Structure of Chalcogenide Glasses From the Rapid Acquisition PDF Technique

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Introduction

Chalcogenide glasses are important technological materials due to their remarkable properties, such as excellent infrared (IR) transmission, large glass forming tendency, and resistance to moisture and chemicals. They are widely used in optoelectronics for infrared elements and electrical switches. These glasses undergo a phase transition which in turn changes their properties. The structural changes relate to the strength in which the networks are linked together in these glasses. They undergo a transition from *floppy* to *rigid* phase with increasing Ge content. However, the details of the relationship between the rigidity transition and the structural properties of these glasses is not yet fully understood.

An IP detector coupled with high-energy synchrotron radiation has been recently successfully used for atomic pair distribution function (PDF) analysis [1], with high probed momentum transfer Q_{max}, from several crystalline materials [2]. Medium-high real-space resolution PDF data analysis from crystalline materials has been performed using image-plate data and shows promising results. Comparable or even better statistics than from conventional X-ray measurements can be achieved with significantly shorter counting times. This new combination of a real-space probe and fast counting time, named RA-PDF, opens up a broad field for future applications to a wide variety of materials of both scientifc and technological interest [2,3].

Measurements were carried out using the RA-PDF method on a series of Ge_xSe_{1-x} samples to systematically study the structure of these glasses, the structural phase transition details, and to explore qualitatively and quantitatively the details of the relationship between the structural parameters and the properties of chalcogenide glasses.

Methods and Materials

High energy X-ray diffraction measurements were performed at the 6-ID-D MU-CAT beam line at the Advanced Photon Source (APS) at Argonne National Laboratory. Chalcogenide glasses Ge_xSe_{1-x}, with x= 15, 18, 20, 22, 23, 26, 28, and 30 were studied using the RA-PDF experimental setup at room temperature. Finely powdered chalcogenide glass samples were prepared by gently grinding their amorphous chunks. The samples were then loaded into hollow flat metal plate sample containers with radius of 0.25 cm and thickness of 1 mm, and sealed between thin Kapton films.

Measurements were carried out in flat-plate transmission geometry. Data acquisition employed the RA-PDF technique, with an X-ray energy of 98.0 keV (λ = 0.126530 Å). A Mar345 image-plate camera, a round disk with a usable diameter of 345 mm, was mounted orthogonal to the beam centered on the IP. Silicon standard sample was used to calibrate the sample-to-detector distance and the tilt of the IP relative to the beam path, using the software Fit2D [4]. The sample to detector distance was 178.4 mm. The count is always adjusted ensure that there are no saturated pixels in the detector. Five scans with irradiation time of 100 seconds were taken for each sample, and then averaged to get better statistics. All raw 2D data were integrated and converted to intensity versus 2θ format using the Fit2D program package [4, 5], where 2θ is the angle between the incident and scattered X-rays. Standard corrections for multiple scattering, polarization, absorption, Compton scattering and Laue diffuse scattering were applied to the integrated data to obtain the reduced total structure function F(Q). Direct Fourier transformation gives the pair distribution function G(r). Data correction and processing utilized the PDFgetX program package [6].

Results

Structural properties of chalcogenide glasses are addressed using the atomic PDF method, well suited for structural determination of this type of materials [1]. The PDF gives the number of atoms in a spherical shell of unit thickness at a distance r from a reference atom. This gives peaks at characteristic distances separating pairs of atoms. Experimental reduced total structure function, *F(Q)=Q(S(Q)-1)*, and corresponding atomic *G(r)*'s for the chalcogenide series are shown in Fig. 1 and Fig. 2 respectively.

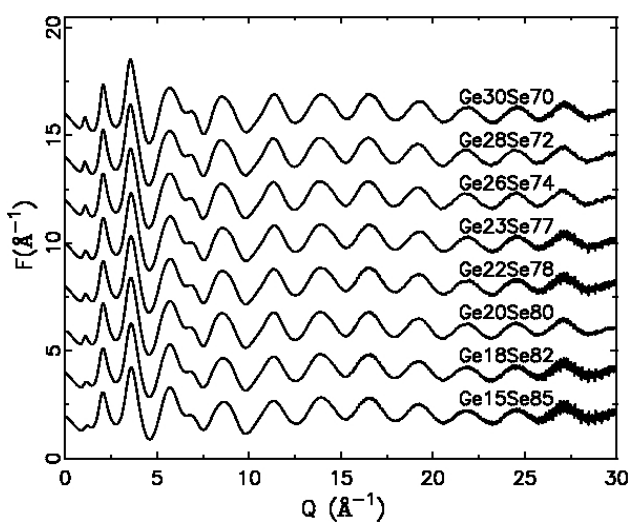

Fig.1. Experimental reduced structure function F(Q)=Q(S(Q)-1) of the chalcogenide glass samples, Ge_xSe_{1-x} (x= 15, 18, 20, 22, 23, 26, 28, and 30). Data were collected at room temperature using the RA-PDF experimental setup.

Fourier transform from reciprocal to real space was carried out up to a very high value of Q, Q_{max}=30Å^{-1}. Beyond that value of

Q the signal to noise ratio was unfavorable in these measurements.

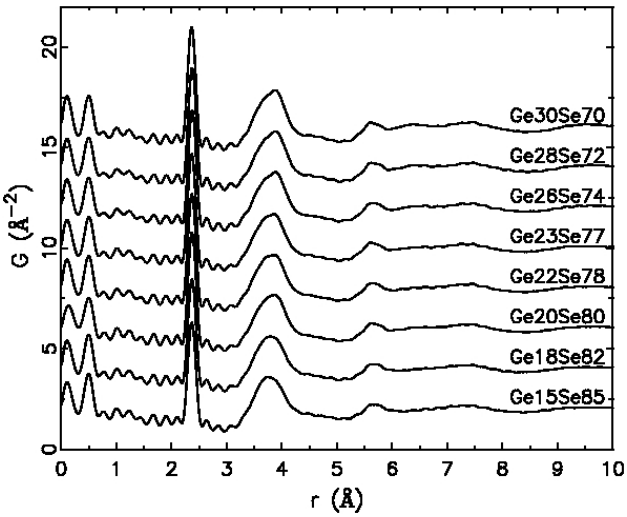

Fig.2. Experimental PDFs corresponding to the data shown in Fig. 1. PDF's shown were obtained from Q-space data through a Fourier transform up to Q_{max}=30Å^{-1}.

Discussion

Initial analysis (not shown) consisting of fitting Gaussian shaped peaks to the experimental G(r)'s for all the samples, and examining the fit results, showed that the first peak occurs at 2.38Å in all the samples. This peak corresponds to the well defined nearest-neighbor Ge-Se distance in chalcogenide glasses. Fit to the second peak, which is due mainly to Se-Se and partially to Ge-Ge distances, and occurs around 3.76Å, revealed an appreciable change in the position of this peak with varying the Ge content. For x>20 a shoulder seems to appear in the second peak. We also studied the behavior of the first sharp diffraction peak (FSDP) of chalcogenide data. This peak occurs at 1.07 Å^{-1}, and sharpens and shifts to lower Q-values as the Ge content increases. Amplitude of the FSDP versus Ge content plot (not shown) revealed that, among the studied samples that have x between 15 and 23, $Ge_{20}Se_{80}$ has the maximum amplitude of the FSDP. This interesting finding is based on single data point, and further experiments are needed on samples with similar Ge-contents (x= 17, 18, 19, 21) to confirm (or otherwise) the existance of the maximum in FSDP, that is possibly due to the change in the connectivity of the structural units in these glasses. Further analysis is in progress.

References:

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