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Rapid structure determination of disordered materials: study of $GeSe_2$ glass

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Abstract

X-ray diffraction experiments on $GeSe_2$ glass employing an Imaging Plate detector system have been carried out and their performance compared to that of traditional experiments employing point-type detectors. Imaging Plate detectors have been found to perform very well delivering good quality data for just a second. The analysis of the experimental data shows that the atomic ordering in $GeSe_2$ glass bears many of the characteristics of a random network of $Ge-Se_4$ tetrahedra.

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A great deal of modern materials do not posses the 3D periodicity and long-range order of crystals and it is this deviation from perfect order that makes them technologically and/or scientifically important. Although non-periodic these materials still posses well defined short-range and some intermediate-range order playing an important role in determining their properties. To understand and gain control over the properties a detailed knowledge of the atomic-scale structure is required. The atomic ordering in disordered materials, in particular glasses, is usually determined by diffraction experiments and described in terms of atomic pair distribution functions (PDF). The atomic PDF peaks at characteristic distances separating pairs of atoms and thus reflects the atomic arrangement. The PDF $G(r) = 4\pi r[\rho(r) - \rho_0]$, is a sine Fourier transform of the so-called total scattering structure function $S(Q)$

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

where ρ_0 and $\rho(r)$ are the average and local atomic number density, respectively, Q is the magnitude of the wave vector and $S(Q)$ is derived from corrected and normalized elastic scattering intensities [1]. The stronger the disorder in a non-crystalline material the weaker the correlations between the positions of the atoms in it and, hence, the lower the number of well-defined peaks in the PDF. Thus by obtaining an experimental atomic PDF and analyzing its peaks and shape one could obtain information about the short and intermediate-range order in the material under study.

Despite the recent great progress in instrumentation structure studies of disordered materials still face some experimental difficulties limiting their large-scale application. One is the relatively long duration of the PDF experiment. Even when the most powerful sources of radiation currently available are employed a diffraction experiment on a disordered material takes many hours to complete. The reason is that the diffraction patterns of disordered 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 employ more efficient, extended-area detectors such as imaging plates (IP) allowing rapid collection of large amounts of diffraction data. Successful applications of IP detectors in structure studies of crystalline materials are

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known for quite some time [2]. Similar experiments on non-crystalline materials are, however, scarce and little is know about the performance of the PDF technique when IP detectors are employed. Results from X-ray diffraction experiments using IPs are shown and the usefulness of this non-traditional approach is discussed in the present work.

The material studied is $GeSe_2$ glass. The reasons are two. First, the material scatters X-rays well, which facilitates the X-ray diffraction experiment. Second, its atomic ordering is relatively well characterized and found to bear many of the characteristics of a random network of corner and edge sharing $Ge-Se_4$ tetrahedra [3–6]. A successful PDF study employing IP detectors should be able to reveal well this basic structural characteristic. The sample 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. Thus prepared bulk glass was gently crushed into fine powder, sealed between thin Kapton foils and subjected to X-ray diffraction experiments.

First, experiments employing a traditional point-type detector were carried out. They were performed at the 1-ID beam line at the Advanced Photon Source (APS), Argonne National laboratory. The measurements were done in symmetric transmission geometry at room temperature. A bent double-Laue Si (111) crystal [7] was used to monochromatize the white beam and deliver intense flux of X-ray photons of energy 80.6 keV. The use of X-rays of such high energy allows to access higher wave vectors and helps reduce several unwanted experimental effects such as absorption and multiple scattering. Furthermore, to reduce the unwanted background, fluorescent and Compton scattering the diffracted X-ray intensities were collected with an intrinsic germanium detector connected to a multi-channel analyzer with pre-set energy windows. This experimental style has proven itself successful in other high-energy X-ray diffraction studies on disordered materials [8]. The data were collected by scanning at constant ΔQ steps of 0.02 $Å^{-1}$. Several diffraction runs were conducted over a period of 8 h and the diffracted intensities collected were averaged to improve the statistical accuracy and reduce any systematic effect due to instabilities in the experimental set up. Thus collected and processed diffraction intensities are shown in Fig. 1a and the structure function $Q[S(Q) - 1]$ extracted from them in Fig. 1b. Note the structure function extends to quite high wave vectors of 35 $Å^{-1}$. Atomic PDFs calculated using the full set of $Q[S(Q) - 1]$ data and a portion of it extending to only 20 $Å^{-1}$ are shown in Fig. 2. All data processing was done using the program RAD [9].

X-ray diffraction experiments using IP detectors were also carried out at the 1-ID beam line at APS using the same sample and employing X-rays of the same energy (80.6 keV). The only difference was that the point Ge solid state detector was replaced by an extended-area IP

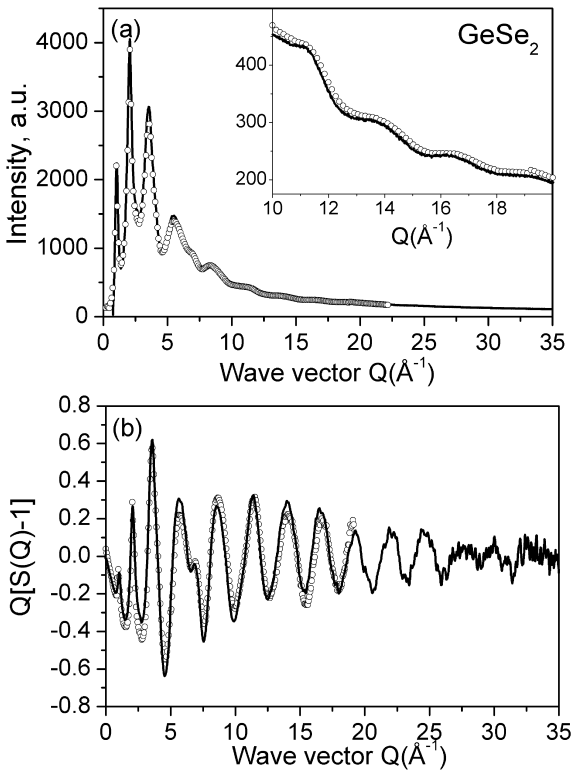

Fig. 1. Background corrected diffraction data (a) and the corresponding reduced structure functions $Q[S(Q) - 1]$. (b) for $GeSe_2$ glass. Data obtained using Ge solid state detector and Imaging Plates are given as solid line and circles, respectively. A portion of the diffraction data is given in the inset on an enlarged scale.

(MAR345) detector allowing to record a large portion of the diffraction pattern of $GeSe_2$ glass at once. The sample to detector distance, the angles of tilt and rotation of the detector with respect to the plane of scattering and the zero position of the incoming X-ray beam were determined by using crystalline Si powder (NIST, a(Si) = 5.43119 Å) as a standard. Extended-area diffraction patterns of crystalline Si and $GeSe_2$ glass are shown in Fig. 3a and b, respectively. Exposure times were 1 s. As can be expected, the diffraction pattern of crystalline Si consists of many sharp rings (Fig. 3a). The rings are only a few and very broad with glassy $GeSe_2$ which lacks the 3D periodicity and perfect order of a crystal. The 2D diffraction pattern of $GeSe_2$ shown in Fig. 3b was subjected to appropriate corrections and reduced to a 1D pattern with the help of the program FIT2D [10]. A comparison between the 1D diffraction patterns of $GeSe_2$ obtained with an energy sensitive Ge detector and an extended-area IP detector is shown in Fig. 1a. The agreement between the two sets of diffraction data is very good. In particular, both diffraction patterns exhibit a peak at 1.01(2) Å with a full width of half maximum (FWHM) of only 0.22 $Å^{-1}$. The presence of a sharp diffraction peak at

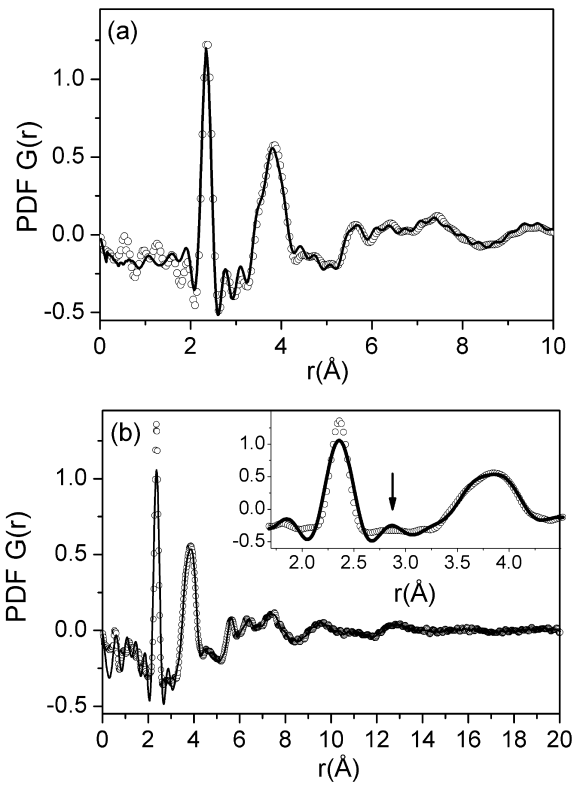

Fig. 2. Experimental atomic PDFs $G(r)$ for $GeSe_2$ glass: (a) Comparison between PDFs derived from Ge (solid line) and IP (circles) detector data both with $Q_{max} = 20$ Å^{-1}. (b) Comparison between high (circles) and medium resolution (solid line) PDF data obtained with $Q_{max} = 35$ Å^{-1} and $Q_{max} = 20$ Å^{-1}, respectively. A portion of the PDF data is given in the inset on an enlarged scale. The termination ripple just below 3 Å in the medium resolution PDF data is marked with an arrow.

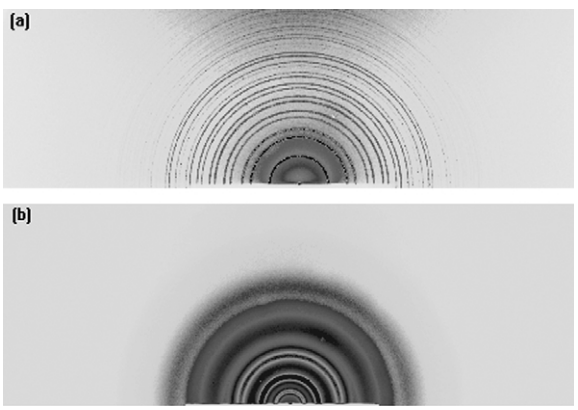

Fig. 3. 2D diffraction patterns of crystalline Si. (a) and $GeSe_2$ glass. (b) Recorded with the use of MAR345 detector. Exposure time—1 s.

low Q values is a characteristic feature of many covalently bonded non-crystalline materials [11]. The result shows that IP detectors are fully capable of resolving the characteristic features in the diffraction patterns of disordered materials. IPs are, however, not sensitive to the energy of the radiation used and some fraction of Compton and fluorescent scattering that is filtered out when Ge detector is employed is present in the diffraction intensities extracted from the IP data. That is why the high-Q intensities collected with IPs appear systematically higher than those obtained with the Ge detector (see the inset of Fig. 1a). This complicates the raw data analysis and derivation of experimental PDFs. Nevertheless, the usual data correction procedures implemented in RAD [9] turned out to be capable of extracting only the elastic scattering and deriving a good quality structure function data up to 20 Å^{-1}, which is about half of the reciprocal space region covered by the traditional experiment. The function agrees well with the one obtained from the Ge detector data (see Fig. 1b). The slight phase shift and intensity differences between the two structure functions seen at Q values larger than 15 Å^{-1} signal the increased difficulties the processing of IP data faces at higher wave vectors. The present IP data, however, are still of very good quality and yield a PDF that agrees very well with the one derived from the Ge detector data with $Q_{max} = 20$ Å^{-1} (see Fig. 2a). A point that deserves mentioning is that atomic PDFs obtained with $Q_{max} \sim 20$ Å^{-1} are indeed of medium resolution and appear with broadened low-r peaks and shape modified by a termination ripple as shown in Fig. 2b. Such experimental artifacts should be carefully accounted for to avoid ambiguities in the PDF data interpretation, especially when fine structural features are an issue.

The first neighbor distance and coordination number in $GeSe_2$ glass were derived from the position and area of the first peak in the PDF obtained from IP data. The first neighbor distance turned out to be 2.37(2) Å which is close to the sum of the covalent radii of Se (1.83 Å) and Ge (0.53 Å). The first neighbor Ge–Se coordination number turned out to be 3.98(3) which is consistent with the presence of $Ge–Se_4$ tetrahedral units. Similar values for the first neighbor Ge–Se separation and coordination number have been found by other studies on crystalline and glassy $GeSe_2$ [3–5,12]. The finding implies that $GeSe_2$ glass is likely to be built of $Ge–Se_4$ tetrahedral units. To verify it we constructed simple model atomic configurations, calculated the corresponding PDFs and compared them to the experimental PDF derived from IP data. The models were based on the structures of the low and high temperature crystalline modifications of $GeSe_2$ [12]. Fragments of the two structures are shown in Fig. 4.

The calculations were done with the help of the program PDFFIT [13]. The increased structural disorder in the glass was simulated by broadening the peaks in the model PDFs into Gaussians, the FWHM of which increased with the radial distance. Also, in comparing with experiment, the model PDFs were convoluted with a Sinc function to account for the relatively low Q_{max} of the IP data. Thus

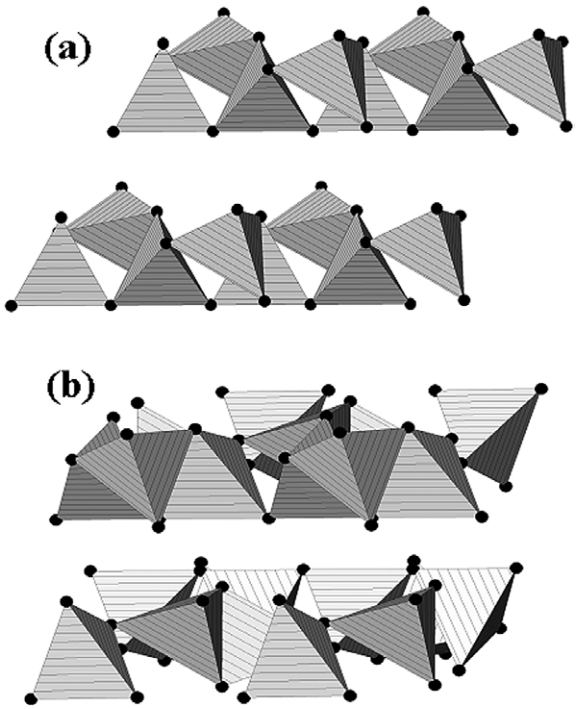

Fig. 4. Fragments from the structures of the low (a) and high-temperature (b) crystalline forms of $GeSe_2$. Both structures are built of $Ge-Se_4$ tetrahedra sharing only corners (a) and both corners and edges (b).

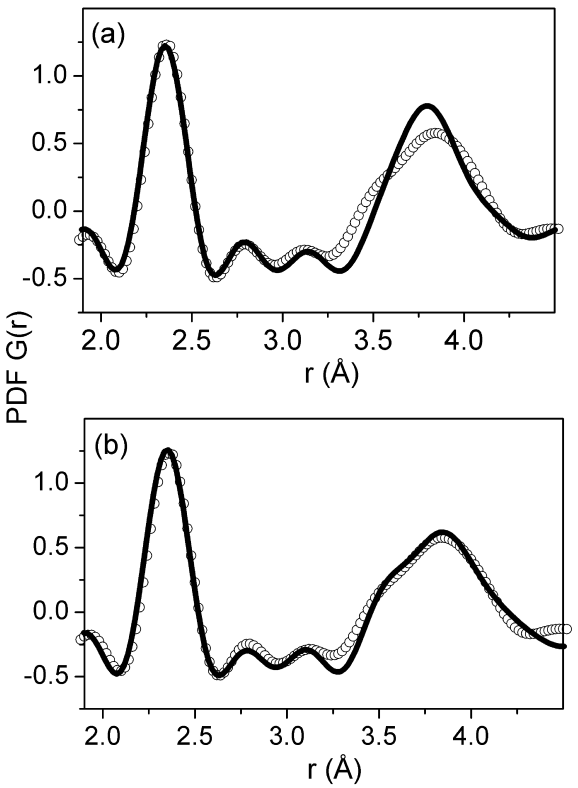

Fig. 5. Comparison between the medium resolution experimental PDF for $GeSe_2$ glass (circles) and model PDFs (line) calculated on the basis of atomic configuration with the structure of the low-temperature (a) and high-temperature modification of crystalline $GeSe_2$ (b). The broadened first PDF peak and the unphysical termination ripple in the data seen between 2.5 and 3.25 Å are well accounted for by convoluting the model with a Sinc function.

calculated model PDFs are shown in Fig. 5. As can be seen in Fig. 5a a model resembling a tetrahedral network of only corner shared tetrahedra reproduces very well the first peak in the experimental PDF but fails to reproduce the pronounced asymmetry of the second PDF peak. Obviously the glass and the low-temperature crystalline modification of $GeSe_2$ share the same basic structural unit, a $Ge-Se_4$ tetrahedron, but do not seem to share the way the $Ge-Se_4$ units are arranged in space. The data presented in Fig. 5b show that a model based on both corner and edge shared tetrahedral units is capable of reproducing all significant details in the experimental data, including the pronounced low-r shoulder of the second PDF peak at approx. 3.6 Å. The result is very much in line with the findings of several previous studies [3–5,14] all suggesting a similarity between the immediate atomic ordering in the glass and that in the high-temperature crystalline phase of $GeSe_2$.

In summary, the present PDF studies confirm the presence of both corner and edge shared tetrahedra in $GeSe_2$ glass and well illustrate the strong similarity between the atomic ordering in the glass and the high-temperature modification of crystalline $GeSe_2$. This outcome clearly shows that imaging plates detectors may be confidently employed in PDF studies of disordered materials. High energy X-ray diffraction with IPs delivers good quality PDF data of medium resolution ($Q_{max} \sim 20$ Å^{-1} or so) for only a fraction of the time (compare 8 h of counting time using a Ge detector versus exposure of one second with MAR345) and may be the only choice when a short duration of the PDF experiment is a must as for example in kinetic studies. The price is that the raw data reduction and PDF derivation are more involved, and include an extra step of processing and reducing the 2D IP data to 1D data. In addition, extra data reduction procedures are to be worked out to remove strong Compton and fluorescent scattering when samples composed of light atomic species are studied and/or very high wave vectors ($Q > 20$ Å^{-1}) are accessed.

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