

## Atomic-Scale Structure of Glasses Using High-Energy X-Ray Diffraction

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**The great potential of high-energy X-ray diffraction to determine fine details in the atomic scale structure is discussed and illustrated with an example of a successful study on GeSe<sub>2</sub> glass.**

## I. Introduction

KNOWLEDGE of the atomic-scale structure is an important prerequisite to understand and control the properties of materials. In the case of crystals, it is obtained solely from the Bragg peaks in their diffraction pattern and is given in terms of a small number of atoms placed in a unit cell subjected to symmetry constraints. However, many materials of technological importance, such as glasses, do not possess the long-range order of conventional crystals and often it is this deviation from perfect order that makes them technologically and/or scientifically important. The diffraction patterns of such non-crystalline materials show only a few sharp, Bragg-like peaks, if any, and a pronounced diffuse component. This renders the standard crystallography and techniques for structure determination inapplicable. The challenge can be met by using the so-called atomic pair distribution function (PDF) technique.

The widely used atomic PDF,  $G(r)$ , is defined as  $G(r) = 4\pi r[\rho(r) - \rho_0]$ , where  $\rho(r)$  and  $\rho_0$  are the local and average atomic number densities, respectively.<sup>1</sup> It peaks at real space distances where the local atomic density deviates from the average one, i.e., where most frequent interatomic distances occur, and thus reflects the structure of materials.

Atomic PDFs are obtained by neutron or X-ray diffraction experiments. A PDF is computed from the diffraction data via a Fourier transformation as follows:

$$G(r) = (2/\pi) \int_{Q=0}^{Q_{\max}} Q[S(Q) - 1] \sin(Qr) dQ \quad (1)$$

where  $Q$  is the magnitude of the wave vector ( $Q = 4\pi \sin\theta/\lambda$ ),  $2\theta$  is the angle between the incoming and outgoing radiation,  $\lambda$  is the wavelength of the radiation used, and  $S(Q)$  is the so-called experimental total structure function. X-ray diffraction studies usually use the Faber–Ziman-type structure function<sup>1</sup> related to the elastic part of the diffracted intensities,  $I^{\text{el}}(Q)$ , as follows:

$$S(Q) = 1 + \left[ I^{\text{el}}(Q) - \sum c_i |f_i(Q)|^2 \right] / \left| \sum c_i f_i(Q) \right|^2 \quad (2)$$

where  $c_i$  and  $f_i(Q)$  are the atomic concentration and X-ray scattering factor, respectively, for the atomic species of type  $i$ . It should be noted that for a material comprising  $n$  atomic species, a single diffraction experiment yields an atomic PDF  $G(r)$  that is a weighted sum of  $n(n+1)/2$  partial PDFs,  $G_{ij}(r)$ ,

each giving the spatial ordering of a particular  $i$ - $j$ -type atomic pair, i.e.,

$$G(r) = \sum_{ij} w_{ij} G_{ij}(r) \quad (3)$$

where  $\sum_{ij} w_{ij} = 100\%$ . Here  $w_{ij}$  are weighting factors reflecting the relative abundance and scattering power of the atomic pairs of type  $i$ - $j$  as follows:

$$w_{ij} = c_i c_j f_i(Q) f_j^*(Q) / \left| \sum c_i f_i(Q) \right|^2 \quad (4)$$

To increase the sensitivity to a particular type of atomic pairs and be able to extract partial PDFs, specialized experimental procedures such as neutron scattering with isotopic substitution<sup>2</sup> and resonant X-ray scattering<sup>3</sup> are usually used. Alternatively, individual first-neighbor atomic pairs in glasses may be revealed by obtaining experimental PDFs with high real space resolution. This could be achieved by using modern sources of radiation such as synchrotrons<sup>4</sup> allowing high values of  $Q$  to be accessed.

Despite the recent great progress in instrumentation, structure studies of non-crystalline materials still face some experimental difficulties limiting their large-scale application. One experimental difficulty is the relatively long duration of the PDF experiment. The reason is that the diffraction patterns of non-crystalline materials are very diffuse in nature and long counting times are required to collect diffraction data with a reasonable statistical accuracy. One solution to the problem is to use more efficient, extended-area detectors allowing rapid collection of large amounts of diffraction data.

In the present paper we demonstrate recent advances in high-energy X-ray diffraction allowing to carry out fast structure studies and obtain high-resolution atomic PDFs for glassy materials. Results from such experiments on GeSe<sub>2</sub> glass are shown.

The chalcogenide GeSe<sub>2</sub> glass has been the subject of numerous spectroscopic,<sup>5</sup> modeling,<sup>6</sup> and diffraction studies<sup>2,7</sup> aimed at determining its atomic ordering and understanding the material's useful photosensitive properties. The studies have revealed that the basic structural unit of the glass is a Ge–Se<sub>4</sub> tetrahedron similar to that occurring in the crystalline compound GeSe<sub>2</sub>. The studies, however, could not agree on the way the Ge–Se<sub>4</sub> tetrahedra are arranged to form a three-dimensional (3D) network in the glass. Two conflicting structural models have been put forward: the first model is the chemically ordered random covalent network model featuring GeSe<sub>2</sub> glass as a more or less random network of corner- and edge-sharing Ge–Se<sub>4</sub> tetrahedra.<sup>7,8</sup> In this model, Ge atoms have only Se atoms as first neighbors and vice versa, and thus pairs of first neighbor-like atoms, i.e., homopolar bonds, may only occur accidentally in very small numbers. The second model views GeSe<sub>2</sub> glass as a collection of fragments of corner- and edge-sharing Ge–Se<sub>4</sub> tetrahedra that are glued together by Se–Se homopolar bonds. In this model, the presence of a substantial number of homopolar bonds is essential for the stability and formation of the glass structure.<sup>2,5,9</sup>

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Here, we used high-energy X-ray diffraction to help resolve the ambiguity.

## II. Experimental Procedure

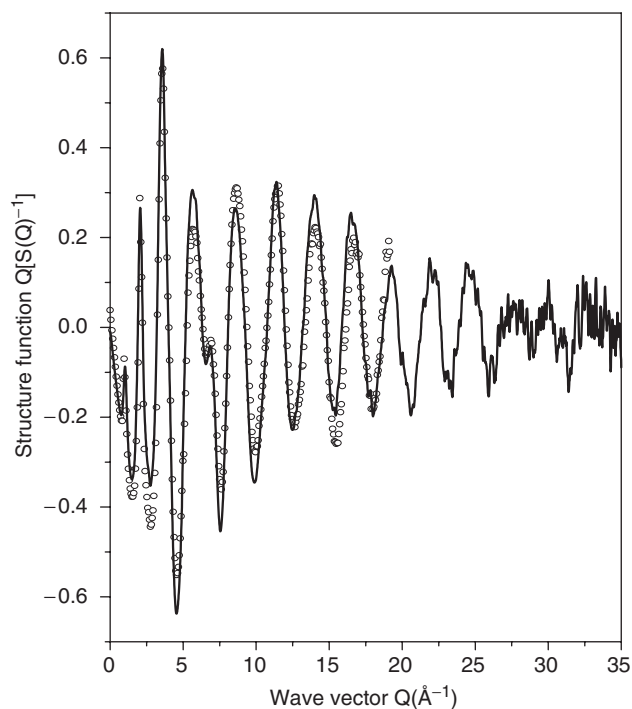
### (1) Sample Preparation

The samples investigated were made by standard procedures involving mixing up high-purity starting materials followed by melting, and rapid quenching of the melt to retain the structurally disordered state. This preparation route resulted in a highly homogeneous non-crystalline sample as confirmed by inspection under an optical microscope and usual X-ray diffraction. Sample stoichiometry was established from the mass balance.

### (2) X-Ray Diffraction Experiments

The diffraction experiments were carried out at the 1-ID beam line at the Advanced Photon Source (APS), Argonne National laboratory. The measurements were carried out in symmetric transmission geometry using X-rays of energy 80.6 keV. An energy-sensitive Ge detector was used to collect the diffraction intensities. The use of X-rays of such a high energy allows to access higher wave vectors and helps reduce several unwanted experimental effects such as absorption and multiple scattering. The data were collected by scanning at constant  $Q$  steps of  $0.02 \text{ \AA}^{-1}$ . Several diffraction runs were conducted over a period of 8–12 h. The diffracted intensities collected were averaged to improve the statistical accuracy and reduce any systematic effect because of instabilities in the experimental set-up. The averaged intensities were normalized in electron units and reduced to the structure function shown in Fig. 1. All data processing was carried out using the program RAD.<sup>10</sup>

To check the performance of large area detectors, the Ge solid-state detector was replaced by an Image Plate (IP) (MAR345, marUSA Inc., Evanston, IL) detector and GeSe<sub>2</sub> glass measured one more time keeping the rest of the experimental set-up unchanged.<sup>11</sup> Exposure times were 1 s. The 2D diffraction pattern of GeSe<sub>2</sub> was subjected to appropriate corrections and reduced to a 1D pattern with the help of the pro-



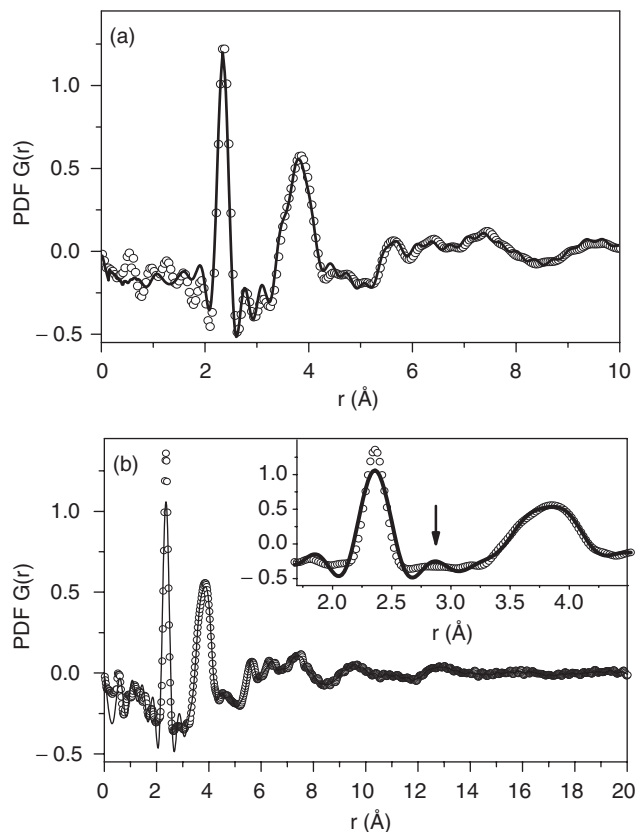
**Fig. 1.** Experimental structure factors for GeSe<sub>2</sub> glass obtained with Ge solid-state detector (solid line) and Image Plate detector (symbols).

gram FIT2D.<sup>12</sup> The latter pattern was processed with the program RAD and reduced to a structure function also shown in Fig. 1.

## III. Results and Discussion

As can be seen in Fig. 1, the structure function for GeSe<sub>2</sub> obtained from single point (Ge) detector data exhibits prominent oscillations up to the maximum value of  $35 \text{ \AA}^{-1}$  reached. This is a very high wave vector allowing to obtain an atomic PDF of high real space resolution as that shown in Fig. 2(b). In Fig. 1(a) structure function for GeSe<sub>2</sub> obtained from 2D (IP) detector data is shown as well. Because IPs are not sensitive to the energy of the radiation used, a fraction of Compton and fluorescent scattering that is filtered out when Ge detector is used is present in the diffraction intensities. This makes the 2D data correction process more involved and, in the present case, limited the  $Q_{\text{max}}$  to a value of  $20 \text{ \AA}^{-1}$ . Nevertheless, the structure function obtained from 2D data agrees well with the one obtained from the Ge detector data (see Fig. 1). The present IP-derived data are of quality good enough to yield a PDF that agrees with the one obtained from the Ge detector data with  $Q_{\text{max}} = 20 \text{ \AA}^{-1}$  (see Fig. 2(a)). A point that deserves mentioning is that atomic PDFs obtained with  $Q_{\text{max}} \sim 20 \text{ \AA}^{-1}$  are indeed of medium resolution and appear with broadened low- $r$  peaks and shape modified by a termination ripple as shown in Fig. 2(b). Such experimental artifacts should be carefully accounted for to avoid ambiguities in the PDF data interpretation, especially when fine structural features are an issue.<sup>2</sup>

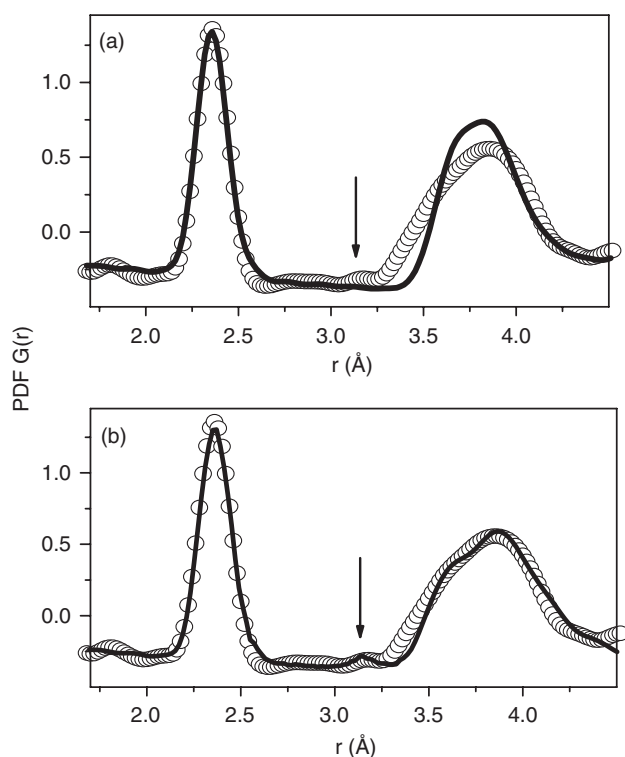
To explore the atomic arrangement in GeSe<sub>2</sub> in detail, we concentrate on the present high-resolution PDF data (those



**Fig. 2.** Experimental atomic pair distribution functions (PDFs) for GeSe<sub>2</sub> glass: (a) Comparison between PDFs derived from Ge (symbols) and Image Plate detectors (line), both, with  $Q_{\text{max}} = 20 \text{ \AA}^{-1}$ . (b) Comparison between high- (symbols) and medium-resolution (line) PDF data obtained with  $Q_{\text{max}} = 35 \text{ \AA}^{-1}$  and  $Q_{\text{max}} = 20 \text{ \AA}^{-1}$ , respectively. A portion of the PDF data is given in the inset on an enlarged scale. The termination ripple just below  $3 \text{ \AA}^{-1}$  in the medium-resolution PDF is marked with an arrow.

obtained from a structure factor with  $Q_{\max} = 35 \text{ \AA}^{-1}$ . The first neighbor distance and coordination number in  $\text{GeSe}_2$  glass were derived from the position and area of the first peak in the high-resolution PDF. The first neighbor distance turned out to be  $2.37(2) \text{ \AA}$ , which is close to the sum of the covalent radii of Se ( $1.83 \text{ \AA}$ ) and Ge ( $0.53 \text{ \AA}$ ). The first neighbor Ge–Se coordination number turned out to be  $3.98(3)$ , which is consistent with the presence of Ge– $\text{Se}_4$  tetrahedral units. Similar values for the first neighbor Ge–Se separation and coordination number have been found by other studies on crystalline<sup>13</sup> and glassy<sup>7</sup>  $\text{GeSe}_2$ . The full-width at half-maximum (FWHM) of the peak, which may serve as a measure of the distortion of the structural units building the glass, turned out to be  $0.19 \text{ \AA}$ . A similar analysis of the first peak in the high-resolution PDF of  $\text{SiO}_2$  glass<sup>4</sup> yields an FWHM value of  $0.12 \text{ \AA}$ . The result shows that Ge– $\text{Se}_4$  tetrahedra in  $\text{GeSe}_2$  glass are almost as well-defined as Si– $\text{O}_4$  ones occurring in silica glass. Furthermore, as can be seen in Fig. 1, the experimental  $Q[S(Q)-1]$  data of  $\text{GeSe}_2$  glass show a well-defined low-frequency oscillation extending to wave vectors as high as  $35 \text{ \AA}^{-1}$ . In glasses where the tetrahedral network is broken and more than one structural unit is present, as is the case with calcium aluminosilicate glasses,<sup>4</sup> the oscillation of the  $Q[S(Q)-1]$  data at higher values of  $Q$  is highly damped and the first PDF peak is very broad and/or highly asymmetric in shape. All these findings suggest that  $\text{GeSe}_2$  glass is a continuous network of well-defined structural units—Ge– $\text{Se}_4$  tetrahedra. To verify this conclusion we constructed simple model atomic configurations, calculated the corresponding PDFs, and compared them with the present high-resolution PDF data. The models were based on the structures of the low- and high-temperature crystalline modifications of  $\text{GeSe}_2$ .<sup>13</sup> The low-temperature modification of  $\text{GeSe}_2$  is built of corner-sharing Ge– $\text{Se}_4$  tetrahedra only. The high-temperature modification of crystalline  $\text{GeSe}_2$  has a structure constructed from both corner- and edge-sharing Ge– $\text{Se}_4$  tetrahedra. No homopolar Ge–Ge and

Se–Se bonds occur in either of the two crystalline modifications. Model atomic configurations with the structure of the two crystalline forms of  $\text{GeSe}_2$  were generated using structure data from literature sources.<sup>13</sup> The increased local structural disorder in the glass was simulated by broadening the peaks in the atomic PDFs into Gaussians, the FWHM of which increased with the radial distance. The lack of a long-range order in the glass was simulated by multiplying the model PDFs with a rapidly decaying exponent. Thus, calculated model PDFs are shown in Fig. 3 over a range of  $r$  values where signatures of homopolar bonds and broken local tetrahedral order are expected to appear.<sup>2</sup> It may be noted that the present models have not only the advantage of approaching the experimental PDF data but also provide a base line between the PDF peaks sloping as  $4\pi r\rho_0$ . Any significant deviation of the experimental data above that base line would indicate the presence of “wrong,” i.e., homopolar bonds and vice versa. As can be seen in Fig. 3(a), a model resembling a tetrahedral network of only corner-sharing tetrahedra reproduces very well the sharp first peak in the experimental PDF but fails to reproduce the experimental data at higher real space distances. Obviously, the glass and the low-temperature crystalline modification of  $\text{GeSe}_2$  share the same basic structural unit but do not seem to share the way the Ge– $\text{Se}_4$  units are arranged in space. The data presented in Fig. 3(b) show that a model based on both corner- and edge-sharing tetrahedral units is capable of reproducing all significant details in the experimental data, including the small bump at approximately  $3.1 \text{ \AA}$  and the pronounced low- $r$  shoulder of the second PDF peak at approximately  $3.6 \text{ \AA}$ . The bump reflects the correlations between Ge atoms centering edge-sharing Ge– $\text{Se}_4$  tetrahedra and the low- $r$  shoulder of the second peak—Ge–Se correlations between those tetrahedra.<sup>13</sup> Both features are missing in the model PDF for the low-temperature crystalline modification of  $\text{GeSe}_2$ , which is an arrangement of only corner-sharing tetrahedra. The result is very much in line with the findings of several previous studies<sup>3,7,8</sup> all suggesting a resemblance between the atomic ordering in the glass and that in the high-temperature crystalline phase of  $\text{GeSe}_2$ . What deserves special attention is the fact that the present high-resolution PDF data appear sensitive enough to reveal the presence of edge-sharing tetrahedra and even the individual Ge–Ge correlations from those tetrahedra, although Ge–Ge correlations contribute as little as 11% ( $w_{\text{Ge-Ge}} = 11\%$ ) to the present PDF data. If another 25% of Ge atoms and 20% of Se atoms in the glass were involved in homopolar bonds, the corresponding atomic correlations should have showed up as extra PDF features at distances close to  $2.32 \text{ \AA}$  (first neighbor Se–Se),  $2.42 \text{ \AA}$  (first neighbor Ge–Ge), and  $2.74 \text{ \AA}$  (second neighbor Se–Se) as discussed by Petri *et al.*<sup>2</sup>, and this is especially true for the Se–Se correlations because they contribute four times ( $w_{\text{Se-Se}} = 46\%$ ) as much as Ge–Ge ones. However, the present experimental PDF data do not show such features, i.e., do not show any evidence that the chemical order in  $\text{GeSe}_2$  glass is broken and a substantial number of Ge and Se atoms participate in structural units other than Ge– $\text{Se}_4$  tetrahedra. Thus, the outcomes of our X-ray diffraction studies appear more consistent with the model picture viewing bulk  $\text{GeSe}_2$  glass as a continuous random network of edge- and corner-shared Ge– $\text{Se}_4$  tetrahedra than with that evoking broken chemical order and a substantial number of homopolar bonds. Then the question arises why the intrinsic chemical order in  $\text{GeSe}_2$  glass may appear broken in some samples as several experimental studies suggest.<sup>2,9</sup> The answer may lie in the fact that  $\text{GeSe}_2$  glasses are usually obtained from quenching from the liquid state where the Ge– $\text{Se}_4$  unit survives but the network of tetrahedra is broken up.<sup>7</sup> If the temperature of quenching is too high and the glass samples are not properly annealed, the broken chemical order and a substantial amount of “wrong” homopolar bonds associated with it may be frozen in the glass network. Previous experiments indicate that indeed this may be the case, because samples<sup>2</sup> quenched from  $\sim 110^\circ\text{C}$  above the liquidus have been found to have 25% of Ge atoms in homopolar bonds while samples<sup>9</sup> quenched from  $50^\circ\text{C}$  above the liquidus have



**Fig. 3.** Comparison between the experimental high-resolution pair distribution function (PDF) for  $\text{GeSe}_2$  glass (circles) and model PDFs (line) calculated on the basis of atomic configuration with the structure of the low-temperature (a) and high-temperature modification of crystalline  $\text{GeSe}_2$  (b). The correlation because of Ge atoms occupying centers of edge-sharing  $\text{GeSe}_2$  tetrahedra is marked with an arrow.

been found to have 15% of Ge atoms in homopolar bonds. This scenario has been further explored and confirmed in a recent study of the crystallization behavior of GeSe<sub>2</sub> glasses obtained by quenching from melt at temperatures exceeding the liquidus by 220 K. The glasses have shown clear signatures of broken chemical order and found to undergo a “trifurcated” crystallization determined by their thermal prehistory.<sup>14</sup> Also, it has been shown that annealing below the glass transition temperature of the type we did heals the broken chemical order in GeSe<sub>2</sub> glass.<sup>15</sup> It appears then that the hotly debated broken chemical order and homopolar bonds in GeSe<sub>2</sub> are more likely to be an artifact of the sample-making process than an integral part of the glass structure.

#### IV. Conclusion

High-energy X-ray diffraction yields high-resolution atomic PDFs ( $Q_{\max} \sim 35 \text{ \AA}^{-1}$ ) for glassy materials allowing very fine structural features to be revealed and important questions about the atomic arrangement to be answered. When coupled to 2D detectors, the diffraction experiments are fast (data collection rates of the order of seconds) but the atomic PDFs obtained are of medium resolution ( $Q_{\max} \sim 20 \text{ \AA}^{-1}$  or so). Such medium-resolution structure data, however, may suffice in many cases when fine structural features are not an issue. The type of experiments discussed in the present work is expected to become more frequently used in structure studies of glasses with the number of synchrotron sources rapidly increasing worldwide.

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