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Breakdown of intermediate range order in AsSe chalcogenide glass

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As-cast amorphous AsSe (a-AsSe) has been characterized by *in-situ* high pressure XRD and Raman spectroscopy up to the pressure of ~ 30 GPa using diamond anvil cell together with *ab-initio* molecular dynamics simulations. A gradual densification has been observed under compression along with the breakdown of intermediate range ordering at ~ 16 GPa. The whole transformation process can be divided into three relatively distinct pressure regimes from 1 bar to 7 GPa, from 7 to 16 GPa, and beyond 16 GPa. Our XRD results together with Raman spectroscopic studies confirm that in the a-AsSe pressure tuning results in network transformations only, without sudden jump in the density. The results obtained by high pressure *ab-initio* molecular dynamics simulations demonstrate the variations in the local structures associated with the experimentally observed transformations. The amorphous-to-amorphous network transformation is found to be reversible upon decompression. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4964798>]

I. INTRODUCTION

Pressure can tune the structure and hence the properties of a material. Many pressure-induced transitions such as amorphous-to-crystalline,^{1–4} crystalline-to-amorphous,^{5–7} amorphous-to-amorphous,^{8,9} liquid-to-liquid,¹⁰ metal-to-semiconductor,¹¹ and metal-to-insulator¹² transitions have been widely reported in a variety of materials. The behavior of amorphous materials under pressure is complex because of their metastability as compared to their thermodynamically stable crystalline counterparts.¹³ In amorphous materials, pressure-induced amorphous-to-amorphous transitions have attracted a great deal of attention of high pressure, condensed matter physics, and materials scientists. Many unusual amorphous-to-amorphous transitions have been reported in a number of network amorphous materials and metallic glasses.^{14–17} Among all amorphous materials, amorphous chalcogenides exhibit amorphous-to-amorphous network transitions under pressure, as they undergo compression because of their relatively open structure at ambient condition as compared to the metallic glasses which are closely packed. High pressure studies on liquid and glassy $\text{Ge}_x\text{Se}_{1-x}$ and $\text{Ge}_x\text{S}_{1-x}$ are the best examples of such network transitions in liquid and glassy chalcogenides. Vaccari *et al.* reported hysteresis in reversible amorphous-to-amorphous transition in GeSe_2 using x-ray absorption fine structure (XAFS) and X-ray diffraction (XRD) measurements.¹⁸ Theoretical study on a- GeSe_2 has shown a gradual pressure-induced insulator-to-metal transition and a gradual amorphous-to-amorphous transition from fourfold-to-sixfold Ge coordination and from twofold-to-fourfold Se coordination.¹⁹ In another study,²⁰

GeSe_2 glass was observed to undergo densification upon pressurization up to ~ 3 GPa through conversion of edge- to corner-sharing tetrahedra, and at pressures ≥ 4 GPa the densification was observed that was contributed to the increase of the coordination numbers around Ge and Se atoms. By performing *in situ* high pressure XRD measurements on GeSe_4 , Skinner *et al.* found the destruction of intermediate range order (IRO) under compression.²¹ Recently, Kalkan *et al.* reported polyamorphism and metallization in tetrahedral GeSe_4 glass.²²

Apart from the conventional $\text{Ge}_x\text{Se}_{1-x}$ and $\text{Ge}_x\text{S}_{1-x}$ glassy systems, As-S and As-Se glassy systems are well known glass formers. Among all As-Se and As-S glassy systems, isostructural As_2Se_3 and As_2S_3 are relatively well studied at ambient conditions. Their glassy structure is characterized by a prepeak of the first sharp diffraction peak (FSDP) in X-ray diffraction (XRD) patterns, which is indicative to the intermediate range order.^{23–27} In glassy and liquid As_2S_3 , the prepeak disappeared as pressure increased, hereby confirming the destruction of intermediate range ordering.^{28,29} However, in these transitions, no sudden drop in the density has been found, and hence the transition was observed to be purely related to a change in the network (i.e., from a loosely packed structure to more packed one). Very recently, in Ge doped As-S glassy system (i.e., in $\text{Ge}_{2.5}\text{As}_{51.25}\text{S}_{46.25}$ glass),³⁰ Kalkan *et al.* reported a reversible amorphous-to-amorphous transition from a molecular network to a more closely packed network. In contrast to As-S glassy systems, As-Se glassy systems have been poorly studied at high pressure. To date, g- As_2Se_3 is the only candidate among all the As-Se glassy systems that has been studied under high pressure conditions. But these studies were limited to the resistivity measurements³¹ and band gap measurements.³² While all other As-Se

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glassy systems remain unexplored under high pressure conditions. Here, we report the results of *in-situ* high pressure synchrotron XRD, Raman spectroscopy measurements, and *Ab-initio* molecular dynamics (AIMD) simulations on stoichiometric amorphous AsSe (a-AsSe). We observed a reversible destruction of intermediate range ordering, and hence the conversion of a quasi-layered (2D) to a closely packed (3D) network amorphous.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

Sample preparation: The residual oxygen content in arsenic and selenium samples of 99.999% purity was reduced using the volatilization technique. The vapor pressure of the oxides of these metals is greater than that of the metals; this has been exploited to remove the oxide species. Selenium was heated at 250 °C and arsenic at 290 °C under vacuum for several hours. After this treatment, the required amounts of As and Se were sealed in a silica tube under vacuum. This mixture was further heated at 650 °C for 12 h in a rocking furnace to ensure good mixing and homogenization of the liquids. To condense a maximum of vapor into the liquid, the temperature was reduced to 500 °C for 1 h. Then, the ampoules were quenched in air and later annealed near the glass-transition temperature ($T_g \approx 175$ °C) of $\text{As}_{50}\text{Se}_{50}$ (AsSe) glass for 10 h to reduce the mechanical stresses induced during the cooling. The amorphous nature of the AsSe sample was confirmed by X-ray diffraction and differential scanning calorimetry.

***In-situ* measurements at high pressure:** Synchrotron radiation XRD and Raman spectroscopic measurements were performed in a Mao-Bell type diamond anvil cell (DAC) with a culet 300 μm in diameter. The sample chamber was a hole of ~ 120 μm diameter drilled in a pre-indented T301 stainless steel gasket. The specimen was loaded into the sample chamber along with ruby as a standard for pressure calibration. A 4:1 mixture of methanol:ethanol was used as a pressure-transmitting media for both the *in-situ* high pressure XRD and Raman spectroscopic measurements.

Angle-dispersive XRD measurements were performed *in-situ* under high pressure at the Extreme Conditions Beamline (ECB) P02.2, PETRAIII, DESY, Hamburg, Germany (Liermann *et al.*, 2015). The energy of the synchrotron radiation was adjusted to 42.7 keV. Two-dimensional diffraction patterns were collected using a Perkin Elmer XRD 1621 ScI-bonded amorphous silicon 2D detector (2048 $\times$ 2048 pixels, 200 $\times$ 200 μm pixel size) mounted orthogonal to the direction of the incident X-ray beam. CeO_2 standard (NIST 674b) was used to measure the sample-to-detector distance and tilt of the detector relative to the beam path. The sample was exposed to an X-ray beam with a diameter of 8(H) $\times$ 3(V) μm^2 for 1 min. The background was collected by exposing X-ray beam on the diamonds of the empty cell (the same cell which was used for the *in-situ* high pressure XRD measurements) which was later used for background subtraction. This method of collecting background has been successfully applied to various other studies and is found to be efficient and accurate. The two-dimensional patterns were integrated into Q -space using the software package Fit2D.³³

Raman experiments were performed using a Renishaw microscope employing a laser of wavelength 785 nm. The laser power was set to 5 mW after optimization to avoid heat- and photo-induced degradation, while still enabling the collection of high-quality Raman spectra.

***Ab-initio* molecular dynamics simulations:** *Ab-initio* molecular dynamics (AIMD) simulations were performed using the Vienna *ab-initio* simulations package (VASP) code³⁴ and the projected augmented wave method (PAW)^{35,36} with generalized gradient approximations. A supercell containing 192 atoms (96 As and 96 Se) was quenched from 2000 K to room temperature (RT) at 0.33 K/fs, and the Nose thermostat³⁷ was used to control the temperature. The mass density was fixed at the measured value for a-AsSe, and the zero-pressure density was obtained by relaxing the box. After quenching to RT, the system was equilibrated for 4000 time steps (3 fs/step), and pressure was applied by uniformly reducing the volume of the box. This method of application of pressure mimics experimental hydrostatic compression and has been previously adopted in many AIMD studies of pressure-induced structural changes. When comparing simulations with experimental results, the spatio-temporal limitation of the AIMD simulations must be taken into account. In the present studies, the small size of the box (192 atoms) may cause statistical fluctuations and lead to different structures. However, the general trend in structural evolution can still be identified.

III. RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of a-AsSe during compression. Under ambient conditions and moderate pressures, there is a pre-peak at $2\theta \approx 3.2^\circ$ in the XRD patterns; this corresponds to intermediate range ordering, i.e., quasi-layered (2D) structure. As the pressure is increased more significantly, the pre-peak shifts to higher 2θ values and loses intensity, finally disappearing at ~ 16.6 GPa (Fig. 1). The loss of this peak reflects the destruction of the intermediate range order (IRO) associated with the quasi-layered (2D) structure and marks the completion of the transformation

FIG. 1. *In-situ* high-pressure XRD patterns of a-AsSe at room temperature in a diamond-anvil cell. Integrated XRD patterns at selected pressures during compression up to 29.5 GPa. The black arrows indicate the appearance of a new feature in XRD patterns at ~ 7.4 GPa and its evolution upon pressurization.

from a quasi-layered (2D) to a closely packed (3D) network amorphous. The progress of this transformation, and the pressures over which it occurs, compares well with the IR spectroscopy measurements on stoichiometric a-As₂Se₃ performed by Struzhkin *et al.*³² It is noted that in XRD patterns a very broad peak (as marked by arrow) appears at ~ 7 GPa, which is an additional indication for the change from a quasi-layered 2D to a 3D network. After 7 GPa, the peak starts getting more pronounced and gains a reasonable height after ~ 16 GPa. This behavior is consistent with the plot of $\lambda/2 \sin \theta$ for the FSDP as a function of pressure (Fig. 2), in which three distinct regions are detectable, and highlighted by solid red, green, and blue lines. The slope of the red line (i.e., -0.004 nm/GPa) indicates that the volume reduces quickly as compared to the reduction of the volume in the pressure regimes indicated by the green (slope, -0.001 nm/GPa) and blue (slope, -0.0007 nm/GPa) lines. In the pressure regime indicated by red line (i.e., ~ 0 –7 GPa), the IRO is quickly destroyed due to the enhancement in the inter-layer interactions and the structure starts transforming from quasi-layered 2D to 3D network. In the green line pressure domain (i.e., from ~ 7 GPa to ~ 16 GPa), quasi-layered 2D network still persists along with the 3D network, and quasi-layered 2D network amorphous is completely transformed into 3D network amorphous at the end of pressure regime (i.e., at ~ 16 GPa). In other words, complete disappearance of IRO is confirmed at ~ 16 GPa. After ~ 16 GPa, up to the maximum pressure achieved in the XRD measurements, pressurization causes the gradual densification of the 3D amorphous as indicated by the blue line.

Figures 3(a) and 3(b) show the high-pressure behavior of a-AsSe during compression and decompression cycles, respectively, observed via Raman spectroscopy. At ambient pressure, the Raman spectrum of a-AsSe consists of a main asymmetric envelope around 220 cm^{-1} , corresponding to the interlayer vibrations of pyramidal AsSe₃ units (which are the basic building blocks of the quasi-layered structure in a-AsSe).³⁸ When the pressure is increased, the intensity of the main envelope decreases and shifts to higher frequencies. The major reduction in the intensity of the main envelope takes place up to ~ 7.6 GPa, and it finally vanishes at

FIG. 2. Data of $\lambda/2 \sin \theta$ of the FSDP in high-pressure XRD patterns of a-AsSe at room temperature as a function of pressure, which is related to the reduced volume of the sample ($V(P)/V(0)$).

FIG. 3. *In-situ* high pressure Raman spectroscopy results for a-AsSe at room temperature. (a) Raman spectra at selected pressures during compression up to 25.3 GPa. (b) Raman spectra at selected pressures during decompression from 25.3 GPa to 0 GPa.

~ 14 GPa, suggesting the completion of the quasi-layered 2D to 3D network transformation. As the layers are forced closer, the AsSe₃ pyramidal units are distorted (i.e., the As-Se-As bond angle is changed). As a result, the band representing the vibrations of AsSe₃ pyramidal units is broadened and reduced in intensity. This behavior is in good agreement with the XRD results in Fig. 1. During decompression, the main envelope of the parent amorphous phase starts to appear back at ~ 11 GPa. With further decrease in pressure, at ~ 1.4 GPa there is a significant increase in the intensity of the main envelope. Finally, upon complete release of pressure, the main envelope which is the indicative of the parent amorphous phase re-gain its shape. This suggests that the pressure-induced amorphous-to-amorphous network transformation in a-AsSe is reversible upon complete pressure release. Similar reversibility in pressure-induced amorphous-to-amorphous transformation has also been observed in other chalcogenide glasses such as GeSe₄, GeS₂, Ge_{2.5}As_{1.25}S_{46.25}, and iso-structural As₂S₃ glasses.^{18,22,28,30}

The nature of the phase transformation demonstrated in the above mentioned experiments has been analyzed from the variations in local structures point of view by using *ab-initio* molecular dynamic (AIMD) simulations. Fig. 4 shows

FIG. 4. Optimized atomic configurations obtained from the high pressure *ab-initio* molecular-dynamics simulations of a-AsSe at various selected pressures. The violet balls represent As atoms and yellow balls represent Se atoms.

a visual representation of quasi-layered (2D) to closely packed (3D) network transformation by showing optimized atomic configurations at three selected pressures. At 0 GPa, quasi-layered (2D) structure is obvious, whereas the structure appears more 3D-like in appearance at elevated pressures (e.g., 10.5 GPa and 21.9 GPa). Fig. 5 shows total and partial As-As, As-Se, and Se-Se pair correlation functions (PCFs) obtained by AIMD simulations. The intensity of the first peak in total PCF decreases with the increase in pressure, while the intensity of the second peak tends to increase with the pressure tuning. The first peak in PCF is found to move towards, higher “ r ” values, whereas the second peak is found towards lower “ r ” values (i.e., the first and second

FIG. 5. Total and partial pair correlation functions at various selected pressures as calculated from *ab-initio* molecular-dynamics simulations of a-AsSe during compression up to 21.9 GPa. The dashed lines in the total, partial As-As, and partial As-Se pair correlation functions represent the approximate peak position of the first peak in the total, partial As-As, and partial As-Se pair correlation functions, whereas two dashed lines in partial Se-Se pair correlation function represent the approximate initial/final (3.8 Å/3.2 Å) positions of the first most prominent peak in the partial Se-Se pair correlation functions.

peaks are found to merge into each other). This behavior of the first and second peaks under pressure indicates the weakening of the covalent bonding, and hereby the enhancement in the van der Waals forces due to the increased interlayer interaction. A similar behavior of the first and second peaks of $g(r)$ has been observed in previous experimental studies on glassy GeSe_4 ²² and liquid GeSe_2 .¹⁰ Concerning As-As, As-Se, and Se-Se PCFs, it is found that the Se-Se PCFs are the most affected, while the As-As PCFs are the least affected as a function of pressure. The first and second peaks of Se-Se PCFs are found to merge into each other with increasing pressure (Fig. 5). The second peak in Se-Se PCFs changes its position from an initial position at ~ 3.8 Å at pressure value of 0.0001 GPa to the final position at 3.2 Å at pressure value of ~ 22 GPa. It means, as the quasi-layered 2D to 3D network transformation proceeds, the Se-Se PCFs are the most affected, pointing to the major player during the transformation.

To investigate the local structure changes associated with the quasi-layered 2D to 3D network transformation, we calculated the total and partial coordination numbers. The

coordination numbers (CNs) have been calculated by using radial distribution function (RDF) method, in which we integrated $4\pi r^2 \rho_0 g(r)$ to the corresponding peak position of total and partial $g(r)$ and multiplying it by 2 (i.e., $C.N = 2 \times \int_0^{r_0} 4\pi r^2 \rho_0 g(r)$). For the total and partial As-As and As-Se CNs, we integrated it up to the first atomic shell peak positions, whereas for the partial Se-Se CN we integrated it up to the 2nd atomic shell peak position. This method of calculating the coordination numbers has been successfully applied in the previous studies.^{39,40} Pressure-induced variations in the total, As-Se and Se-Se partial coordination numbers are seemed to follow three trends in three pressure regimes (Fig. 6). The numerical values of pressures that onset these regimes are nearly the same to that of the pressure values that onset the regimes seen in XRD experiment (Fig. 2). The average value of 2nd shell Se-Se coordination number is ~ 5.1 at 0 GPa and is increased to ~ 6.8 at ~ 7 GPa, while it remains almost unchanged in the pressure range of ~ 7 –15 GPa. Further increase in pressure results in the decrease of the 2nd shell Se-Se coordination number from ~ 6.9 at ~ 15 GPa to ~ 6.3 at ~ 22 GPa. The average value of the 1st shell As-Se coordination number decreases from ~ 3.1 at 0 GPa to ~ 2.8 at ~ 7 GPa, and then it slightly increases from ~ 2.8 to ~ 3 in the pressure range of ~ 7 –15 GPa. With further increase in pressure, the average value of the 1st shell As-Se coordination number is further increased from ~ 3 at ~ 15 GPa to ~ 4.3 at ~ 22 GPa. In talking about the average value of the 1st shell As-As coordination number, it increases gradually from ~ 1.1 at 0 GPa to ~ 1.6 at ~ 22 GPa. On the other hand, the 1st shell total average coordination number initially reduces from ~ 2.2 at 0 GPa to ~ 2 at ~ 7 GPa, increases from ~ 2 at ~ 7 GPa to ~ 2.5 at ~ 15 GPa, and then finally increases more from ~ 2.5 at ~ 15 GPa to ~ 3.3 at ~ 22 GPa. It can be concluded that as the quasi-layered 2D to 3D network transformation proceeds,

FIG. 6. Pressure dependence of average total and partial coordination numbers as calculated from *ab-initio* molecular-dynamics simulations of a-AsSe during compression up to 21.9 GPa. The average total and partial As-As, As-Se coordination numbers correspond to the first shell coordination, whereas the partial Se-Se coordination number corresponds to the second shell coordination. The solid lines are guide to the eyes along the various trends in the data. The red color dashed lines separate the transformation process into three pressure regimes.

similar to the pair correlation functions (Fig. 5), Se-Se coordination is the most affected, while As-As coordination is the least affected under pressure.

IV. CONCLUSIONS

In summary, we performed *in-situ* high pressure XRD, Raman spectroscopic measurements, and *ab-initio* molecular dynamic simulations on stoichiometric a-AsSe chalcogenide. We observed a gradual densification upon compression up to ~ 30 GPa along with breakdown of IRO associated with the quasi-layered 2D to 3D network transformation at 16 GPa. The gradual densification and associated network transformation under pressure can be divided into three pressure regimes: (i) 0–7 GPa pressure regime: in this pressure regime, IRO quickly collapses due to enhancement in inter-layer interactions, and quasi-layered (2D) network amorphous starts transforming into 3D network amorphous, but overall structure still remains quasi-layered 2D network amorphous in this regime. (ii) 7–16 GPa pressure regime: in this pressure regime, quasi-layered 2D network amorphous is completely transformed into 3D network amorphous. (iii) 16–30 GPa pressure regime: in this pressure regime, densification of 3D network amorphous occurs. In the aforementioned three pressure regimes, volume and coordination numbers of the specimen change with different paces. The amorphous-to-amorphous transformation under compression is found to be reversible upon decompression. Such kind of structural transformation in the intermediate range ordering as a function of pressure is expected to occur in other amorphous As-Se systems as well. Our current work will help the materials scientists and physicist to understand the behavior of network glassy/amorphous materials under pressure. Further studies are needed to explore the behavior of the network glasses and liquids under pressure. These studies should address the pressure-induced structural transformations along with the associated pressure-induced variations in the physical properties (e.g., resistivity) of network glasses and liquids.

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