The topology of bulk quenched Ge
x
Se
1−
x
(0 ≤ x ≤ 0.4) glasses

I. Petri & P. S. Salmon

Department of Physics, University of Bath, Bath BA2 7AY, UK

The topology of bulk quenched Ge
x
Se
1−
x
glasses at compositions x = 0, 0.2, 0.25, 0.33 and 0.4 was studied by using neutron diffraction to measure the Bhatia–Thornton number–number partial structure factor, SNN(Q), where Q is the scattering vector. The results were analysed by reference to the recently measured full set of partial pair distribution functions for glassy GeSe2 which help to illustrate the origin of the main structural features and give insights into the chemical ordering. Addition of Ge to glassy Se imposes an additional length scale on the atomic ordering, associated with intermediate ranged Ge–Ge correlations, which is manifested by a so called first sharp diffraction peak at QFSDP = 1 Å⁻¹ that reaches its maximum height at the GeSe2 composition. The results are consistent with the ‘8-N’ rule and may be interpreted in terms of a chemically ordered continuous random network. However, the full set of partial pair distribution functions measured for glassy GeSe2 show that deviations from this model do occur and may, therefore, be expected for other glasses near this composition.

The object of this paper is to study the change in topology of bulk quenched Ge
x
Se
1−
x
glasses over a wide composition range by using neutron diffraction to measure the Bhatia–Thornton number–number partial structure factor, SNN(Q), where Q is the magnitude of the scattering vector. The Ge–Se system was chosen for investigation since it is a much studied covalently bonded glass former whose network connectivity over the glass forming region 0 ≤ x ≤ 0.4 can be changed by altering the Ge:Se ratio. On the basis of mean field constraint theory, there is a rigidity percolation threshold at x = 0.2 corresponding to a mean coordination number n = 2.4. Evidence for such a transition and related phenomena near this threshold value has been found from Raman spectroscopy and temperature modulated differential scanning calorimetry measurements. The present work complements other neutron diffraction experiments on the composition and temperature dependence of the structure of both the liquid and glassy phases of Ge
x
Se
1−
x
. Other studies on the composition dependence of the glass structure have been made using both direct and indirect methods, including x-ray absorption fine structure (EXAFS), x-ray emission and Raman spectroscopy. Unexpected deviations from the ‘8-N’ rule were observed in some of this work. In the present investigation, the diffraction patterns for the glassy phase were measured over an extended Q range which will reduce the distortion of the corresponding real space functions. Furthermore, advantage is taken of the recently measured full set of partial pair distribution functions, gNN(r), for glassy GeSe2 in the interpretation of the results.

The total structure factor S1(Q) measured in a neutron diffraction experiment on a binary system comprising Ge and Se of natural isotopic abundance reduces, at a good level of approximation, to the single partial structure factor SNN(Q) since the coherent scattering lengths of Ge and Se are similar. The Fourier transform of this function, gNN(r), contains information on the topology of the system as it describes the sites of the scattering nuclei but is not concerned with their chemical identity. For many binary glasses and their corresponding liquids, SNN(Q) has a characteristic three peak structure for 0 ≤ Qr1 ≤ 10, where r1 is the nearest neighbour distance, which is manifest in the corresponding SNN(Q). The first of these peaks occurs at low values of Qr1 between 1.7 and 3.1 for many oxide, halide and chalcogenide structurally disordered systems as is the so-called first sharp diffraction peak (FSDP). It is a signature that the bond takes a significant directional character and arises from the intermediate ranged atomic ordering. The present experiments on glassy Ge
x
Se
1−
x
will, therefore, provide information on the network topology at both short and intermediate atomic length scales.

Theory

In a neutron diffraction study of a binary Ge–Se compound, the coherent scattered intensity can be represented by the total structure factor

S1(Q) = SNN(Q) − 1 + A {SNC(Q)/(1 − x) − 1} + BSNC(Q)

(1)

where x denotes the atomic fraction of Ge, b the coherent scattering length of chemical species, \( b_b = b_{Ge} + (1 - x) b_{Se} \), \( A = x(1 - x)/b_b^2 \) and \( B = 2ab/b_b \). In Equation (1), SNN(Q), SNC(Q) and SNC(Q) are the Bhatia–Thornton number–number, concentration–concentration and number–concentration distribution functions.
to first order, be neglected. The total pair distribution function follows from the Fourier transform relation

\[ G_\tau (r) = \frac{1}{2\pi n_0 r} \int_0^\infty dQ S_\tau (Q) \sin (Qr) \]

\[ = \left[ g_{NN} (r) - 1 \right] + A g_{CC} (r) + x (1 - x) B g_{NC} (r) \]  
(2)

where \( n_0 \) is the atomic number density. In terms of the partial pair distribution functions for the Ge and Se atomic species

\[ g_{NN} (r) = x^2 g_{GeSe} (r) + (1 - x)^2 g_{SeSe} (r) + 2x (1 - x) g_{GeSe} (r) \]  
(3a)

\[ g_{CC} (r) = x (1 - x) [g_{GeSe} (r) + g_{SeSe} (r) - 2g_{GeSe} (r)] \]  
(3b)

\[ g_{NC} (r) = x g_{GeSe} (r) - (1 - x)^2 g_{SeSe} (r) + (1 - 2x) g_{GeSe} (r) \]  
(3c)

whence it follows that

\[ G_\tau (r) = C [g_{GeSe} (r) - 1] + D [g_{SeSe} (r) - 1] + E [g_{GeSe} (r) - 1] \]  
(4)

where \( C = 2x (1 - x) b_0 \) and \( D = (1 - x)^2 b_0 \) and \( E = x^2 b_0 \). If the scattering lengths of the atomic species are equal then \( \Delta = 0 \) and the functions \( S_{NN} (Q) \) and \( s_{NN} (r) \) are given directly by Equations (1) and (2). Since \( n_0^\text{Ge} = (1 - x) n_0^\text{Se} \) it follows from the definition of \( g_{NN} (r) \) that the average coordination number, irrespective of species type, is given by

\[ \pi = 4 \pi n_0 \int r^2 g_{NN} (r) \, dr \]

where \( n_0^\alpha \) is the mean number of particles of type \( \alpha \) contained in a volume defined by two concentric spheres of radii \( r_i \) and \( r_o \), centred on a particle of type \( \alpha \). For a binary Ge-Se system comprising elements of natural isotopic abundance the neutron scattering lengths are comparable at \( b_{Ge} = 8.185(20) \) fm and \( b_{Se} = 7.9709(9) \) fm (Ref. 25). The weighting coefficients for the investigated glasses are given in Table 1 and show that \( S_{NN} (Q) \) accounts for the majority of \( S_\tau (Q) \), i.e. the contribution from the other partial structure factors can, to first order, be neglected.

In practice, the reciprocal space data sets are limited by the measurement window function \( M (Q) \) of the diffractometer where \( M (Q < Q_{\text{max}}) = 1 \) and \( M (Q > Q_{\text{max}}) = 0 \) and it is convenient to consider the function

\[ D' (r) = \frac{1}{\pi^{\frac{3}{2}}} \int dQ S_\tau (Q) M (Q) \sin (Qr) \]

\[ = 4 \pi n_0 G_\tau (r) \, \delta (M (r)) \]  
(6)

where \( \delta \) denotes the one dimensional convolution operator and \( M (r) \) is the real-space representation of \( M (Q) \). Since \( G_\tau (r) \) is dominated by \( g_{NN} (r) \) and \( M (Q = 0) = 1 \) it then follows that

\[ D' (r) = (4 \pi n_0 g_{NN} (r)) \delta (M (r)) - 4 \pi n_0 \]  
(7)

To obtain reliable coordination numbers for the glasses it proved necessary to take into explicit account the effect of the finite \( Q_{\text{max}} \). The first peak of \( D' (r) \) was therefore fitted to a sum of \( G \) Gaussians representing the individual \( \delta (M (r)) = 4 \pi n_0 g_{NN} (r) \), convoluted with \( M (r) \).

**Experimental method**

Glassy Ge\textsubscript{0.75}Se\textsubscript{0.25} samples were prepared by loading Ge lumps (99-9999%, Aldrich) and Se pellets (99-999%, Johnson Matthey) into silica ampoules of 5 mm internal diameter and 1 mm wall thickness in a high purity argon filled glove box (–1 ppm oxygen, <10 ppm water). The ampoules had been cleaned using chromic acid prior to etching with a 40% solution of hydrofluoric acid. The sample filled ampoules were then evacuated to a pressure of \( 10^{-5} \) torr, purged three times with helium gas and after ~12 h they were sealed. Next, the ampoules were loaded into a rocking furnace and were heated at 1°C min\(^{-1}\) to 1000°C, pausing for 1 h at both the melting and boiling points of Se and at the melting point of Ge. After 48 h the ampoules were slowly cooled to either 850°C (\( x = 0.33 \)), 750°C (\( x = 0.25 \) or 0.4) or 650°C (\( x = 0.2 \)) where they were quenched in an ice/salt water mixture at –5°C. Glassy Se was prepared by heating the ampoule at 1°C min\(^{-1}\) to 210°C, near the melting point of Se, where it was equilibrated for 3 h. It was then heated at the same rate to 450°C, left for ~12 h and finally quenched in an ice/salt water mixture at ~5°C. The glass transition temperature, \( T_g \), of the samples was measured using a TA Instruments Thermal Analyser 2000 machine operating at a scan rate of 10°C min\(^{-1}\). Both the onset and midpoint temperatures of the transition were recorded (Table 1) and lie within the range of values given in the literature for Ge\textsubscript{0.75}Se\textsubscript{0.25} glasses (Ref. 2, 5, 26-9).

The neutron diffraction experiment on the \( x = 0.2 \) sample was performed using the D4B instrument at the Institut Laue-Langevin (Grenoble, France) operating at an incident wavelength of 0.7047 Å. The remaining experiments were made using the SANDALS instrument at the ISIS pulsed neutron source (Rutherford Appleton Laboratory, UK). The glasses were in the form of a coarsely ground powder and were con-

<table>
<thead>
<tr>
<th>Glass</th>
<th>( x )</th>
<th>A B C</th>
<th>D E</th>
<th>T(_g) (onset) (°C)</th>
<th>T(_g) (midpoint) (°C)</th>
<th>( n_0 ) (Å(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge\textsubscript{0.75}Se\textsubscript{0.25}</td>
<td>0.2</td>
<td>1.15×10(^{-4})</td>
<td>0.0537</td>
<td>0.3251</td>
<td>0.6331</td>
<td>0.0417</td>
</tr>
<tr>
<td>Ge\textsubscript{0.75}Se\textsubscript{0.25}</td>
<td>0.25</td>
<td>1.35×10(^{-4})</td>
<td>0.0536</td>
<td>0.3800</td>
<td>0.5550</td>
<td>0.0650</td>
</tr>
<tr>
<td>Ge\textsubscript{0.75}Se\textsubscript{0.25}</td>
<td>0.33</td>
<td>1.99×10(^{-4})</td>
<td>0.0535</td>
<td>0.4483</td>
<td>0.4366</td>
<td>0.1151</td>
</tr>
<tr>
<td>Ge\textsubscript{0.75}Se\textsubscript{0.25}</td>
<td>0.4</td>
<td>1.71×10(^{-4})</td>
<td>0.0534</td>
<td>0.4825</td>
<td>0.3524</td>
<td>0.1652</td>
</tr>
</tbody>
</table>
The measured $S_{\text{NN}}(Q)$, as obtained from Equation (1) by assuming $A=B=0$, are shown in Figure 1. As $x$ is increased from zero, the most striking change is the appearance of an FSDP at a position $Q_{\text{FSDP}}$ = $1 \text{ Å}^{-1}$ (see Table 2), i.e. a new intermediate ranged atomic length scale of periodicity $2\pi Q_{\text{FSDP}}$ develops as Ge is added to pure Se. The extent of these oscillations in real space is controlled by the coherence length $2\pi \Delta Q_{\text{FSDP}}$, the full width at half maximum of the FSDP, was obtained by reflecting the low $Q$ part of the peak about $Q_{\text{FSDP}}$. The magnitude of the oscillations is controlled by the height of the FSDP which first increases with $x$, reaching its maximum at GeSe$_{2}$, before subsequently decreasing. The resolution function, $\Delta Q/Q$, of the D4B and SANDALS instruments in the region of the FSDP are roughly comparable at $\pm 2\%$. The $g_{\text{NN}}(r)$ functions for the Ge$_x$Se$_{1-x}$ glasses are shown in Figure 2 and were obtained from Equation (2) by assuming $A=B=0$ and using reciprocal space data sets truncated at a maximum value $Q_{\text{max}}$ of either 15.95 $\text{ Å}^{-1}$ ($x=0$) or 19.95 $\text{ Å}^{-1}$ (all other $x$). The peak positions and coordination numbers are summarised in Table 3. Simple integration of the first peak in $g_{\text{NN}}(r)$ from its first to second minimum gave $n$ values that were too high compared with those expected on the basis of the ‘8-N’ rule and the measured $g_{\text{NN}}(r)$ for GeSe$_{2}$. The $n$ values of Table 3 were, therefore, obtained by taking into explicit account the finite measurement window function of the diffractometer through the peak fitting procedure described in the Theory section.

**Table 2.** Parameters describing $S_{\text{NN}}(Q)$ for glassy Ge$_x$Se$_{1-x}$ where $Q_{\text{FSDP}}$ (ε=FSDP, 2, 3 or 4) denotes peak position

<table>
<thead>
<tr>
<th>Glass</th>
<th>$Q_{\text{FSDP}}$ (Å$^{-1}$)</th>
<th>Height of FSDP (Å$^{-1}$)</th>
<th>$Q_{1}$ (Å$^{-1}$)</th>
<th>$Q_{2}$ (Å$^{-1}$)</th>
<th>$Q_{\text{NN}}(Q_{1})$</th>
<th>$S_{\text{NN}}(Q_{1})$</th>
<th>$S_{\text{NN}}(Q_{2})$</th>
<th>$S_{\text{NN}}(Q_{\text{FSDP}})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.92(2)</td>
<td>2.06(5)</td>
<td>2.50(2)</td>
<td>1.79(4)</td>
<td>1.76(2)</td>
</tr>
<tr>
<td>GeSe$_{0.5}$</td>
<td>1.04(2)</td>
<td>0.596(5)</td>
<td>0.34(1)</td>
<td>2.02(2)</td>
<td>1.75</td>
<td>2.01</td>
<td>1.357(1)</td>
<td>0.401</td>
</tr>
<tr>
<td>GeSe$_{0.3}$</td>
<td>0.99(2)</td>
<td>0.796(5)</td>
<td>0.30(1)</td>
<td>2.02(2)</td>
<td>1.74</td>
<td>2.00</td>
<td>1.417(1)</td>
<td>0.626</td>
</tr>
<tr>
<td>GeSe$_{0.5}$</td>
<td>0.94(2)</td>
<td>0.627(5)</td>
<td>0.29(1)</td>
<td>2.02(2)</td>
<td>1.78</td>
<td>2.00</td>
<td>1.327(1)</td>
<td>0.547</td>
</tr>
</tbody>
</table>
Table 3. Interatomic distances and coordination numbers for glassy GeSe\textsubscript{x-x} \textsubscript{2-x-y}, where \( r_1 \) and \( r_2 \) give the positions of the first and second peaks in \( g_{nn}(r) \)

<table>
<thead>
<tr>
<th>Glass</th>
<th>( r_1(\text{Å}) )</th>
<th>( r_2(\text{Å}) )</th>
<th>( \bar{n} )</th>
<th>( \bar{n}(\text{`8-N' rule}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se</td>
<td>2.34(2)</td>
<td>1.573</td>
<td>2.03(5)</td>
<td>2</td>
</tr>
<tr>
<td>GeSe\textsubscript{2}</td>
<td>2.35(2)</td>
<td>1.647</td>
<td>2.54(5)</td>
<td>2.67</td>
</tr>
<tr>
<td>GeSe\textsubscript{3}</td>
<td>2.35(2)</td>
<td>1.647</td>
<td>2.51(5)</td>
<td>2.51</td>
</tr>
<tr>
<td>GeSe\textsubscript{4}</td>
<td>2.37(2)</td>
<td>1.616</td>
<td>2.68(5)</td>
<td>2.68</td>
</tr>
</tbody>
</table>

believed to consist mainly of chains with perhaps a few rings.\(^{(19)}\)

When 20 mol\% Ge is added to form GeSe\textsubscript{2}, it is anticipated to break-up and cross link the Se chain structure by forming four fold coordinated units on the basis of the `8-N' rule. The small shift of the first peak position in \( g_{nn}(r) \) to 2.35(2) Å is then consistent with the formation of Ge(Se\textsubscript{1/2})\textsubscript{4} tetrahedra having a Ge–Se bonding distance of \( \bar{n} \)=2·36 Å, as found from the measured \( g_{nn}(r) \) for glassy GeSe\textsubscript{2}.\(^{(20)}\) An increase of the first peak position could also be compatible with the formation of homopolar Ge–Ge bonds that appear at \( \bar{n} \)=2·36 Å, as found from the measured \( g_{nn}(r) \) for glassy GeSe\textsubscript{2}.\(^{(20)}\)

Recent neutron diffraction experiments on glassy GeSe\textsubscript{2}\(^{(20)}\) using the method of isotopic substitution show that the chemical order of the network is broken with a maximum of 25(5)% Ge and 20(5)% Se being involved in homopolar bonds. However, the ratio of the number of Ge–Ge (or Se–Se) bonds to the total number of bonds in the glass is small at \( \approx \)4%. Further, the basic building block of the glass is the Ge(Se\textsubscript{1/2})\textsubscript{4} tetrahedral unit. The analysis of the neutron diffraction results for the GeSe\textsubscript{x-x} \textsubscript{2-x-y} glasses will therefore proceed on the basis that heteropolar bonding is preferred, a strategy that is in keeping with most previous investigations.\(^{(5,9,10,13–18)}\)

For glassy GeSe\textsubscript{2}, the first peak in \( g_{nn}(r) \) gives a coordination number \( \bar{n} \)=2·44(6) and is consistent with the CON model wherein \( \bar{n} \)=4, \( \bar{n} \)=2(1–x)/x, \( \bar{n} \)=2(1–x)/x and \( \bar{n} \)=2(1–x)/x. A higher value \( \bar{n} \)=2·64(18) was measured in a previous neutron diffraction experiment\(^{(6)}\) corresponding to \( \bar{n} \)=4 and G-e-Se and Se-Se bonds are allowed on the Se rich side of the GeSe\textsubscript{2} composition (x<1/3) while only G-e-Se bonds are allowed on the Ge rich side (x>1/3).\(^{(13,15)}\) At the stoichiometric composition x=1/3 only G-e-Se bonds are allowed and the network is completely chemically ordered. The expected coordination numbers for the CON are \( \bar{n} \)=4, \( \bar{n} \)=2(1–3x)/(1–x) and \( \bar{n} \)=0 on the Se rich side and \( \bar{n} \)=2(1–x)/x, \( \bar{n} \)=2(1–x)/x and \( \bar{n} \)=2(1–x)/x on the Ge rich side. However, both the RCN and CON models give the same mean coordination number of \( \bar{n} \)=2(1+x), i.e. this \( \bar{n} \) value is simply a condition that must hold if, in accordance with the `8-N' rule, Ge is fourfold coordinated and Se is twofold coordinated in GeSe\textsubscript{x-x} \textsubscript{2-x-y} glasses.
As the full set of $g_{\text{Ge}}(r)$ for glassy GeSe$_{1.5}$ has been measured\(^{[20]}\) and the fundamental building block in this glass, the Ge(Se$_4$)$_2$ tetrahedron, is also present in GeSe$_{1.5}$, the $g_{\text{Ge}}(r)$ for GeSe$_{1.5}$ were used to construct $G(r)$ for GeSe$_{1.5}$ by applying suitable weighting factors, Equation (4). A differently, $G_{\text{Ge}}(r)$ was constructed by using the measured $g_{\text{GeSe}}(r)$ for glassy Se (Figure 2) in place of that for glassy GeSe$_{1.5}$. For the purpose of these comparisons the r space functions were all derived by truncating the corresponding reciprocal space functions at the same maximum value $Q_{\text{max}}=15.95$ Å$^{-1}$. The results shown in Figure 3 demonstrate that, while neither of these combinations reproduce $G_{\text{Ge}}(r)$ for GeSe$_{1.5}$, the correlations contributing to the main features in $G_{\text{Ge}}(r)$ can be identified.

On the addition of Ge to form glassy GeSe$_{1.5}$, n increases to 2-51(5) and the ratio of the first and second peak positions, $r_{1}/r_{2}$, increases to 1.609 which is closer to the ratio $r_{1}/r_{2}=1.633$ expected for perfect Ge(Se$_4$)$_2$ tetrahedra. Figure 3 shows that by using the weighted $g_{\text{Ge}}(r)$ for GeSe$_{1.5}$ better agreement with $G_{\text{Ge}}(r)$ is obtained for GeSe$_{1.5}$ compared with GeSe$_{1.5}$. A Ge(Se$_4$)$_2$ tetrahedron motif is formed with increasing r the first peak of $G_{\text{Ge}}(r)$ is better represented by $g_{\text{GeSe}}(r)$ for glassy GeSe$_{1.5}$ and the second peak position moves to higher r as it gains an increased contribution from Se- Se correlations within tetrahedra. The CON model gives coordination numbers of $n_{\text{Ge}}=4$, $n_{\text{Se}}=2/3$ and $n_{\text{Ge}}=2.5$ which compare with values of $n_{\text{Ge}}=4-1(2)$, $n_{\text{Se}}=0-4(2)$ and $n_{\text{Ge}}=2-35(17)$ obtained from EXAFS experiments\(^{[14]}\) and $n_{\text{Ge}}=3.95$, $n_{\text{Se}}=0-75$ and $n_{\text{Ge}}=2-54$ obtained from a differential anomalous x-ray scattering study\(^{[27]}\). Overall, the diffraction results are consistent with several Raman spectroscopy studies of GeSe$_{1.5}$ glasses where both (Se) chains and Ge(Se$_4$)$_2$ tetrahedra are found at small x values\(^{[15,17,18]}\).

For GeSe$_{1.5}$, the comparison of Figure 3 with the measured CON model gives coordination numbers of $n_{\text{Ge}}=4$, $n_{\text{Se}}=2/3$ and $n_{\text{Ge}}=2-5$ which compare with values of $n_{\text{Ge}}=4-1(2)$, $n_{\text{Se}}=0-4(2)$ and $n_{\text{Ge}}=2-35(17)$ obtained from EXAFS experiments\(^{[14]}\) and $n_{\text{Ge}}=3.95$, $n_{\text{Se}}=0-75$ and $n_{\text{Ge}}=2-54$ obtained from a differential anomalous x-ray scattering study\(^{[27]}\). Overall, the diffraction results are consistent with several Raman spectroscopy studies of GeSe$_{1.5}$ glasses where both (Se) chains and Ge(Se$_4$)$_2$ tetrahedra are found at small x values\(^{[15,17,18]}\).

Conclusions

The structure of the GeSe$_{1.5}$ ($0 \leq x \leq 0.4$) glasses was analysed by experimental and computational means. The results confirm that the glass is a semi-liquid with a continuous random network model. However, the full set of $g_{\text{Ge}}(r)$ measured for glassy GeSe$_{1.5}$ show that deviations from this model do occur and may, therefore, be expected for other glasses near this composition.

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References