act as chain terminators and they also bond to intrachain Te-sites forming B-sites.

In these chalcogen halide glasses, the presence of one-fold coordinated halogen atoms serves to mechanically constrain the Te_n -chain network. This behavior follows directly from constraint theory of glasses. This factor certainly represents one of the reasons why alloying Te with a halogen drastically elevates the glass forming tendency.

Average Length of Chain-fragment in Ternary Glasses

The bimodal (I_1, I_2) distribution of ^{125}Te sites observed in the present ternary glass system fortunately permits separating the contribution in the lineshape of 2-fold coordinated Te-sites from the 4-fold coordinated ones. In the Se-alloying experiments (Fig. 8) we were thus able to establish the critical Se concentration z_c at which all 2-fold coordinated Te-sites in a chain are fully substituted by Se. Experimentally this is realized when $I_1/I_2 \rightarrow 0$, or $I_1 \rightarrow 0$. Consequently, the ratio $z_c/(3-z_c)$ has another physical meaning: it provides a direct measure of the concentration of 2-fold to 4-fold coordinated chalcogen sites in a chain fragment and this information permits estimating the length of the chains as we show next.

If the chains in the glasses were infinite in extent, i. e. $n = \infty$, where n is the number of Te_3Cl_2 formula units as in crystalline Te_3Cl_2 , then one expects $z_c/(3-z_c) = 2$ since there are twice as many 2-fold coordinated Te-sites as 4-fold coordinated ones. The previous relation yields $z_c = 2.0$. On the other hand, if the chains were much smaller in length, say $n = 4$ formula units long, then simple counting of sites reveals $z_c = 2.25$. Finally, for a chain fragment that is only $n = 2$ formula units long, a count of the sites populated reveals $z_c/(3-z_c) = 5$ or $z_c = 2.5$. Thus z_c spans a range of $2.0 < z_c < 2.5$ as the chain length varies in the range as $\infty > n > 2$.

The value of $z_c = 2.5$ deduced from the Mössbauer intensity ratio I_1/I_2 measurements (Fig. 8) in the present ternary glass system, thus implies that the average length of the chains is given by $n = 2$. Exactly the same average length of the chain fragments was inferred quite independently from earlier [2] ^{129}I Mössbauer emission spectroscopy measurements on the stoichiometric glasses $\text{Te}_3(\text{Br or Cl})_2$. Remarkably, it appears that the average length of $n = 2$ of the chain fragments is independent of Se and Br contents of the glasses for the region of the phase diagram presently studied. While a chain-length of $n = 2$ can be easily rationalized for Series I samples, it is less obvious to understand such a result for Series II samples. One possible interpretation is to think of the Te_7Br_3 glasses of series II to be composed of two types of $n = 2$ chain fragments. One of these fragments contains halogens as terminations only (Te_6Br_2) while the other fragment of Te_6Br_4 stoichiometry contains a pair of intrachain halogens in addition to a pair of halogens acting as terminations as shown in Figure 2b. A glass stoichiometry close to Te_7Br_3 would then result if on an average for every Te_6Br_4 chain-fragment one had a pair of Te_6Br_2 fragments in the network.

Conclusions

The principal conclusions on the ternary Te-Se-Cl(Br) chalcogen halide glass system emerging from the present work are as follows. (a) The low glass transition temperatures T_g , which range from $70 \sim 90^\circ\text{C}$ in the present ternary glass system, are characteristic of a network possessing a low ~ 2 average coordination number. (b) ^{125}Te Mössbauer hyperfine structure results reveal that both 2-fold and 4-fold coordinated Te-sites are populated in the glasses with the quadrupole splitting of the former sites (site-1) $\Delta \sim 12$ mm/s while that of the latter sites (site-2) $\Delta_2 \sim 5$ mm/s. (c) The ^{125}Te site intensity ratio I_1/I_2 decreases linearly as Se replaces Te in the ternary glasses and extrapolates to 0 at $z = z_c = 2.5$. The reduction in I_1/I_2 reveals that Se replaces 2-fold coordinated Te sites in the chains before the 4-fold coordinated ones. (d) The average length of the chains in the Se-alloyed glasses, suggested by the value of $z_c = 2.5$, corresponds to $n = 2$ formula units of Te_3Cl_2 , i. e. 1.5 nm, and this length appears to be independent of Se and Br content of the glasses in the region of the phase diagram studied presently.

Acknowledgements

It is a pleasure to acknowledge the assistance of Melissa Gibbs, Ted Hunt and Victoria Morris in facilitating the neutron irradiations at the University

of Missouri Research Reactor, and Professor Jacque Lucas for his interest and encouragement in this work. This work was supported by the National Science Foundation grants DMR-92-07166 and DMR-93-09061.

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