

# Partial structure analysis of glassy $\text{As}_2\text{Se}_3$ using anomalous X-ray scattering

S. Hosokawa<sup>a,b,\*</sup>, Y. Wang<sup>c</sup>, W.-C. Pilgrim<sup>b</sup>, J.-F. Bézar<sup>d</sup>,  
S. Mamedov<sup>e,1</sup>, P. Boolchand<sup>e</sup>

<sup>a</sup> Center for Materials Research Using Third-Generation Synchrotron Facilities, Hiroshima Institute of Technology, Hiroshima 731-5193, Japan

<sup>b</sup> Institut für Physikalische-, Kern-, und Makromolekulare Chemie, Philipps Universität Marburg, D-35032 Marburg, Germany

<sup>c</sup> Handai Frontier Research Center, Graduate School of Engineering, Osaka University, Suita 565-0871, Japan

<sup>d</sup> Laboratoire de Cristallographie, CNRS, F-38042 Grenoble, cedex, France

<sup>e</sup> Department of Electrical, Computer Engineering and Computer Science, University of Cincinnati, Cincinnati, OH 45221-0030, USA

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## Abstract

Anomalous X-ray scattering experiments have been performed on glassy  $\text{As}_2\text{Se}_3$  at room temperature in order to clarify the role of each constituent for short- and intermediate-range order. The experiments were performed using intense X-rays from a third-generation synchrotron facility, ESRF. Differential structure factors,  $\Delta_i S(Q)$ , close to the As and Se K edges were obtained from a detailed analysis. The prepeak around  $Q = 12 \text{ nm}^{-1}$  in the total structure factor,  $S(Q)$ , indicating evidence of intermediate-range order, is dominated by the As–As correlation around  $12 \text{ nm}^{-1}$  and the Se–Se correlation around  $14.5 \text{ nm}^{-1}$ . The origin of the prepeak is carefully discussed. © 2006 Elsevier B.V. All rights reserved.

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## 1. Introduction

$\text{As}_2\text{Se}_3$  is well known as a prototype semiconductor having a strong glass forming ability. Physical properties of glassy  $\text{As}_2\text{Se}_3$  have intensively been investigated from an experimental as well as a theoretical point of view [1]. Studies of X-ray [2] and neutron [3] diffraction, as well as X-ray absorption fine structure [4], showed that glassy  $\text{As}_2\text{Se}_3$  has a short-range order (SRO) similar to the crystal, i.e., threefold coordinated As and twofold coordinated Se are covalently bound to each other. The occurrence of a prepeak

around  $12 \text{ nm}^{-1}$  in the total structure factor,  $S(Q)$ , in glassy  $\text{As}_2\text{Se}_3$  measured by diffraction methods presents evidence of intermediate-range order (IRO). Although the IRO is recognized to play an important role in the properties of glassy  $\text{As}_2\text{Se}_3$ , the origin of the prepeak is still open to discussion.

In order to clarify the role of each constituent for the SRO and IRO in glassy  $\text{As}_2\text{Se}_3$ , we have carried out an anomalous X-ray scattering (AXS) experiment. In this paper, we present differential structure factors,  $\Delta_i S(Q)$ , derived from a detailed analysis of the X-ray scattering data close to the As and Se K edges, and discuss the SRO and IRO in glassy  $\text{As}_2\text{Se}_3$ .

## 2. Experimental procedure

The bulk glass sample was obtained by quenching the melts in a quartz ampoule containing the mixed com-

\* Corresponding author. Address: Center for Materials Research Using Third-Generation Synchrotron Facilities, Hiroshima Institute of Technology, Hiroshima 731-5193, Japan. Tel.: +81 82 921 6095; fax: +81 82 921 9444.

E-mail address: [hosokawa@cc.it-hiroshima.ac.jp](mailto:hosokawa@cc.it-hiroshima.ac.jp) (S. Hosokawa).

<sup>1</sup> Present address: Horiba Jobin Yvon Inc., Edison, NJ 08820-3012, USA.

pound. The purity of the starting materials was 99.999%. The melt was homogenized at 600 °C for at least 48 h before the sample was quenched in water. The AXS experiments were performed at two energies below each K edge (20 and 200 eV below the As K edge of 11867 eV and the Se K edge of 12658 eV) at the beamline BM02 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The diffraction measurements were carried out in reflectance geometry using an  $\omega - 2\theta$  diffractometer installed on the beamline.

In order to obtain  $\Delta_i S(Q)$ s with high statistical quality, two requirements needed to be fulfilled: (1) A sufficient energy resolution to discriminate the elastic signal from the fluorescence and Compton contributions, and (2) a high enough number of scattered X-ray photons in a reasonable data acquisition time. Therefore, we chose a graphite crystal analyzer providing a good Bragg reflection, which was placed on a 40-cm long arm to obtain a good energy resolution of about 60 eV FWHM [5], and the  $K_\beta$  fluorescence and Compton scattering intensities are estimated to be less than 0.2% at energies where the elastic spectra were measured. Energy scans were performed at several  $Q$  values to estimate these contributions for the data reduction.

Following the procedure in the literature [5], we derived the  $\Delta_i S(Q)$ , which were obtained from the difference between two diffraction data sets around each K edge. In a binary system,  $\Delta_i S(Q)$  can be written as a linear combination of three partial structure factors,  $S_{ij}(Q)$ , each weighted by a factor,

$$W_{ij}(Q, E) = c_i c_j \Delta_A (f_i(Q, E) f_j^*(Q, E)) / \Delta_A (\langle f(Q, E) \rangle^2).$$

Here,  $c_i$  is the concentration,  $\Delta_A()$  is the difference of the function in the parentheses close to the A edge,  $\langle \rangle$  is the chemical average, and  $f_i(Q, E) = f_{0i}(Q) + f'_i(E) + i f''_i(E)$  is the complex atomic form factor of the  $i$ th element, where  $f_{0i}$  is the usual energy-independent term and  $f'_i$  and  $f''_i$  are the real and imaginary parts of the anomalous contributions, respectively. Theoretical values taken from the literature [6,7] were used for the usual and anomalous terms in  $f_i(Q, E)$ . In Table 1, the  $W_{ij}$  values are given for  $\Delta_i S(Q)$  close to the As and Se K edges, together with those for  $S(Q)$  at  $Q = 22.5 \text{ nm}^{-1}$  (the first maximum position in  $S(Q)$ ). It should be noted that  $S_{\text{SeSe}}(Q)$  is very small in  $\Delta_{\text{As}} S(Q)$  and  $S_{\text{AsAs}}(Q)$  is negligible in  $\Delta_{\text{Se}} S(Q)$ .

Table 1  
Weighting factors,  $W_{ij}$ , given for  $\Delta_i S(Q)$  around the As and Se K edges, together with those for  $S(Q)$ , at  $Q = 22.5 \text{ nm}^{-1}$  (the first maximum position in  $S(Q)$ )

	$\Delta_{\text{As}} S(Q)$	$\Delta_{\text{Se}} S(Q)$	$S(Q)$
$W_{\text{AsAs}}$	0.328	-0.038	0.143
$W_{\text{AsSe}}$	0.604	0.404	0.470
$W_{\text{SeSe}}$	0.068	0.634	0.387

### 3. Results

Fig. 1 shows  $\Delta_i S(Q)$ s of glassy  $\text{As}_2\text{Se}_3$  close to the As (crosses) and Se (circles) K edges. For comparison,  $S(Q)$  measured at  $E = 11667 \text{ eV}$  (200 eV below the As K edge) is also shown by the solid line in the figure.  $\Delta_{\text{As}} S(Q)$  has a distinct and sharp prepeak around  $Q = 12 \text{ nm}^{-1}$ , the position of which almost coincides with that in  $S(Q)$  although the latter is much broader. It should be noted that any structure at this  $Q$  position could hardly be seen in  $\Delta_{\text{Se}} S(Q)$ , while  $\Delta_{\text{Se}} S(Q)$  also shows a shoulder at the higher  $Q$  value of  $14.5 \text{ nm}^{-1}$ , where  $\Delta_{\text{As}} S(Q)$  has no indication. This finding could be hardly seen in the previous AXS result due to the poor statistical quality [8].

### 4. Discussion

In the previous experiment [8], the  $\Delta_i S(Q)$  spectra could be measured for a limited  $Q$  range up to about  $60 \text{ nm}^{-1}$ . Therefore the pair correlation functions,  $\Delta_i g(r)$ , gave limited information on only the position of the first peak, i.e., the bond length of the SRO. In contrast, the present  $\Delta_i S(Q)$  results extend the  $Q$  range up to about  $100 \text{ nm}^{-1}$ , which allows further spatial information on the second-neighbour shell to be obtained. Crosses and circles in Fig. 2 show  $\Delta_i g(r)$ s for glassy  $\text{As}_2\text{Se}_3$  close to the As and Se K edges, respectively. The nearest-neighbour distances around both the As and Se atoms are  $0.242 \pm 0.002 \text{ nm}$ , which coincides with the scattering [2,3] and XAFS [4] results within the experimental error. This result strongly supports the SRO model that glassy  $\text{As}_2\text{Se}_3$  has an SRO similar to the crystal, preferring heteropolar As–Se bonds.

As regards the second shell region of  $r = 0.3\text{--}0.4 \text{ nm}$ , more reasonable results could be obtained in comparison to the previous AXS study [8]. Since  $\Delta_{\text{As}} g(r)$  comprises almost no Se–Se correlation contribution, as shown in Table 1, the second large peak at  $r = 0.370 \text{ nm}$  in  $\Delta_{\text{As}} g(r)$  can be assigned as the As–Se–As configuration with a bond

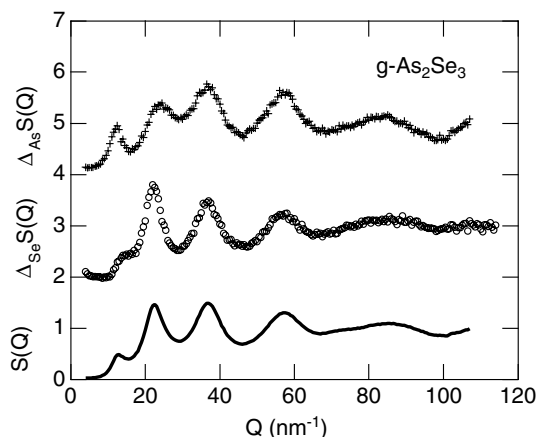


Fig. 1.  $\Delta_i S(Q)$ s of glassy  $\text{As}_2\text{Se}_3$  close to the As (crosses) and Se (circles) K edges, together with  $S(Q)$  (solid line) measured at  $E = 11667 \text{ eV}$  (200 eV below the As K edge).

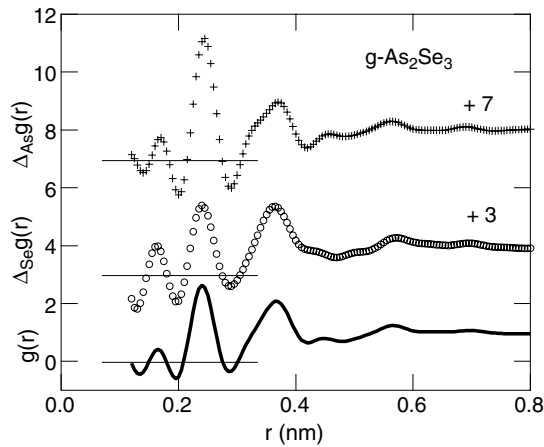


Fig. 2.  $\Delta_i g(r)$ s of glassy  $\text{As}_2\text{Se}_3$  close to the As (crosses) and Se (circles) K edges, together with  $g(r)$  (solid line) measured at  $E = 11667$  eV (200 eV below the As K edge).

angle of  $\sim 100^\circ$ . Due to the same reason, the second large peak at  $r = 0.364$  nm in  $\Delta_{\text{Se}}g(r)$  may be made of the Se–As–Se conformation in the  $\text{As}(\text{Se}_{1/2})_3$  pyramid with a bond angle of  $\sim 98^\circ$ . These values are similar to those in the crystal [9], which strongly supports the chemically-ordered continuous-random-network model for glassy  $\text{As}_2\text{Se}_3$ .

On the other hand, it is difficult to assign the shoulder at  $r \sim 0.325$  nm. Since the magnitudes of the shoulder have the same order as  $W_{\text{AsSe}}$  in Table 1, it could be formed by an As–Se correlation. A candidate is a conformation between an As atom at the top of an  $\text{As}(\text{Se}_{1/2})_3$  pyramid and a Se atom additionally attached to a Se atom at the bottom of the pyramid. This configuration, however, induces a substantial number of homopolar Se–Se bonds, and forms a small As–Se–Se angle of  $\sim 84^\circ$ . Due to the still limited  $Q$  range of  $\Delta_i S(Q)$ , a ripple from the truncation error is expected to appear in the same  $r$  range, although  $\Delta_{\text{Se}}S(Q)$  shows a very small signal at  $r \sim 0.325$  nm. This prevents the further discussion on the atomic conformation in the intermediate distance range.

As mentioned in the introduction section, the appearance of the prepeak around  $12 \text{ nm}^{-1}$  in  $S(Q)$  reveals the existence of IRO. As clearly seen in Fig. 1, the  $\Delta_i S(Q)$ s close to the As and Se K edges differ from each other, in particular at the prepeak position, i.e.,  $\Delta_{\text{As}}S(Q)$  shows a prominent prepeak at  $Q \sim 12 \text{ nm}^{-1}$ , while  $\Delta_{\text{Se}}S(Q)$  shows a shoulder at the different  $Q$  value of  $\sim 14.5 \text{ nm}^{-1}$ . As seen in Table 1,  $\Delta_{\text{As}}S(Q)$  is a linear combination of mainly  $S_{\text{AsAs}}(Q)$  and  $S_{\text{AsSe}}(Q)$ , while  $\Delta_{\text{Se}}S(Q)$  consists mainly of  $S_{\text{AsSe}}(Q)$  and  $S_{\text{SeSe}}(Q)$ . Therefore it appears plausible that the main part of the prepeak originates from the As–As correlation, and its higher  $Q$  side around  $14.5 \text{ nm}^{-1}$  from the Se–Se correlation.

For a further understanding of the IRO in glassy  $\text{As}_2\text{Se}_3$ , the origin of the prepeak should be discussed. It was believed for a long time that the prepeak at  $Q = Q_p \sim 12 \text{ nm}^{-1}$  indicated the existence of an IRO with a correlation length  $r = 2\pi/Q_p \sim 0.52$  nm in real space. Several

models were proposed to explain the origin of this correlation, such as a layer structure similar to the crystal, clusters, or voids. As seen in Fig. 2, however, there is no special indication of a correlation at a length of 0.52 nm. Therefore, the origin of the prepeak should be considered in a different way, similar to the speculation for the prepeak in glassy  $\text{GeSe}_2$  [5]. As seen in Fig. 2, the interatomic distance of the As–(Se)–As is well defined to be  $\sim 0.367$  nm, and the second shell around an As-atom contains three As neighbours. If the atomic arrangement of this As sublattice has an amorphous As-like structure [10],  $S_{\text{AsAs}}(Q)$  should have a peak at a  $Q$  position corresponding to the first peak position in  $S(Q)$  of amorphous As,  $21.9 \text{ nm}^{-1}$ . The scaling factor can be given by the ratio of the As–As interatomic distances,  $0.245/0.367$ . The resultant  $Q_p$  position is  $14.6 \text{ nm}^{-1}$ , which is larger than the present value of  $12 \text{ nm}^{-1}$ . Thus, a modification of the As sub-lattice structure from amorphous As configuration is needed for a further understanding.

## 5. Conclusion

AXS experiments have been performed on glassy  $\text{As}_2\text{Se}_3$  at room temperature in order to clarify the role of each constituent for the SRO and IRO. The experiments were performed using intense X-rays from a third-generation synchrotron facility, ESRF.  $\Delta_i S(Q)$ s close to the As and Se K edges were obtained from a detailed analysis. From the results of  $\Delta_i g(r)$ s, the SRO and the second-shell IRO are discussed, revealing the chemically-ordered continuous-random-network picture, except for a shoulder at  $r \sim 0.325$  nm. The prepeak around  $Q = 12 \text{ nm}^{-1}$  in  $S(Q)$ , indicating evidence of IRO, is dominated by the As–As correlation around  $Q \sim 12 \text{ nm}^{-1}$  and the Se–Se correlation at higher  $Q$  of  $\sim 14.5 \text{ nm}^{-1}$ . The origin of the prepeak is carefully discussed.

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