High-pressure behavior of As_2O_3: Amorphous-amorphous and crystalline-amorphous transitions

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(Received 14 September 2007; revised manuscript received 31 March 2008; published 24 April 2008)

The room temperature compression of As_2O_3 has been studied by *in situ* diamond anvil cell Raman and x-ray diffraction up to a pressure of 35 GPa. Upon compression, we discovered a crystal-to-amorphous transition in arsenolite, while claudetite, which is another crystalline polymorph of As_2O_3, remains crystalline up to at least 40 GPa. We have also observed an amorphous-amorphous transition in As_2O_3 glass at 25 GPa. This transition is characterized by a dramatic change in the Raman spectrum, which is reversible upon decompression. *In situ* diamond anvil cell x-ray diffraction of As_2O_3 glass reveals that the amorphous-amorphous transition is associated with an increase in the arsenic coordination. The amorphous-amorphous transition is reversible with little hysteresis.

DOI: 10.1103/PhysRevB.77.144113 PACS number(s): 61.43.Fs, 61.05.C−, 78.30.−j, 81.40.Vw

I. INTRODUCTION

There are three known crystalline As_2O_3 polymorphs, arsenolite, claudetite I, and claudetite II.[1–3] All three polymorphs are built from an assembly of AsO_3 pyramids. In each structure, the As-O bond distance is close to 1.8 Å and the closest As-As distance is approximately 3.2 Å. Arsenolite is the low temperature polymorph [stable below 110 °C (Ref. 4)] that crystallizes into a cubic lattice. In the arsenolite structure, the AsO_3 building blocks are assembled together to form adamantane structured As_4O_6 molecular units (Fig. 1).[1] Claudetite I and II are formed at high temperature and crystallize into a monoclinic lattice. In both forms, each oxygen atom is shared between two AsO_3 pyramids to form a layered structure.[2,3]

Since 1939, As_2O_3 is known to be a good glass forming substance.[5] The local structure of the glass is well known and based on AsO_3 pyramids. However, the linkage of these building blocks is not as well understood. Imaoka and Hasegawa[6] concluded that a structure consisting of three-membered rings of AsO_3 pyramids was most consistent with their x-ray diffraction data. Similarly, Clare *et al.*[7] found their neutron data to be consistent with a random network of corner sharing AsO_3 pyramids with the presence of three-membered rings similar to those found in As_4O_6 molecules. These authors also specified that the interplanar distances of either claudetite form are inconsistent with the data. Papatheodorou and Solin,[8] by using Raman spectroscopy, interpreted the structure of As_2O_3 glass (g-As_2O_3) at high temperature to be layerlike, similar to claudetite. Based on their Raman and infrared data, Galeener *et al.*[9] concluded that the structure of g-As_2O_3 is a continuous random network of AsO_3 pyramidal units, which is in some way similar to that of GeO_2 glass. The more recent study by Yannopoulos *et al.*[10] indicated that As_2O_3 is a strong liquid ($m \approx 19$) similar to SiO_2.[11] These data would indicate that the structure of liquid As_2O_3 is a continuous three-dimensional network and not a layered structure or a molecular liquid.

To date, there have been few reports of As_2O_3 at high pressure. In 1967, White *et al.*[4] reported the high-pressure phase diagram of As_2O_3 up to 10 GPa. In 1999, Grzechnik[12] reported the compressibility and vibrational modes for arsenolite up to 16 GPa. In that study, the author did not observe

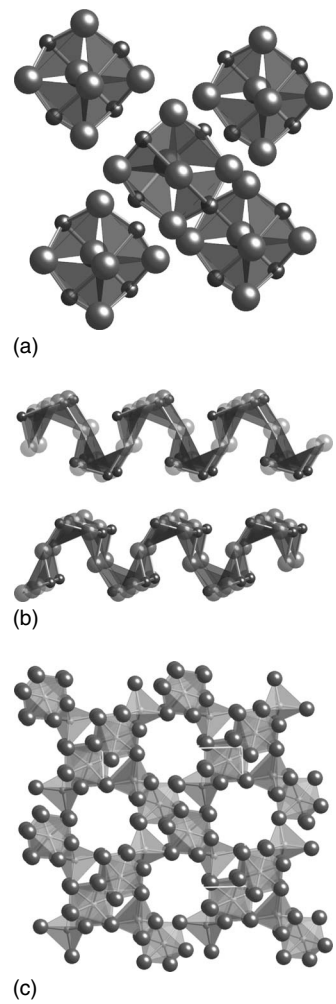

FIG. 1. Structure of (a) arsenolite (c-As_2O_3), (b) claudetite I (m-As_2O_3), and (c) As_2O_5. In each figure, the large spheres represent the O atoms and the small spheres represent the As atoms.

any structural change in arsenolite. In 2006, Andrikopoulos *et al.*[13] reported the pressure dependence of As_2O_3 glass Raman spectrum up to 9.4 GPa. In that study, the authors reported a broadening and a decrease in the intensity of the Raman bands. They interpreted the changes in the local order to be from cagelike structures to layerlike ones. They also concluded that the high-pressure structural modification is retained after pressure release. Finally, in 2007, Mei *et al.*[14] studied the structural changes in pressure densified glassy As_2O_3 as well as the pressure dependence of the Raman spectrum up to 11.6 GPa. They concluded that the only structural difference between the samples recovered from 10 and 23 GPa and the starting glass is a small decrease in the As-As-As/O angle, which indicates a slightly tighter packing of AsO_3 pyramids with increasing density. Below, we extend the range of pressure to 40 GPa and show that significant structural changes in As_2O_3 happen in the 20–40 GPa region.

II. EXPERIMENTAL METHODS

We synthesized both crystalline and glassy As_2O_3 from a starting material of 99.99% As_2O_3, which is purchased from Alfa Aesar (Lot No. 032681). The samples produced were thermally quenched g-As_2O_3, arsenolite (cubic, c-As_2O_3), and claudetite (monoclinic, m-As_2O_3). The g-As_2O_3 sample was made by heating the crystalline arsenolite form of As_2O_3 to 800 °C in a vacuum-sealed quartz tube (melting point As_2O_3=312.3 °C). The glass was formed by letting the liquid cool in air, which is made by removing the sealed quartz tube from the furnace. The claudetite crystals were synthesized from crystalline arsenolite, which is sealed in a Pyrex tube with a trace amount of water and heated to 180 °C for 72 h. The claudetite sample was characterized by using both x-ray diffraction and Raman spectroscopy.

In situ high-pressure experiments were performed by using a cylindrical type diamond anvil cell (DAC).[15] The cell was fitted with 200 μm culet diamonds for the spectroscopy experiments and 300 μm culets for the x-ray diffraction experiments. In all of the cases, the sample (piece of glass, piece of claudetite crystal, or crystalline powder of arsenolite) was packed along with a few pieces of ruby smaller than 1 μm in a 90 μm diameter hole electroeroded in a rhenium gasket by using an electric discharge machine (Hylozoic Products) without a pressure transmitting medium. The pressure was determined by using the ruby fluorescence technique[16] in all of our high-pressure experiments that used a diamond anvil cell.

The Raman spectroscopy experiments were performed by using a custom-built notch filter based micro-Raman system that used a frequency-doubled yttrium aluminum garnet Verdi laser (Coherent, Inc.), which generates a narrow frequency single line at 532 nm. The laser excitation was focused onto the diamond anvil cell by using a 20× long working distance Mitutoyo objective. The laser power after the objective was maintained between 5 and 7 mW to prevent damaging the sample. The signal was collected into a Shamrock 303i spectrometer (Andor Technology, Inc.) after removing the laser light by using two Kaiser supernotch filters. The signal was then diffracted off a 1200 grooves/mm grating and collected into a back-thinned Andor DV401-BR-DD charge coupled device detector. The spectral resolution of the system was 2 cm^{-1}, which was high enough for the study of glasses and amorphous materials.

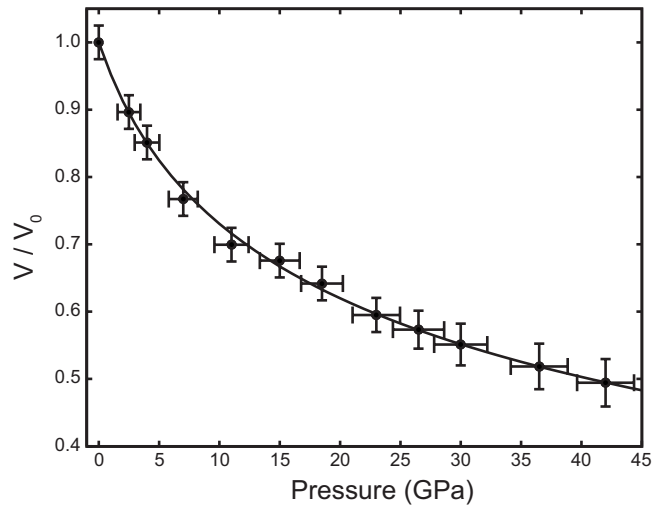

FIG. 2. Equation of state for As_2O_3 glass. The solid line overlaid on the data is the Birch–Murnaghan equation of state fit of the data ($B_0=18\pm2$ GPa and $B_0'=3.5\pm0.5$ GPa).

The x-ray diffraction experiment on g-As_2O_3 was performed on sector 1 at the Advanced Photon Source (Argonne National Laboratory, Il) by using a 50×50 μm^2 focused beam at a wavelength of 0.1241 Å (100 keV). The diamond anvil cell was fitted with one perforated diamond anvil on the upstream side of the cell to reduce the Compton scattering from diamond. The typical sample to detector distance was about 245 mm. The detector was a highly sensitive, low background GE Revolution amorphous Si area detector. The data were calibrated by using the diffraction pattern from CeO_2. The two-dimensional data were radially integrated by using the program[17] FIT2D and manually processed by using the method described in a previous paper.[18] Due to experimental time constraints, we selected four pressures at which to collect the diffraction data: 4, 17, 22, and 32 GPa. To properly normalize the radial distribution functions and extract coordination numbers, we carefully measured the equation of state of As_2O_3 glass, which is presented in Fig. 2. We directly measured the equation of state by measuring the volume of a sample of As_2O_3 glass packed in the gasket hole of the diamond anvil cell. The area of the cylindrical sample was measured by using digital images of the sample at each pressure point. The thickness of the sample was determined by measuring the distance between the two opposite diamond tables (face of the diamond parallel to the culet facing the outside of the cell) while taking into account the change in the diamond heights with pressure. The change in the diamond anvil heights with pressure was calibrated by using the known equation of state of KBr and CsCl.[19] We confirm the initial slope of the equation of state up to 7 GPa by measuring the equation of state in a pentane-isopentane hydrostatic medium. A fit of the As_2O_3 data collected up to 42 GPa to a Birch–Murnaghan equation of state gave $B_0=18\pm2$ GPa and $B_0'=3.5\pm0.5$ GPa (Fig. 2).

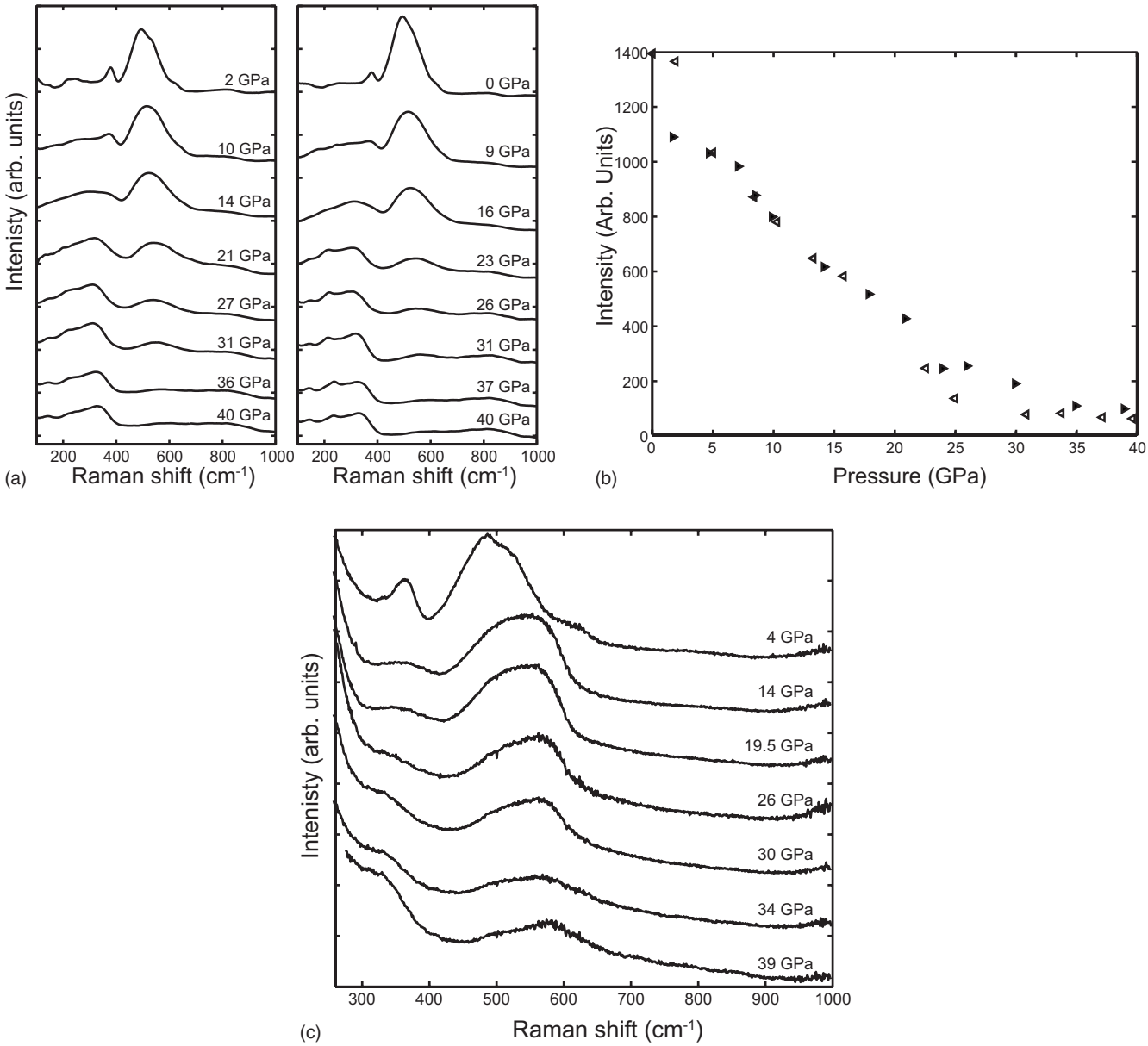

FIG. 3. (a) Raman spectra of As_2O_3 glass (g-As_2O_3) from ambient up to 40 GPa during compression (left) and decompression (right). The intensity of each spectrum collected at pressures >22 GPa was multiplied by 2. (b) Integrated intensity from 400 to 800 cm^{-1} as a function of pressure for g-As_2O_3. The solid triangles pointing to the right indicate data collected upon compression and the empty triangles pointing to the left indicate data collected upon decompression. (c) Raman spectra of As_2O_3 glass from ambient to 39 GPa measured by using a 785 nm laser excitation wavelength.

III. EXPERIMENTAL RESULTS

A. Raman spectroscopic study

1. Compression-decompression of g-As_2O_3

The Raman spectrum of As_2O_3 glass is composed of a very intense broad feature centered about 500 cm^{-1} preceded by a less intense and sharper feature centered at 380 cm^{-1}. According to Andrikopoulos *et al.*,[13] the large feature can be separated into four components (480, 525, 550, and 610 cm^{-1}). The 380 and 525 cm^{-1} peaks are characteristic of cagelike regions of the glass, and the 480 and 550 cm^{-1} peaks are assigned to layerlike configurations.[13,20]

We measured the *in situ* the Raman spectrum of As_2O_3 glass in the diamond anvil cell up to 40 GPa (Fig. 3). Upon compression, the Raman scattering intensity progressively decreases. The main feature in the glass spectrum also seems to become less resolved, and at 15 GPa, the four peaks are not discernable and only a broad feature centered around 500 cm^{-1} can be observed. Above 20 GPa, a different feature appears below 400 cm^{-1}, while the large peak between 400 and 600 cm^{-1} dramatically weakens. Beyond 30 GPa, the 500 cm^{-1} feature has completely disappeared and only the low frequency feature is present on the pattern. Upon decompression, the dramatic change in the Raman spectrum appears to be reversible and the large feature between 400

and 600 cm^{-1} regains intensity below 25 GPa. After a complete decompression of the sample, the Raman spectra are almost identical. The reversibility of the changes in the Raman spectra shows little or no hysteresis [Fig. 3(b)], which is possibly due to the rigid nature of the AsO_3 pyramids.

It should also be noticed that upon compression, the sample changes color from completely clear to yellow, then red, and, finally, completely black above 45 GPa. This phenomenon is also observed in similar glasses such as As_2S_3.[21] Since the absorption of the sample at 532 nm significantly increases above 30 GPa, we also reproduced the experiment by using a lower energy laser wavelength of 785 nm and observed the same transition [Fig. 3(c)]. This was done to ensure that no photoinduced effects were being caused by the Raman excitation laser.

2. Compression-decompression of arsenolite

Arsenolite has 20 internal vibrational modes, of which 10 are Raman active (two A_{1g}, two E_g, and four F_{2g}) and 4 are IR active (F_{1u}). The Raman spectrum of arsenolite shows seven strong vibrations between 100 and 1000 cm^{-1} (Fig. 4). The peak at 559 and 368 cm^{-1} are assigned to out of phase and in phase breathing of As and O in the As_4O_6 molecule, respectively.[12] The peaks at 182 and 413 cm^{-1} are assigned to the bending of As-O-As. The peaks at 780 and 470 cm^{-1} are due to As-O-As stretching. Finally, the peak at 266 cm^{-1} is an As-O-As wagging mode.[22]

Upon compression to 15 GPa, the Raman spectrum shows changes in relative intensities as previously reported by Grzechnik.[12] Along with the changes, the Raman scattering intensity of the peaks have become much weaker and some broad features start to appear underneath the spectrum. The spectra collected at higher pressures ($P > 25$ GPa) show a dramatic decrease in remaining intensity of the arsenolite vibrations. The pattern starts to look more and more like that of g-As_2O_3 at the same pressures. The strong 370 cm^{-1} arsenolite peak due to the breathing of As_4O_6 units drastically reduces in intensity. Above 30 GPa, the patterns do not show any sharp band, and only a large broad feature is visible below 400 cm^{-1}. To confirm that the sample is, indeed, amorphizing, we also performed the same experiment by using x-ray diffraction [Fig. 4(b)] and observed that the sample does lose long-range order and become amorphous with respect to x-ray diffraction as well.

Upon decompression, the pattern remains unchanged down to 28 GPa. At 25 GPa, one weak arsenolite peak appears at 346 cm^{-1} on top of the broad background and a different broad feature appears between 400 and 600 cm^{-1}. Upon further decompression, the intensity of the low wave number broad feature decreases and completely disappears below 15 GPa. The intensity of the feature centered at 500 cm^{-1} increases and a few more arsenolite peaks become visible. When the experiment is repeated by using a 785 nm laser excitation line, the exact same result is observed.

3. Compression of claudetite

The Raman spectrum of claudetite was previously described by Mercier and Sourisseau.[23] A factor group analysis

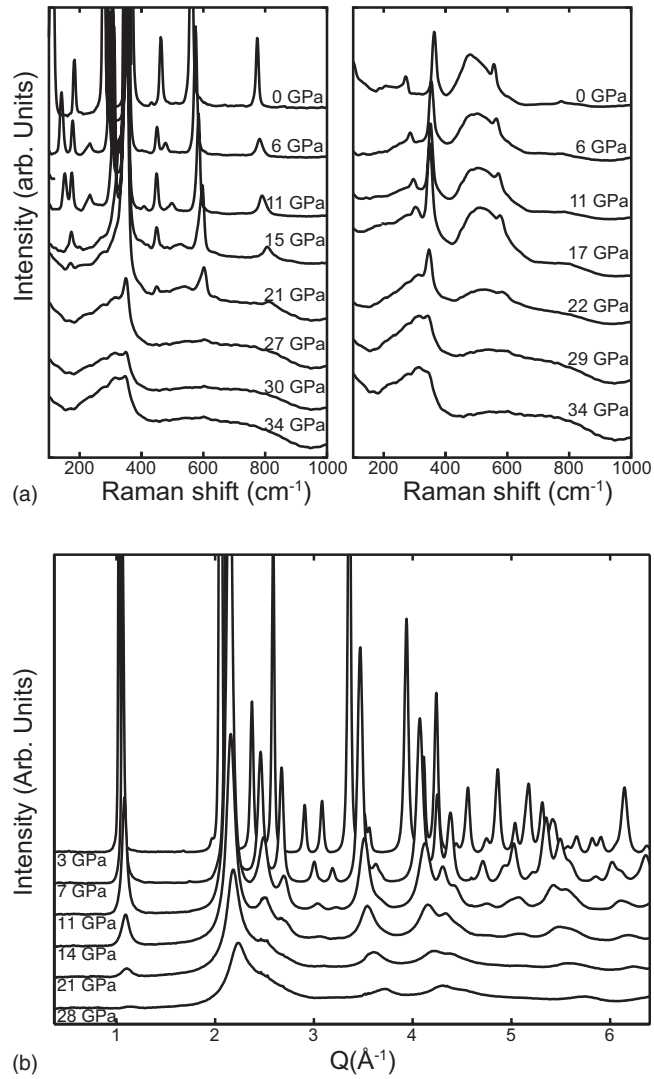

FIG. 4. (a) Raman spectra of arsenolite c-As_2O_3 from ambient up to 34 GPa during compression (left) and decompression (right). (b) X-ray diffraction patterns for arsenolite as a function of increasing pressure.

of the claudetite structure shows that there are 54 internal modes, of which 14 B_g and 13 A_g modes are Raman active and 14 B_u and 13 A_u modes are infrared active. The Raman spectrum of claudetite at 2.5 GPa displays nine major peaks below 400 cm^{-1}, one very strong peak at 474.5 cm^{-1} (breathing mode of O normal to the layers), followed by three less intense peaks at 559 (symmetric stretching of the AsO_3 pyramids), 638.5, and 652.5 cm^{-1} (asymmetric stretching of the AsO_3 pyramids) and, finally, three weaker peaks between 700 and 900 cm^{-1} (asymmetric stretching of the AsO_3 pyramids) (Fig. 5). Upon compression, the main features of the spectrum remain unchanged and some additional peaks seem to appear. Two intense peaks appear on either side of the main band and the relative intensity of the weak peaks below 400 cm^{-1} (symmetric deformation of the AsO_3 pyramids) increases as compared to that of the strongest peak. Up to 40 GPa, the sample remained clearly crystalline in character and the main peak retains the same full width at half maximum. The apparent broadening above 30

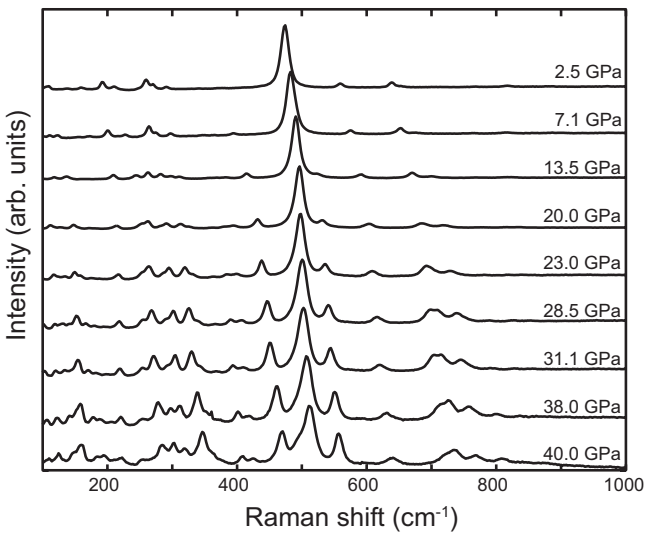

FIG. 5. High-pressure Raman spectra of claudetite (m-As_2O_3) from ambient up to 40 GPa.

GPa is due only to the splitting of the peak. At 40 GPa, we can clearly observe a shoulder developing on the high energy side of that peak. No pressure-induced amorphization was observed within our experimental pressure range for the claudetite polymorph. Only minor changes occur, which result in the appearance of some other Raman active vibrations and some changes in relative intensity.

4. Diamond anvil cell Raman spectroscopy summary

The Raman study of As_2O_3 showed that an amorphous-amorphous transition[24] occurs upon compression of g-As_2O_3 above 20 GPa (Fig. 3). This transition is characterized by a rapid decrease in intensity of the 550 cm^{-1} mode and a corresponding appearance of an additional low frequency mode at 350 cm^{-1}, which begins to appear above 20 GPa. That transition is reversible upon decompression with little or no hysteresis [Fig. 3(b)]. The compression of arsenolite also yielded pressure-induced amorphization (Fig. 4). The arsenolite pattern progressively gives way to an amorphous pattern between 16 and 27 GPa. At 27 GPa, the pattern is very similar to that obtained for glassy As_2O_3 at the same pressure. Finally, we also compressed claudetite and observe no pressure-induced amorphization. Andrikopoulos *et al.*[13] previously described the changes in the glass spectrum below 10 GPa to be due to a reduction in the intensity of modes characteristic of the cagelike configuration with respect to the modes assigned to the layerlike regions. This observation would, in fact, not be consistent with the subsequent disappearance of the Raman intensity in the 400–600 cm^{-1} region since claudetite, which is the layered structure form of As_2O_3, is kinetically stable at ambient temperature up to at least 40 GPa. Both arsenolite and As_2O_3 glass transform into the same structure above the same transition pressure. Therefore, the Raman studies presented here would suggest that the low-pressure glass structure (glass synthesized at room pressure) is more closely related to the arsenolite structure, which is in agreement with the neutron diffraction results of Clare *et al.*[7]

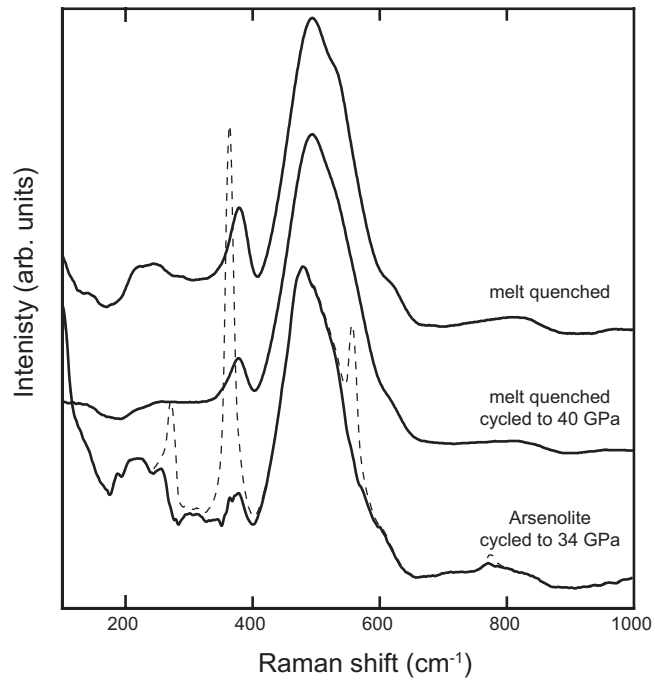

FIG. 6. Comparison of thermally quenched g-As_2O_3 before and after pressurization to 40 GPa along with pressure amorphized c-As_2O_3 (arsenolite) at room pressure (dashed line). We also plotted with a solid line the pressure amorphized pattern after the subtraction of the arsenolite peaks (dashed line) to better visualize the Raman spectrum of the amorphous material.

In Fig. 6, we can see that there is a little or no difference between the Raman spectra of g-As_2O_3 and pressure cycled (to 40 GPa) g-As_2O_3. Along with the two patterns of g-As_2O_3, we plotted the pattern of pressure amorphized arsenolite. To clarify Fig. 6, we subtracted the arsenolite spectrum from the pressure amorphized pattern. We see in Fig. 6 that the pressure amorphized spectrum shows no significant difference from the g-As_2O_3 pattern. This observation indicates a very similar structure for the pressure amorphized arsenolite, the pressure cycled As_2O_3 glass, and the thermally quenched As_2O_3 glass. Mei *et al.*[14] reported an *ex situ* structural investigation of As_2O_3 glass recovered from 10 and 23 GPa. They concluded that the structure of the recovered glass is very similar to that of the starting glass material with only a small amount of residual densification. This result is consistent with our results from samples recovered from 40 GPa.

B. X-ray diffraction study of g-As_2O_3

To better understand the local structural changes occurring across the transition observed in our Raman spectroscopy study, we performed an *in situ* DAC x-ray diffraction experiment. We collected data upon compression from 4 up to 32 GPa and on the pressure quenched sample.

The total structure factor at each pressure is presented in Fig. 7. The ambient pattern was previously collected outside the DAC by Mei *et al.*[14] The sharp weak peaks sitting on top of the broad amorphous diffraction pattern at high pressure

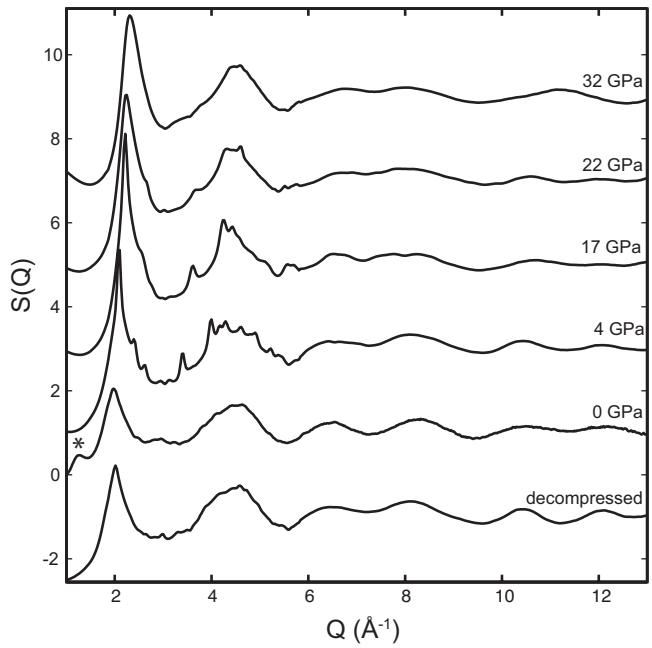

FIG. 7. Total structure factor $S(Q)$ before compression at ambient outside the diamond anvil cell (RP) and as a function of pressure *in situ* in the diamond anvil, and, finally, after decompression still in the diamond anvil cell. The high-pressure data are successively vertically shifted up by 2 units and the decompressed plot is shifted down by 2 units. The * on the room pressure data indicates the first sharp diffraction peak. The peak is not observed in any of the other patterns. The sharp peaks in the diffraction patterns at 4 and 17 GPa are due to a small amount (<1%) of arsenolite present in the sample.

are due to a small amount of crystalline arsenolite present in the glass. Arsenolite recrystallizes readily from the glass when a trace amount of moisture is present. The relative intensity of the peaks as compared to the broad features characteristic of the glass indicates that only a very small fraction (a few percent) of the sample is crystalline. The total structure factor of g-As_2O_3 shows a very weak first sharp diffraction peak, which disappears completely upon initial compression. This change would indicate a loss of medium range order upon compression of As_2O_3 glass, which is associated with the shrinkage of open regions in the network. Up to 17 GPa, the short-range order of the glass ($Q>5$ Å^{-1}) shows a general broadening of the oscillations. From 17 up to 32 GPa, some changes become noticeable as the oscillations are clearly different from that observed at ambient conditions. These changes indicate significant structural modifications in the short-range order of g-As_2O_3 at the highest pressures. The principal peak shifts from 1.97 to 2.31 Å^{-1} with an increase in height of almost 60%, which is associated with an increase in the amount of extended range order with pressure.[25]

The first peak in the pair distribution function shown in Fig. 8 results from the As-O bonds. The maximum in the distribution of As-O bond distance change from 1.79 ± 0.01 Å to 1.82 ± 0.01 Å between 0 and 32 GPa and returns to 1.79 ± 0.01 Å in the decompressed glass. The bond distances can be compared to the ambient As-O distances of c-As_2O_3 and m-As_2O_3 polymorphs, which are 1.79 and 1.72–1.81 Å, respectively. At ambient, the second peak arises from As-As correlations. The position of the peak slightly changes with pressure from 3.19 ± 0.01 Å down to 3.14 ± 0.01 Å at 32 GPa. These changes in the As-As and As-O distances indicate a decrease in the As-O-As angle from $126.0\pm1.0°$ at ambient to $120.0\pm1.0°$ at 32 GPa if we assume that the bond angle distribution is symmetric. Along with the shortening of the correlation distance, the distribu-

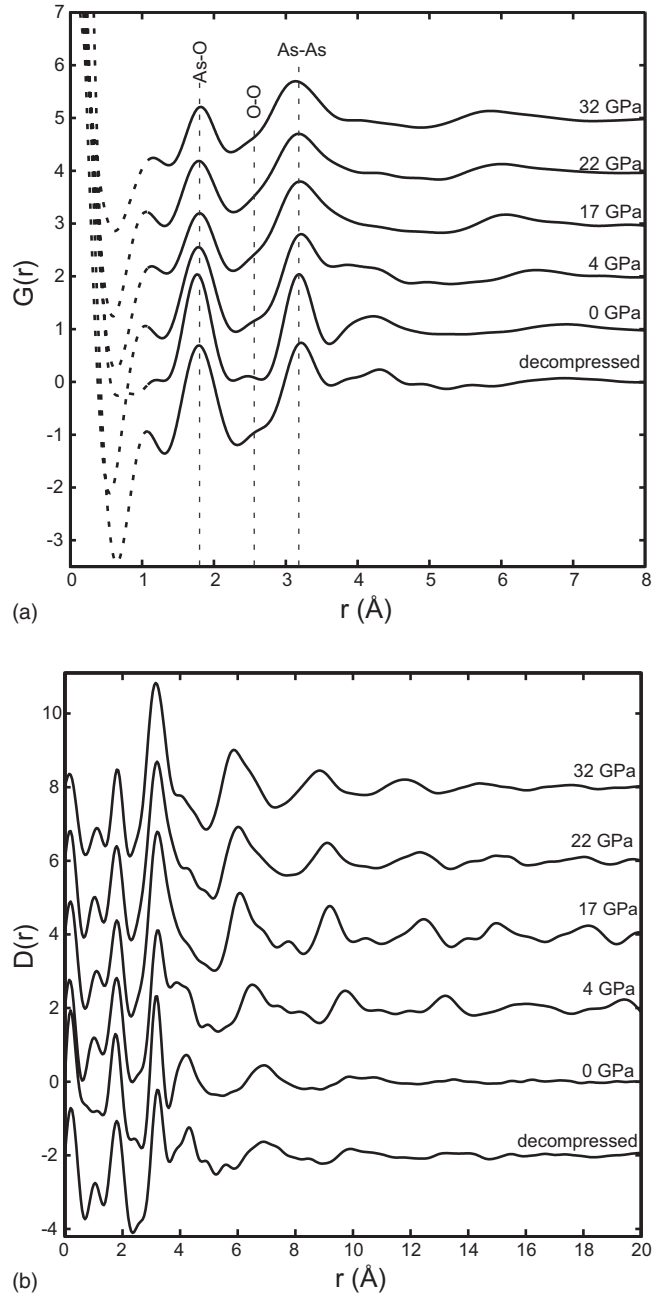

FIG. 8. (a) Total pair distribution function $G(r)$ and (b) differential distribution function $D(r)=4\pi\rho[G(r)-1]$ data for g-As_2O_3 before compression at ambient and as a function of pressure *in situ* in the diamond anvil cell at 4, 17, 22, and 32 GPa and after decompression still in the diamond anvil cell. The high-pressure data are successively vertically shifted up by 1 unit and the decompressed plot is shifted down by 1 unit.

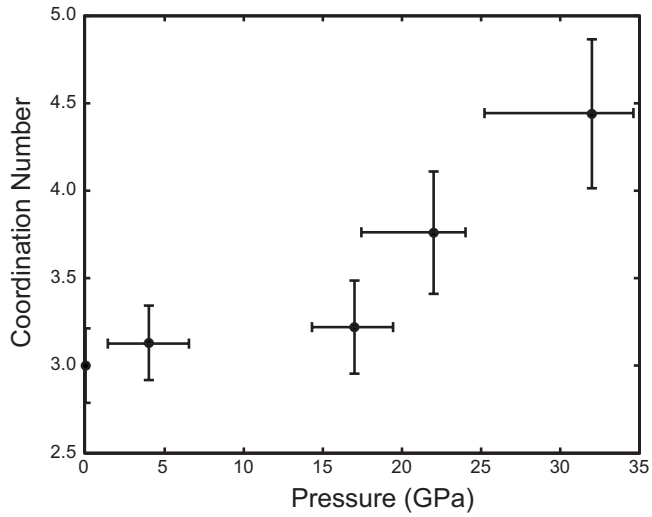

FIG. 9. Coordination number determined from the $G(r)$ data for g-As_2O_3 as a function of pressure.

tion noticeably broadens above 4 GPa. The broad peak centered at about 4 Å at ambient pressure merges with the 3.2 Å peak with increasing pressure, which indicates a less discrete distribution of As-As correlation distances. Upon pressure release, the total pair distribution function sharpens back up and the feature centered at 4 Å is once again resolved from the sharp 3.2 Å peak. Mei *et al.*[14] previously reported this observation for g-As_2O_3 samples quenched from 10 and 23 GPa.

The analysis of the total pair distribution function also provides the number of oxygen atoms in the first coordination shell of arsenic. We know from previous studies that arsenic is coordinated to three oxygens (AsO_3 units) at room pressure.[6,7] The integration under the As-O peak of $G(r)r^2$ assuming form factors independent of Q for the room pressure data gives a coordination number of 3.1 ± 0.2, which is very close to the previously reported value.[7] At 32 GPa, we obtain a coordination number of 4.6 ± 0.4. Therefore, there is a clear increase in the first coordination shell of As (Fig. 9). The plot indicates that only a very little change in the coordination number is observed up to 17 GPa. However, between 17 and 22 GPa, the coordination increased from 3.2 to almost 3.8.

Upon pressure release, the As coordination comes back to the initial configuration, wherein arsenic is surrounded by three oxygen in the first coordination shell.

IV. DISCUSSION

Our experimental data on As_2O_3 indicate that some structural changes occur in As_2O_3 glass between 17 and 30 GPa. The x-ray diffraction data indicate an increase in the coordination number of oxygen atoms around As above 17 GPa. The average coordination number goes from 3.0 ± 0.2 below 17 GPa to 4.6 ± 0.4 at 32 GPa.

The As-O bond length very slightly elongates with pressure and its distribution remains sharp. In As_2O_5, arsenic is in four- and sixfold coordinations with O [Fig. 1(c)]. However, the bond distance for each As-O environment is very different. The ^{IV}As-O bonds are 1.66–1.71 Å, while the ^{VI}As-O bonds are 1.78–1.82 Å. Our x-ray data clearly show that the As-O bond distance only increases and shows no indication of any short As-O bond corresponding to AsO_4 tetrahedra. This observation is consistent with a model wherein the As-O coordination changes from 3 to 6. The present analysis of the diffraction data does not show any obvious indication of four- or five-coordinated environments upon compression. The data do not show any plateau in the coordination number at 4, unlike in the case of GeO_2,[26] wherein the coordination plateaus at 5, or B_2O_3,[27] wherein the coordination plateaus at 4. This also indicates the absence of four-coordinated As.

The interpretation of the Raman data does not provide a direct indication of the coordination of As since the main peak position that is characteristic of octahedral AsO_6 in As_2O_5 is the peak at 568 cm^{-1} at ambient conditions.[28] This is comparable to the main peak in c-As_2O_3, which sits at about 560 cm^{-1}. In the As_2O_5 structure, the Raman peaks characteristic of AsO_4 tetrahedra are all fairly weak and lie mostly between 800 and 950 cm^{-1}.[28] From the analysis of the Raman intensity between 400 and 600 cm^{-1}, we very clearly see that there is no significant sign of any hysteresis in the transition, which is surprising since there is a large change in the structure of the glass with a change in coordination. We also observed that whether we start from an arsenolite crystalline sample (lowest potential energy phase) or a glass sample (higher potential energy phase), the transition occurs at the same pressure and the high density amorphous phase has the same structure according to Raman spectroscopy. Upon decompression, the sample recovered at room pressure from amorphization of arsenolite or pressure cycling of As_2O_3 glass is nearly identical to the As_2O_3 glass melt quenched at room pressure (Fig. 6 and 7). The only significant difference is in the Raman intensity of the peak at 377 cm^{-1}, which corresponds to cagelike As_4O_6 units.[20]

The transition in As_2O_3 can be compared to that in Bi_2O_3 and B_2O_3, both of which display a change in coordination upon compression.[29,27] Bi_2O_3 pressure amorphizes just like arsenolite and is recovered into an amorphous phase at ambient pressure.[29] The authors also reported a strong coloration of the Bi_2O_3 sample with pressure just like what we observed for As_2O_3 glass and arsenolite. The Bi_2O_3 sample changed from pale yellow at room pressure to bright red at 24 GPa. The study on B_2O_3 shows that the coordination shell changes progressively from three to four oxygen atoms surrounding each B upon compression.[27] The change is continuous and the data showed that the ratio of BO_3 to BO_4 changes with pressure.

V. CONCLUSION

In conclusion, we studied As_2O_3 up to 40 GPa. Above 20 GPa, we see the onset of a structural transformation that results in a complete loss of the Raman intensity above 400 cm^{-1} in g-As_2O_3 and c-As_2O_3 (arsenolite). c-As_2O_3 amorphizes above 20 GPa into a phase with a structure very consistent with that of g-As_2O_3 at the same pressure. The

Raman spectrum of the low-pressure glass is recovered upon decompression in both c-As_2O_3 and g-As_2O_3. The compression of m-As_2O_3 (claudetite) displayed no sign of amorphization. This observation is consistent with the previous reports, which suggested that the structure of g-As_2O_3 is much more closely related to that of c-As_2O_3 than that of m-As_2O_3.[6,7]

Based on the x-ray diffraction data collected on g-As_2O_3 as a function of pressure, it was concluded that an increase in the average As coordination number from three oxygen atoms to almost five at 32 GPa occurred. The increase in coordination appears to start only above 17 GPa. Based on the known crystalline As-O bond lengths, the transition is interpreted as a progressive change in the ratio of three-coordinated and six-coordinated As-O polyhedra without the formation of four-coordinated As. This transition is comparable to that of B_2O_3, which progressively changes from threefold to fourfold coordination. The amorphous-amorphous transition in As_2O_3 shows no hysteresis.

ACKNOWLEDGMENTS

R. T. Hart is thanked for his help during the initial stages of the study. The use of the Advanced Photon Source was supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38. This work was supported by the National Science Foundation (Chemistry Division, Grant No. 0612553), U.S. Department of Energy, and Carnegie/DOE Alliance Center (DOE-NNSA) CDAC.

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