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Compositional changes of the first sharp diffraction peak in binary selenide glasses

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Compositional changes of the first sharp diffraction peak (FSDP) in the measured structure factor have been studied for several binary selenide glasses using pulsed-neutron and high-energy x-ray diffraction techniques. The observed variations in the FSDP (factor of 10 in the amplitude and ≈ 0.5 Å^{-1} in the peak position) reflect multiple aspects in the glass network on both the short- and intermediate-range scales and are also correlated with macroscopic properties. An empirical relation has been discovered relating the compositional dependence of the FSDP position to the local coordination number of the guest atom.

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The first sharp diffraction peak (FSDP), a prominent low-Q feature in the structure factor $S(Q)$ of network glasses, has been a subject of extended interest in the last two decades. Nevertheless, the origin of the FSDP is still a matter of debate, although it is clear that it can arise for different reasons in different systems.[1] Indeed in a number of reviews[1,2] it has been shown that any type of the glass with a one-dimensional (1D), 2D, or 3D network can exhibit a well-pronounced FSDP in the scattering vector range of $0.8 \leqslant Q_1 \leqslant 1.6$ Å^{-1}. Neutron diffraction with isotopic substitution[3,4] and anomalous x-ray scattering[5] clearly show that the main contribution to the FSDP usually comes from network-forming cation-cation (NFC) correlations. In this study we have carried out time-of-flight neutron and high-energy x-ray diffraction measurements on complementary binary selenide glassy systems (Ge-Se, As-Se, Te-Se) as well as additional P-Se glass compositions and compared to literature data on Si-Se glass.[6] The results show that the FSDP contains considerable structural information on both the intermediate- and short-range-order length scales—for example, the appearance of homopolar NFC-NFC bonds, random vs nonrandom distribution of the NFC-related structural units, and changes in the dominant structural motif. The extensive comparisons reported here reveal that multiple aspects of the NFC correlations are clearly revealed in trends of the FSDP parameters.

Many early models of the FSDP were based on layer structures.[7] For a dense random packing of small structural units, following the Percus-Yevick solution of the hard-sphere problem, the position and amplitude of the FSDP are reproduced well for stoichiometric glasses.[2] On the other hand, the void model[8] explains a remarkable difference in the neutron FSDP height for alkali silicate glasses. The FSDP shows at least two anomalies: (i) it remains invariant or even becomes more intense and narrow with increasing temperature in contrast to the usual broadening of peaks in $S(Q)$,[9,10] and (ii) it decreases in amplitude with increasing pressure.[11,12] The NFC correlations reflect an intermediate-range ordering (IRO) in the glass network since a characteristic length scale deduced from the FSDP position, $L_1 \approx 2\pi/Q_1 = 3.5$–$8$ Å, covers usually 2–3 interatomic distances.[2] In contrast to extensive studies of the FSDP as a function of temperature and to a lesser extent pressure, surprisingly very little attention has been paid to the compositional dependence of the FSDP parameters except for previous works on the binary selenide systems P-Se (Ref. 13) and Si-Se (Ref. 6).

The selenide binaries $A_x\text{Se}_{1-x}$, where A is an element of group IV, V, or VI, are very suitable model materials for these studies since they exhibit a very large glass-forming range from pure vitreous Se ($x=0$) to $x=0.4-0.7$. In addition, $A_x\text{Se}_{1-x}$ glasses remain homogeneous on mesoscopic scale over the entire vitreous domain, contrary to phase-separated S-rich binaries.[14] Many recent theories such as rigidity percolation were tested using these glasses.[15,16]

Neutron diffraction experiments were carried out at IPNS (Argonne National Laboratory, USA) and ISIS (Rutherford-Appleton Laboratory, UK) spallation neutron sources. High-energy x-ray scattering experiments were performed at the European Synchrotron Radiation Facility (Grenoble, France) and the Advanced Photon Source (Argonne National Laboratory). The neutron and high-energy x-ray data analyses followed standard procedures as described in Refs. 6, 17, and 18, respectively. In order to extract the FSDP parameters (position, amplitude, and width), a parabolic function was used to approximate the background underneath the FSDP in $S(Q)$ at low Q, allowing the FSDP to be isolated and fitted with a Gaussian or Lorentzian. Neither function reproduced the exact shape of the most intense FSDP's but the former was significantly better for the less intense peaks and was therefore used systematically for all systems investigated.

The low-Q part of the $S(Q)$ for the binary glasses exhibits remarkable changes with composition (Fig. 1). With increasing NFC content, the FSDP becomes a factor of 10 more intense and shifts to lower Q by 0.5 Å^{-1}. Such an enormous

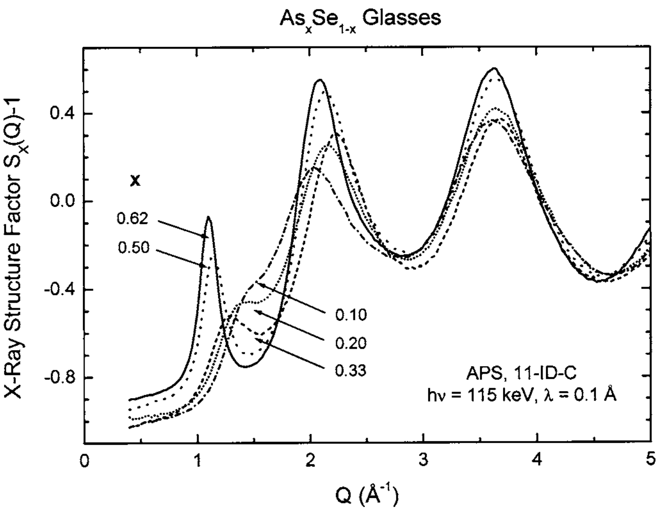

FIG. 1. Low-Q part of the x-ray structure factor $S_X(Q)$ for selected compositions in the As$_x$Se$_{1-x}$ system.

change is not exhibited by any other peak in the structure factor. Plotting the FSDP amplitude (Fig. 2) and position (Fig. 3) as a function of the NFC concentration, several characteristic composition regions appear for the group-IV (Ge$_x$Se$_{1-x}$, Si$_x$Se$_{1-x}$) and group-V (As$_x$Se$_{1-x}$, P$_x$Se$_{1-x}$)) alloys. On the other hand, the chainlike group-VI alloy Te$_x$Se$_{1-x}$ does not show any dramatic evolution. The astonishing trends in the FSDP parameters discussed below are not related to a simple change in the scattering factors as a function of the NFC content and have a structural origin. For example, Ge, As, and Se as well as Si and P are neighbors in the periodic table; consequently, their x-ray scattering factors are similar within ±4%. The neutron coherent scattering lengths for Ge and Se are also nearly identical ($\bar{b}_{\mathrm{Ge}}/\bar{b}_{\mathrm{Se}}=1.036$); those for P, Te, and As are similar within ±13%. In addition, the normalized Faber-Ziman NFC-NFC weighting factor increases monotonically with x, in contrast to the non-monotonic behavior of the FSDP amplitude for the group-IV glasses.

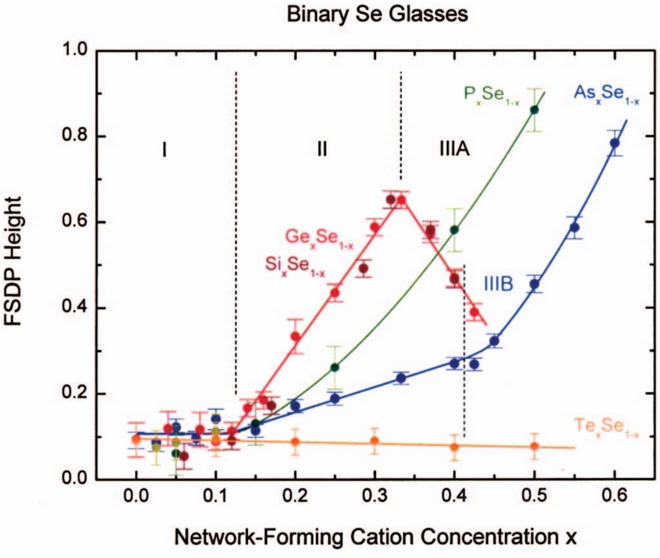

FIG. 2. (Color) Amplitude of the FSDP in binary selenide glasses as a function of x. Only neutron diffraction data are plotted: (dark red circles) Si$_x$Se$_{1-x}$ (Ref. 6), (red circles) Ge$_x$Se$_{1-x}$ (this work), (green circles) P$_x$Se$_{1-x}$ (Ref. 13), (dark yellow circles) P$_x$Se$_{1-x}$ (this work), (blue circles) As$_x$Se$_{1-x}$ (this work), and (orange circles) Te$_x$Se$_{1-x}$ (this work). The solid lines are drawn as a guide for the eye. Limits of the regions I, II, and IIIA for group-IV glasses and IIIB for As$_x$Se$_{1-x}$ system are shown by dashed lines.

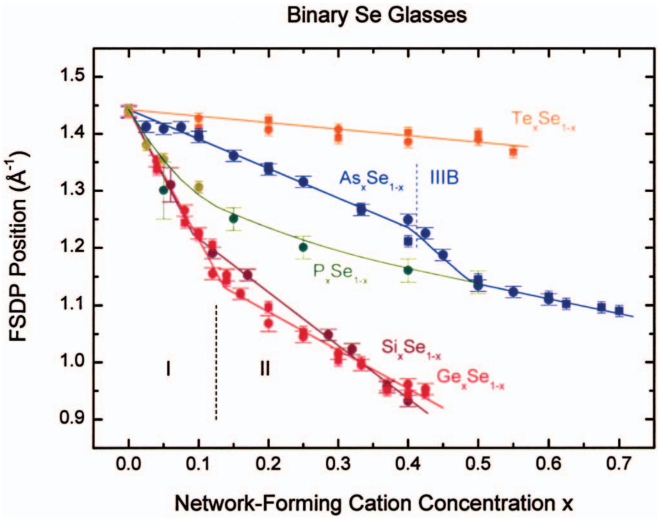

FIG. 3. (Color) FSDP position in binary selenide glasses as a function of x: (dark red circles) Si$_x$Se$_{1-x}$ (ND, Ref. 6), (red circles, squares) Ge$_x$Se$_{1-x}$ (ND and XRD, this work), (blue circles, squares) As$_x$Se$_{1-x}$ (ND and XRD, this work), (orange circles, squares) Te$_x$Se$_{1-x}$ (ND and XRD, this work), (green circles) P$_x$Se$_{1-x}$ (ND, Ref. 13), and (dark yellow circles) P$_x$Se$_{1-x}$ (ND, this work). The initial slope of the lines is given in the text. The solid line for P$_x$Se$_{1-x}$ represents calculated Q_1 values (see text for details). The dashed lines show limits for the regions I, II, and IIIB (As$_x$Se$_{1-x}$).

Region I: random distribution of the NFC-related structural units at $x \leqslant 0.10-0.15$. The FSDP amplitude remains almost constant in this region (Fig. 2), while characteristic trends appear in the FSDP position as a function of composition (Fig. 3). In particular, we note a distinct difference in the initial slope $\partial Q_1/\partial x$ for the group-IV (−2.2 Å^{-1} atom^{-1}, $x \leqslant 0.10-0.15$), group-V As$_x$Se$_{1-x}$ (−0.52 Å^{-1} atom^{-1}, $x \leqslant 0.4$), and group-VI (−0.11 Å^{-1} atom^{-1}, $x \leqslant 0.55$) systems. The invariant FSDP amplitude in this composition range suggests a random distribution of NFC-related structural units in the disordered selenium network. Consequently, only a few additional NFC-NFC correlations appear with $L_1 = 3.5-5.5$ Å compared to more probable periodicities of 7 Å $\leqslant r_{\mathrm{NFC-NFC}} \leqslant$ 14 Å, for a stochastic scenario. Direct evidence of the random-nonrandom NFC distribution is demonstrated in the Ge$_x$Se$_{1-x}$ system. The absence of short Ge-Ge correlations at ≈3.0 Å below $x \approx 0.10$, characteristic of edge-sharing (ES) GeSe$_{4/2}$ tetrahedra,[4,10] indicates a random distribution of GeSe$_{4/2}$ units. The short Ge-Ge distances clearly appear at $x \geqslant 0.14$, indicating an agglomeration of GeSe$_{4/2}$ into a mixture of corner-sharing (CS) and ES GeSe$_{4/2}$ tetrahedra. The fraction of ES GeSe$_{4/2}$ units, f_{ES}, increases monotonically up to $f_{\mathrm{ES}}=0.39$ for the stoichiometric composition (not shown), which is consistent with previous diffraction results.[4,10] CS and ES $GeSe_{4/2}$ tetrahedra probably form large rings, similar to the eight-membered rings in HT-$GeSe_2$,[20] giving rise to Ge-Ge intraring correlations at 5–7 Å and to a significant increase of the FSDP. MD simulations[21] show the existence of large 6–9 fold rings consisting of 12–18 atoms in the structure of glassy $GeSe_2$. Raman data[22] are also consistent with the edge sharing above $x \approx 0.1$, and recent ^{77}Se NMR results also confirm agglomeration of $GeSe_{4/2}$ tetrahedra at $x \geqslant 0.11$.[23] A nonmonotonic change in the entropy of viscous flow at $x \approx 0.1$ (Ref. 24) and in thermal relaxation above $x \approx 0.12$ (Ref. 25) correlate with a drastic change in the network topology. Similar edge-sharing starts also in the Si-Se system at $x \approx 0.1$ according to Raman spectroscopy.[22]

The remarkably different slopes for twofold-, threefold-, and fourfold-coordinated guest species reflect the magnitude of changes in the intermediate- and short-range order as determined by real-space functions and spectroscopic data. As expected, the group-IV NFC's exhibit the strongest effect, while isomorphous Te has the lowest one. An empirical equation was found to relate these initial slopes to the guest n (Ref. 19) and host n_0 local coordination numbers:

$$\frac{\partial Q_1}{\partial x}(n) = \frac{\partial Q_1}{\partial x}(n_0)\left(\frac{3\pi}{2}\right)^{n-n_0}, \tag{1}$$

where $\partial Q_1/\partial x(n_0)$ is the initial slope for the Te_xSe_{1-x} glasses since $n=n_0=2$ in this case.

It is interesting to note that the term $(3\pi/2)$ appears for a disordered binary system of hard spheres as a result of chemical ordering and relates the position of the first peak in the Bhatia-Thornton concentration-concentration structure factor $S_{CC}(Q)$ to the sphere diameter d (Ref. 30):

$$Q_1^{CC} \cong \frac{3\pi}{2d}. \tag{2}$$

The void model[8] introduces a very similar approach for cation-centred spherical clusters in network glasses. Preferential chemical ordering clearly exists in binary selenide glasses; therefore, it is probably not surprising to have the term $(3\pi/2)$ in Eq. (1) relating the composition change in Q_1 (and in the correlation length L_1) to a number of additional bonds per guest atom, compared to the local host connectivity.

Region II: network formation by NFC-related structural units at $0.10–0.15 \leqslant x \leqslant 0.2–0.4$. Above group-IV and -V atom concentrations of 0.10–0.15, the FSDP amplitude increases dramatically, reaching a maximum for the group-IV systems at the stoichiometric ASe_2 composition $x=0.33$. In contrast, the FSDP amplitude in the group-V system does not reach a maximum but the rate of increase changes from nearly linear to parabolic at $x \approx 0.2$ (P-Se) and 0.4 (As-Se).

Regions IIIA and IIIB: homopolar NFC-NFC bonds at $x \geqslant 0.2–0.4$. The appearance of homopolar NFC-NFC first-neighbor correlations in the glass structure dramatically changes the FSDP amplitude. As already mentioned, this effect is different for the group-IV and -V systems. The sharp decrease in the FSDP amplitude observed in both Ge_xSe_{1-x} and Si_xSe_{1-x} above the stoichiometric composition $x=0.33$ (region IIIA) is related to the change in the structural role played by the group-IV atoms. They no longer behave as network-forming cations but depolymerize the network as a modifier, as evidenced by the nearly linear decrease of the glass transition temperature T_g by 80–100 K, similar to the typical modifier behavior found in Ag-Ge-Se and Cu-As-Se glasses. The FSDP also disappears progressively in metal chalcogenide glasses with increasing metal content.[26] In contrast, in the group-V systems, the network polymerization remains essentially invariant when P-P (≈ 2.23 Å) or As-As (≈ 2.53 Å) homopolar bonds appear in the network at $x \approx 0.2$ and $x=0.4$, respectively (region IIIB), consistent with ^{31}P NMR, ^{75}As NQR, and Raman spectroscopy results.[27–29] The parabolic increase of the FSDP amplitude in this case appears to be related to additional intermediate-range correlations caused by the neighboring phosphorus or arsenic atoms in dimers and/or to a progressive appearance of P_4Se_3/As_4Se_3 cage molecules above $x \approx 0.5$ (Ref. 28).

The behavior of the P-Se system is more complicated due to multiple phosphorus sites (fourfold and threefold coordinated) observed at low x in neutron diffraction, ^{31}P MAS-NMR, and Raman spectroscopy studies.[13,27,28] Our high-resolution diffraction results in r space also suggest mixed phosphorus coordination at $x \leqslant 0.1$. The solid line in Fig. 3, calculated using phosphorus distributions between fourfold- and threefold-coordinated sites and P-P-related structural units derived from NMR, Raman, and neutron diffraction data, reproduces the experimental FSDP position as well as the continuous change of $\partial Q_1/\partial x$ from a nearly fourfold-coordinated to a threefold-coordinated value at $x \approx 0.2$. A further decrease in Q_1 must be related to the appearance of structural units with homopolar P-P bonds, including P_4Se_3 cage molecules. In this composition range ($x \geqslant 0.2$), we have used the $\partial Q_1/\partial x$ slope from the As_xSe_{1-x} system at $0.5 \leqslant x \leqslant 0.7$, where a significant concentration of As-As bonds was found using diffraction measurements and ^{75}As NQR.[29] It is interesting to note that the Q_1 values for the two group-V systems are finally merging in this composition range.

The observed structural features and trends at the IRO level *do not* correlate with rigidity percolation limits[15,16] which predict specific changes in the glass network dynamics at $x=0.2$ for tetrahedral systems and at $x=0.4$ for trigonal ones. It seems that the network dynamics and static IRO structure are not closely related in the case of binary selenide glasses. A similar conclusion concerning phosphorus speciation in the P-Se system was made earlier based on ^{31}P magic angle spinning (MAS) NMR results.[27]

Summarizing, we have found that the compositional evolution of the intermediate-range order is closely related to variations in the local order. Consequently, the FSDP reflects multiple changes in the glass network on both the short- and intermediate-range scales: random vs nonrandom distribution of the NFC-related structural units, homopolar NFC-NFC bond formation, network-forming vs modifierlike behavior, the appearance of cage molecules, and the effect of local coordination of the guest atoms, and these changes also correlate with macroscopic properties.

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Honkimäki (ESRF), M. Miloshova and M. Fourmentin(Université du Littoral), and M.-L. Saboungi (CRMD) are gratefully acknowledged for their help with the experiments and many useful discussions. The work at Argonne and Oak Ridge was supported by the U.S. Department of Energy, Office of Science, under Contract Nos. 31-109-ENG-38 and DE-AC05-00OR22725. The work at the Université du Littoral (France) was supported by the European Union within the Interreg III program.

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