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Atomic-scale structure of GeSe₂ glass revisited: a continuous or broken network of Ge–(Se_{1/2})₄ tetrahedra?

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Abstract

The atomic-scale structure of germanium diselenide (GeSe₂) glass has been revisited using a combination of high-energy x-ray diffraction and constrained reverse Monte Carlo simulations. The study shows that the glass structure may be very well described in terms of a continuous network of corner- and edge-sharing Ge–Se₄ tetrahedra. The result is in contrast to other recent studies asserting that the chemical order and, hence, network integrity in GeSe₂ glass are intrinsically broken. It is suggested that more elaborate studies are necessary to resolve the controversy.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Glasses with the AB₂ stoichiometry (A = Si, Ge; B = O, S, Se) enjoy a wide range of practical applications and, for this reason, have been the subject of great scientific interest [1]. Special attention has been paid to determining the atomic-scale structure since a good knowledge of it is a prerequisite to understanding and, hence, gaining control over their useful properties. It is firmly established that the basic structural units of oxide AB₂ glasses are A–(B_{1/2})₄ tetrahedra (here B = O) that share their vertices and form a continuous random network [2, 3]. The situation is, however, not very clear with non-oxide AB₂ glasses, in particular with GeSe₂. Two conflicting structural models have been put forward. The first features the glass as a chemically ordered, continuous random network of both corner- and edge-sharing Ge–(Se_{1/2})₄ tetrahedra (here A = Ge, B = Se) [4]. In this model homopolar bonds, i.e. pairs of first-neighbor-like atoms, may occur accidentally in very small numbers. The second model views GeSe₂ glass as a chemically inhomogeneous aggregate of two different phases, with only the majority one based on Ge–(Se_{1/2})₄ tetrahedra. In this model, the presence of a substantial number of homopolar, i.e. Ge–Ge and Se–Se bonds, is a fundamental feature of the glass

structure. The former model dates back to the earlier studies on GeSe₂ glass [5] while the latter is gaining popularity lately on the grounds of more recent spectroscopic [6], and isotopic substitution neutron diffraction experiments [7]. However, the findings of a number of other recent studies are difficult to reconcile with the idea that the structural integrity of GeSe₂ glass is intrinsically broken. First, both x-ray and neutron scattering experiments [8] have found that the intensity of the first sharp diffraction peak (FSDP) in Ge_xSe_{1–x} glasses reaches a maximum at the stoichiometric composition $x = 1/3$. Also, the extended, i.e. beyond intermediate, atomic ordering in GeSe₂ has also been found to be very high [9]. These findings show that the degree of connectivity of the tetrahedral network in GeSe₂ glass is indeed very high. Second, theoretical studies consistently have either failed [10] to show the presence of any or to reproduce [11] the substantial number of Ge–Ge homopolar bonds in GeSe₂ glass suggested in [6, 7]. Indeed the latter disagreement may not come as a surprise since simple estimates based on the difference between the strength of single homopolar (e.g. Ge–Ge) and heteropolar (e.g. Ge–Se) bonds show [6] that the degree of broken chemical order in GeSe₂ glass suggested in [7] greatly exceeds that expected. The present work addresses the controversy with the GeSe₂ atomic-scale structure by employing high-energy x-ray diffraction (XRD) and constrained reverse Monte Carlo (RMC) simulations. This approach was chosen for the following

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reasons: first, high-energy x-rays have proven to be very useful in revealing fine structural features of oxide AB_2 glasses [12] and are quite, or at least as much as the neutrons used so far [7], sensitive to Ge–Ge correlations in $GeSe_2$ glass. For reference, the atomic scattering amplitudes for naturally occurring Ge and Se have a very similar contrast for x-rays ($f(Ge) = 32$ and $f(Se) = 34$) and neutrons ($b(Ge) = 8.18$ fm and $b(Se) = 7.9$ fm), resulting in a comparable sensitivity of the two radiations to Ge–Ge correlations in $GeSe_2$ glass. However, high-energy XRD has the advantage of providing data of superb statistical accuracy and very low experimental artifacts (e.g. Fourier termination ripples) in the region of the first-neighbor-like atom distances of interest. Second, constrained RMC allows us to extract the individual contributions of Ge–Ge, Ge–Se and Se–Se atomic pairs to the experimental diffraction data without the danger of convoluting them together. The latter could happen if a set of multiple but relatively ill-conditioned experimental data is employed to tackle this task. In particular, isotopic substitution neutron diffraction experiments have relied on three datasets with $w(Ge-Ge)$ of 11%, 7.5% and 3%, respectively, to evaluate the individual contribution of Ge–Ge pair correlations to the experimental data [7]. Here $w(Ge-Ge)$ is the weighting factor of Ge–Ge pair correlations to a given diffraction dataset [13, 14]. A partial correlation function evaluated from datasets with fairly similar and fading sensitivities to the atomic pair under question should be looked at with caution.

Using our approach we show that the atomic-scale structure of $GeSe_2$ glass may be described very well as a continuous network of edge- and corner-sharing $Ge-(Se_{1/2})_4$ tetrahedra that are not broken but floppy enough to allow the appearance of a small number of shorter (~ 2.3 Å) than usual (~ 3.8 Å) Se–Se interatomic distances. The network does not involve a substantial number of Ge–Ge homopolar bonds, nor does it accommodate a second structural motif/phase and, in this sense, is chemically fully ordered.

2. Experimental details

2.1. Sample preparation

The sample of $GeSe_2$ glass studied was made by standard procedures using 99.999% pure Ge and Se. The starting ingredients were vacuum sealed in a quartz tube, heated to 1300 K for 48 h and finally quenched in ice water. Then the sample was annealed at 600 K, which is approximately 60 K below the glass transition temperature, for 24 h. Then the prepared bulk glass was gently crushed into fine powder, sealed between thin Kapton foils and subjected to high-energy XRD experiments.

2.2. High-energy x-ray diffraction experiments

The experiments were conducted using x-rays of energy 80.6 keV in transmission geometry at the 1-ID beamline at the Advanced Photon Source, Argonne National Laboratory. The use of high-energy x-rays helps reduce several unwanted experimental effects such as absorption and multiple scattering, and also allows us to access higher wavevectors. This results in

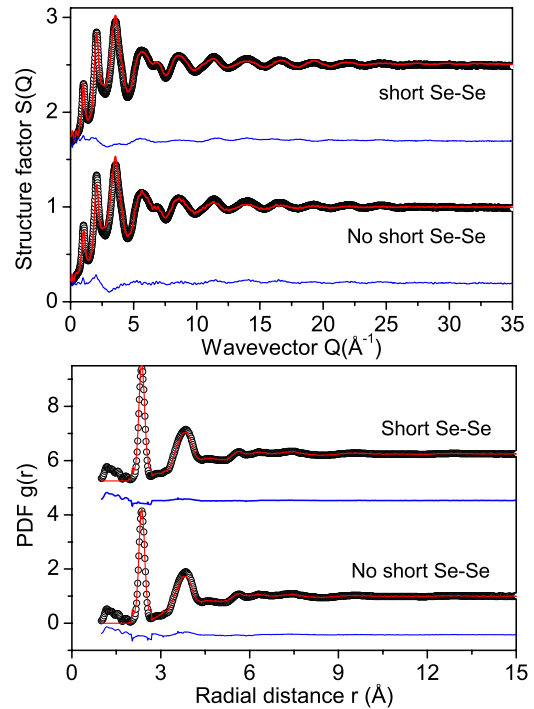


Figure 1. Experimental (symbols) and model (line in red) structure factors (upper part) and atomic PDFs (lower part) for $GeSe_2$. The model data are based on RMC-generated configurations with and without Se–Se distances shorter than 3 Å. The residual difference between the experimental and model data is given below each dataset (line in blue).

atomic pair distribution functions (PDF) of a greatly improved quality and resolution [12, 13]. The experimental Faber–Ziman-type [14] structure factor $S(Q)$ for $GeSe_2$ glass and its Fourier counterpart, the atomic PDF $g(r) = \rho(r)/\rho_0$, are shown in figure 1. Here $\rho(r)$ and ρ_0 are the local and average atomic number density, and Q and r are the wavevector and radial distance, respectively.

3. Results

As can be seen in figure 1, $S(Q)$ shows prominent oscillations up to the maximum value of $Q = 35$ Å⁻¹ reached in the present experiment. It agrees very well with the more recent XRD $S(Q)$ data of Murakami *et al* [15]. The corresponding $g(r)$ has a very well-defined first peak located at 2.37(2) Å, followed by a broad maximum at 3.9(1) Å, and a few more small-amplitude peaks at longer interatomic distances. The position of the first $g(r)$ peak is close to the sum of the covalent radii of Ge (0.53 Å) and Se (1.83 Å). Its area gives a coordination number of 3.98(3), which is consistent with the presence of $Ge-(Se_{1/2})_4$ tetrahedral units. The experimental $S(Q)$ and PDF $g(r)$ are typical for AB_2 glasses built of only one type of well-defined structural unit. In glasses where the tetrahedral network is broken and more than one structural unit is present, the oscillation of the $S(Q)$ data at higher values of Q is highly damped and the first PDF peak is very broad and/or highly asymmetric in shape [12]. These experimental observations, in line with the results of

previous studies, suggest that GeSe₂ glass is a highly connected (i.e. continuous) network of well-defined structural units—Ge–(Se_{1/2})₄ tetrahedra.

As already shown (see figure 3 in [13]) the low-*r* region (up to 4 Å) of the experimental PDF data may be very well approximated by a model based on the high-temperature crystalline modification of GeSe₂ that is built of edge- and corner-sharing Ge–(Se_{1/2})₄ tetrahedra. The model is an approximation since it is based on a crystalline, i.e. periodic, structure but still useful since it shows that the low-*r* region of the experimental PDF data may be explained entirely in terms of an assembly of coupled Ge–(Se_{1/2})₄ units, contrary to what others have suggested [7]. Here we take the next step by building a non-periodic structural model and refining it against the whole range of experimental XRD data, both in real and reciprocal space.

4. Modeling

The modeling was done by constrained reverse Monte Carlo simulations [16]. The method involves the building of atomic configurations in a simulation box and refining them against experimental, structure-sensitive data such as $S(Q)$ and $g(r)$ s. The refinement is done by varying the atomic coordinates in a random manner so as to obtain the best possible agreement between the model computed and experimentally determined $S(Q)$ and $g(r)$ s within plausible structural constraints [17]. Usually, the imposed constraints include the glass's chemical composition, density, distances of closest interatomic approach and first coordination numbers. The constraints applied here are based on indisputable experimental observations, namely that (i) well-defined Ge–(Se_{1/2})₄ tetrahedra are present in GeSe₂ glass and (ii) these tetrahedra may share their corners or edges. Indeed the approach of testing and refining constrained, three-dimensional (3D) structural models against experimental, one-dimensional (1D) diffraction data is not new. Routinely the 3D structure of crystalline materials is obtained by fitting their powder XRD patterns (1D datasets) with models constrained within the symmetry elements of 230 space groups [18]. The model that is of a minimal complexity, fits the experimental diffraction data very well, and is consistent with theoretical predictions, is usually the one adopted and used as a structural basis for explaining the material's properties. The modeling of the structure of GeSe₂ glass done here is based on the same (Occam's razor) universal principle. Models with different sizes were constructed to ensure that effects due to the inherent periodicity of the RMC simulation box do not affect the modeling outcome. One of the models contained 1500 (500 Ge and 1000 Se) atoms, the other 15 000 (5000 Ge and 10 000 Se) atoms. Both were constrained to have Ge–Se first coordination sphere distances in the range of 2.0–2.7 Å. This is the range of distances where the first peak in the experimental PDF shows up. Initially Ge atoms from the model configurations had 4 Se atoms as first neighbors, and all Se atoms had two Ge as first neighbors. Those values correspond to the experimentally determined first coordination numbers and reflect the presence of Ge–(Se_{1/2})₄ structural units in the glass. In order to establish if homopolar bonds

exist in the glass, four different configurations were produced by refining the two initial models against the experimental diffraction data. Two configurations (one small and one large) were produced by excluding the possibility of the generation of first-neighbor-like atom pairs, i.e. homopolar bonds. This was done by enforcing the minimum Ge–Ge and Se–Se interatomic distances to be not less than 3.0 Å, which is the low-*r* limit of the second peak in the experimental PDF. The other two configurations (one small and one large) had Ge–Ge and Se–Se distances of minimum approach as short as 1.9 Å to allow the generation of homopolar bonds, should they exist. RMC simulations were run until all important details in the experimental data, in both real and reciprocal space, were reproduced very well. Calculations were done with the help of the program RMC++ [19]. Structural models which resulted from the small and large size initial configurations that were refined under the same conditions turned out to be virtually indistinguishable. The result shows that the structural solution found here is model-size-independent. For that reason hereafter we show only results for the two, larger-size (15 000 atoms) model configurations.

5. Discussion

As can be seen in figure 1 both configurations fit the experimental data very well (goodness-of-fit factors less than a few per cent) with the one where shorter Ge–Ge and Se–Se distances were allowed, performing somewhat better at reproducing the sharper features of the experimental data (compare the difference curves in figure 1). This is an indication that the presence of first-neighbor-like pairs of atoms in GeSe₂ glass is consistent with the experimental diffraction data. Partial structural factors, partial atomic PDFs and bond angle distributions for the two model configurations are shown in figures 2 and 3, respectively. The partial $S(Q)$ and $g(r)$ are similar in shape to those obtained in previous studies [7, 10, 11] but differ in some important details, as discussed below. There is a very small bump at 2.4 Å in the partial $g_{\text{GeGe}}(r)$ for the model configuration where shorter Ge–Ge distances are allowed and, as expected, no such bump is present in the partial $g_{\text{GeGe}}(r)$ for the configuration where they are not. The bump corresponds to a Ge–Ge first coordination number of 0.021. By taking the ratio of this coordination number to that of the total Ge coordination number an estimate can be made of the amount of Ge–Ge homopolar bonds in the model. It equates to a value of 0.34% which is within the limits of the statistical noise in the data. Therefore, it may be concluded that the level of Ge–Ge homopolar bonding in GeSe₂ glass is insignificant, contrary to the findings of previous spectroscopy (~2% Ge–Ge homopolar bonds) and neutron (~4% Ge–Ge homopolar bonds) diffraction studies. The present finding is, however, well in line with the results of several theoretical studies on GeSe₂ [10, 11b]. Distances comparable to those (2.3 Å) assigned to Se–Se homopolar bonds are clearly seen in the partial $g_{\text{SeSe}}(r)$ for the configuration where they are allowed. The corresponding coordination number is 0.14. It equates to a value of 2.19% 'shorter than usual' Se–Se bonds, which compares to the value of 4% reported in previous studies [6, 7, 10b, 11]. Since the

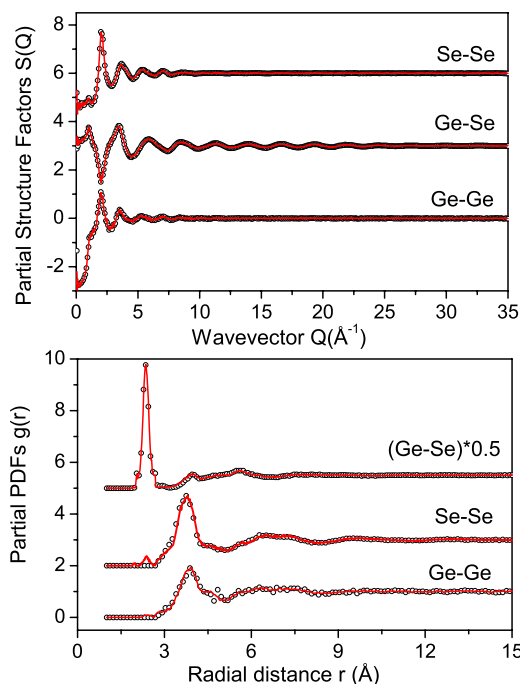


Figure 2. Partial structure and atomic PDFs for GeSe_2 derived from RMC models refined against the experimental total $S(Q)$ and $g(r)$ shown in figure 1. Datasets shown by a solid line (in red) and symbols correspond to models with and without ‘short’ Se–Se distances, respectively.

amount of Ge–Ge ‘homopolar’ bonds is negligible, and the distribution of Se–Ge–Se and Ge–Se–Ge bond angles peak (see figure 3) at values typical for well-defined tetrahedral units [7, 10, 11] it is unlikely that the Se–Se distances of length 2.3 Å seen in the partial $g_{\text{SeSe}}(r)$ data are due to Se–Se ‘homopolar’ bonds coming from disassociated Ge– $(\text{Se}_{1/2})_4$ tetrahedra. Geometrical analysis of both model atomic configurations, with and without ‘2.3 Å’ Se–Se distances, shows that they are a fully connected network of edge-sharing Ge– $(\text{Se}_{1/2})_4$ tetrahedra, as shown in figure 4. The ratio of edge- to corner-sharing tetrahedra in both configurations is approximately $31 \pm 1\%$, which is consistent with the findings of previous studies [6, 7, 10, 11]. By taking the ratio between the Ge–Se and Se–Se first-neighbor distances it is possible to compare the degree of perfection of Ge– $(\text{Se}_{1/2})_4$ tetrahedra in the two model configurations to that of an ideal one, which has a ratio of $\sqrt{3/8} = 0.612$. The ratio is 0.615 for the configuration with no ‘homopolar’ bonds, showing that Ge– $(\text{Se}_{1/2})_4$ tetrahedra in it are almost perfect. That ratio is 0.621 for the configuration with ‘homopolar’ bonds, indicating that the Ge– $(\text{Se}_{1/2})_4$ tetrahedra in it are distorted. That is why the distribution of Se–Ge–Se bond angles in the latter atomic configuration is somewhat broader than that in the former (see figure 3)². The distorted Ge– $(\text{Se}_{1/2})_4$ tetrahedra in GeSe_2 are,

² Note that the bond angle distribution resulting from the present RMC studies is broader than those predicted by *ab initio* simulations. This is likely due to the fact that the *ab initio* constructed models are, as a rule, much smaller in size (just a few hundred atoms) than our model (~15 000 atoms) and so are not sensitive to the likely presence of larger size rings, i.e. larger bond angles, in GeSe_2 glass. In addition, RMC explicitly takes into account the usual thermal disorder in glasses while *ab initio* models do not always.

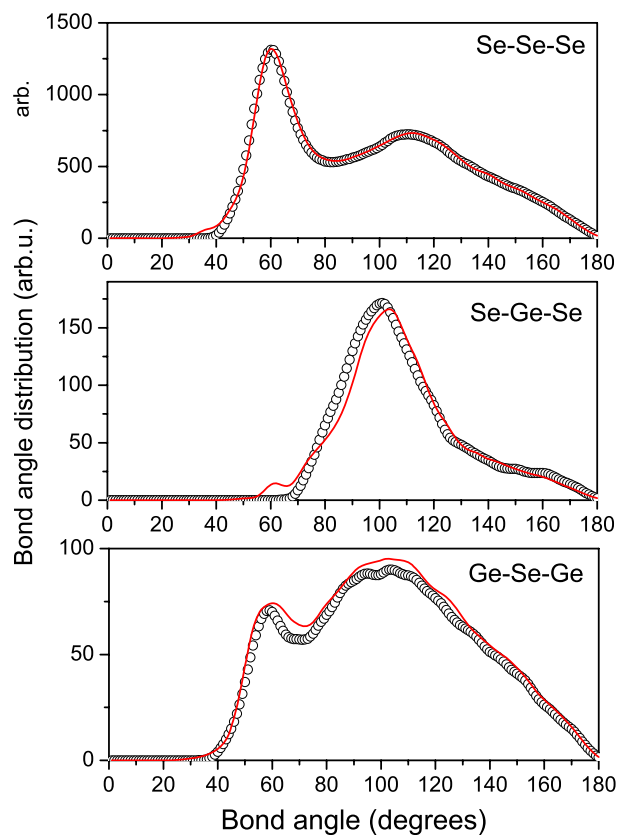


Figure 3. Bond angle distributions in GeSe_2 as derived from RMC-generated models with (line in red) and without (symbols) ‘short’ Se–Se distances.

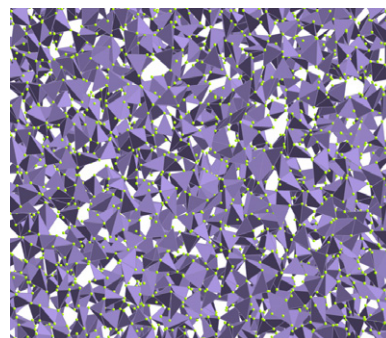


Figure 4. A fragment from the RMC-generated structural model for GeSe_2 where ‘short’ Se–Se distances are allowed. The model features a fully connected network of edge- and corner-sharing Ge– Se_4 tetrahedra.

however, still much more regular than the Ge– $(\text{Se}_{1/2})_4$ units in molten GeSe_2 , which show a ratio of 0.645 [7]. The presence of substantially distorted Ge– $(\text{Se}_{1/2})_4$ tetrahedra in GeSe_2 glass has also been suggested by recent multiscale modeling studies (see figure 5 in [10b]). A closer look at the model configuration with ‘2.3 Å’ Se–Se distances (see figure 5, lower part) shows that they come from Ge– $(\text{Se}_{1/2})_4$ units that are either quite distorted and/or approach each other closely, i.e. that they all have either inter- or intra-tetrahedral origin, and in that sense, may not be identified categorically as ‘homopolar’ Se–Se bonds from a second phase as done in [7].

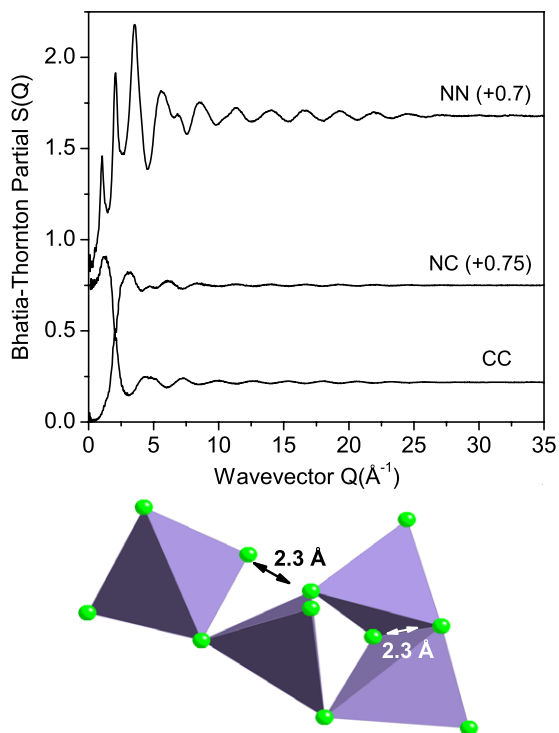


Figure 5. Bhatia–Thornton partial $S(Q)$ s for GeSe_2 derived from the Faber–Ziman-type partial $S(Q)$ s shown in figure 2 (upper part). A small fragment from an RMC-generated model for GeSe_2 showing ‘short’ Se–Se distances with a purely intra- or inter-tetrahedral origin.

In summary, the interatomic bonding in non-oxide AB_2 glasses is very covalent when compared to that in their oxide counterparts. For example, the ionicity of the Ge–Se bond is 7%, comparing to 40% in Ge–O. As a result $\text{A}-(\text{O}_{1/2})_4$ tetrahedra ($\text{A} = \text{Si}, \text{Ge}$) are quite rigid and share only vertices in the oxide AB_2 glasses. As the present and other studies [10b] have shown, $\text{Ge}-(\text{Se}_{1/2})_4$ tetrahedra appear quite floppy and share both vertices and edges in GeSe_2 glass. However, as we show here, these floppy tetrahedral units may still form a continuous random network that is fully chemically ordered at the atomic scale. The lack of any chemical disorder in GeSe_2 glass is demonstrated by the absence of any FSDP in the Bhatia–Thornton [20] concentration–concentration structure factor $S_{\text{cc}}(Q)$ shown in figure 5 (upper part). The FSDP seen at $1.01(1) \text{ \AA}$ in the experimental total $S(Q)$, i.e. the extended medium-range order in GeSe_2 glass [9], arises from the geometrical characteristics of the random tetrahedral network (see the number–number $S_{\text{NN}}(Q)$ in figure 5), in particular those involving both Ge and Se atoms (see $S_{\text{GeSe}}(Q)$ in figure 2) regardless of the presence of shorter ($\sim 2.3 \text{ \AA}$) than usual ($\sim 3.8 \text{ \AA}$) Se–Se distances in the glass.

6. Conclusions

Previous studies claim that a substantial number of Ge–Ge homopolar bonds is required to reproduce the experimental $g(r)$ for GeSe_2 glass in good detail (p S1519 in [7a]; [15]). Here we show that this is not necessarily the case by using experimental $g(r)$ data of a comparable sensitivity to Ge–Ge

correlations (compare $w(\text{Ge–Ge}) = 11\%$ in the present study versus $w(\text{Ge–Ge}) \sim 3\text{--}11\%$ in [7a]). The controversy may be due to the fact that we and others [7, 15] have studied different GeSe_2 samples that may or may not have had a substantial number of Ge–Ge homopolar bonds. For example, if the temperature/rate of quenching/deposition is too high and/or the glass is not annealed thermally the broken chemical order and a substantial amount of ‘wrong’ homopolar bonds found in molten GeSe_2 may be frozen in the glass network. Indeed this possibility has been explored, and confirmed, in a recent experimental study of the crystallization behavior of GeSe_2 glasses obtained by quenching from the melt at temperatures exceeding the liquidus by 220 K. These glasses have shown clear signatures of broken chemical order and found to undergo a ‘trifurcated’ crystallization determined by their thermal prehistory [21]. Computer simulations, in particular molecular dynamics, too have indicated that ‘homopolar’ Ge–Ge bonds may or may not appear in structural models of GeSe_2 glass depending on how ‘fast’ the computer simulations are done [11b]. If this is the case, the hotly debated ‘homopolar’ Ge–Ge bonds and the ‘broken’ chemical order in GeSe_2 glass are more related to the history of glass preparation than to some fundamental property of the glass structure. One way to resolve the controversy is to carry out a systematic study on a series of GeSe_2 samples quenched/annealed at different rates/temperatures using a combination of structural probes that will ensure several, highly reliable datasets for each sample. The structural probes may include isotopic substitution neutron diffraction targeting the Ge–Ge correlations in a more sensitive way than done previously [7], total and resonant XRD (Ge and/or Se edges) as well as spectroscopy (e.g. Raman). Other approaches to resolving the controversy are also possible. One thing is sure: until the controversy is resolved dismissing the structural model viewing GeSe_2 as a continuous random network of $\text{Ge}-(\text{S}_{1/2})_4$ tetrahedra and/or introducing new classes of disordered network forming materials [20] is premature.

Acknowledgments

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