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Local structure of As_2O_3 glass from first principles simulations

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ABSTRACT

We model As_2O_3 glass from the liquid state using *ab initio* molecular dynamics simulations and probe its atomic structure using various analyzing techniques. The model is almost free from coordination and chemical defects and has an average coordination number of 2.38. The AsO_3 pyramids are randomly connected *via* corner sharing to form the glass state. The glass network presents six membered hexagonal-like rings similar to those formed in the As_4O_6 molecules but isolated or complete As_4O_6 molecules do not exist. The glass state mainly consists of layer-like and incomplete As_4O_6-like structures.

1. Introduction

Arsenic trioxide (As_2O_3) with some practical applications [1,2] has three crystal forms: arsenolite, claudetite-I, and claudetite-II [3–5] (see Fig. 1). Arsenolite has a cubic symmetry and consists of adamantine structured As_4O_6 molecules. Both claudetite-I and claudetite-II have a monoclinic lattice and are built of infinite As_2O_3 layers. The key local structural unit of all these crystalline phases is AsO_3 pyramids.

As_2O_3 is known as a good glass former too. The basic structural component of glassy As_2O_3 (*g*-As_2O_3) is also AsO_3 pyramids, similar to the crystalline phases. However it is still not well known how they are linked each other to form a glass state. Experiments proposed different structural arrangements of AsO_3 pyramids for *g*-As_2O_3. The first experiment based on Raman spectroscopy indicated that *g*-As_2O_3 could be characterized as a distorted layer-like monoclinic crystalline phase, claudetite [6]. However Raman and infrared data did not confirm a disordered layer-like state and instead proposed a continuous random network of AsO_3 pyramidal units [7]. In another infrared and Raman study, it was suggested that the glass phase was composed of the pyramidal units that were corner connected to form a continuous random network that has both layer-like and As_4O_6 molecular-like order [8]. According to x-ray diffraction experiment [9], *g*-As_2O_3 consisted of three membered rings of AsO_3 pyramids. On the other hand, the neutron diffraction study [10] proposed a random network of corner-sharing AsO_3 pyramids and the existence of three membered rings, similar to those formed in the As_4O_6 molecules (indeed As_4O_6 molecules has six membered hexagonal-like rings but in these experiments they are refereed as a three membered rings of AsO_3 pyramids). The physical origin of the discrepancy reported in these experiments is not clear but might be related to some experimental processes such as quenching rate, sample stoichiometry *etc.*

Alternative to experiments, computer simulations have been proven to be a powerful technique to investigate materials, in particular at the atomistic level. They can provide information that cannot be openly exposed in experiments. Actually it is quite surprising that there has been no attempt to prompt the atomic structure of *g*-As_2O_3 from quantum mechanical simulations, to our knowledge. Lack of such an investigation stimulates us to focus on this material. Here we generate *g*-As_2O_3 from the liquid state using an *ab initio* molecular dynamics (MD) technique. Our findings support the layer-like configurations and the presence of incomplete As_4O_6-like structures.

2. Methodology

We employed the SIESTA *ab initio* code [11] to generate the glass model. The SIESTA is based on the first-principles pseudopotential method within the density functional theory. The pseudopotentials were due to the Troullier and Martins scheme [12]. The exchange correlation energy was estimated by the generalized gradient approximation (GGA) of PBE [13]. The double zeta plus polarized orbitals were chosen as a basis set. For the Brillouin zone integration, Γ point sampling was used. The NPT (constant number of atoms, constant pressure, and constant temperature) ensemble was selected to perform the MD simulations. Each time step of the MD simulations is one femtosecond (fs). The velocity rescaling approach was employed to control temperature. The volume of the supercell at zero pressure was equilibrated using the Parrinello Rahman technique [14] but shear deformations were not allowed. A randomly distributed amorphous configuration used to model amorphous Si_2N_3 was chosen as a starting structure. Si and N

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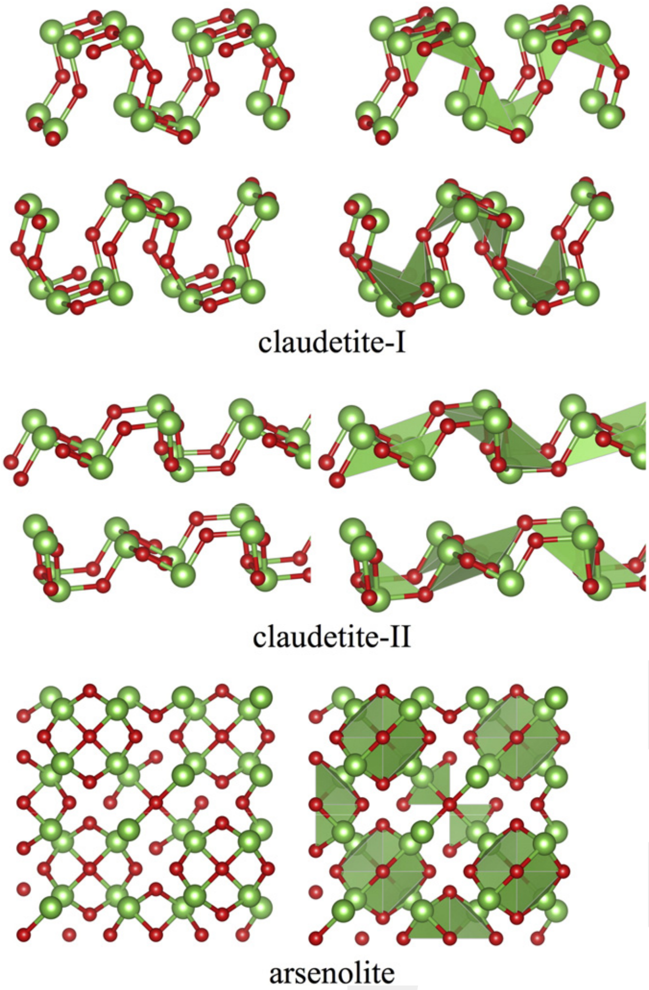

Fig. 1. Ball and stick and polyhedral representation of crystalline As_2O_3 phases.

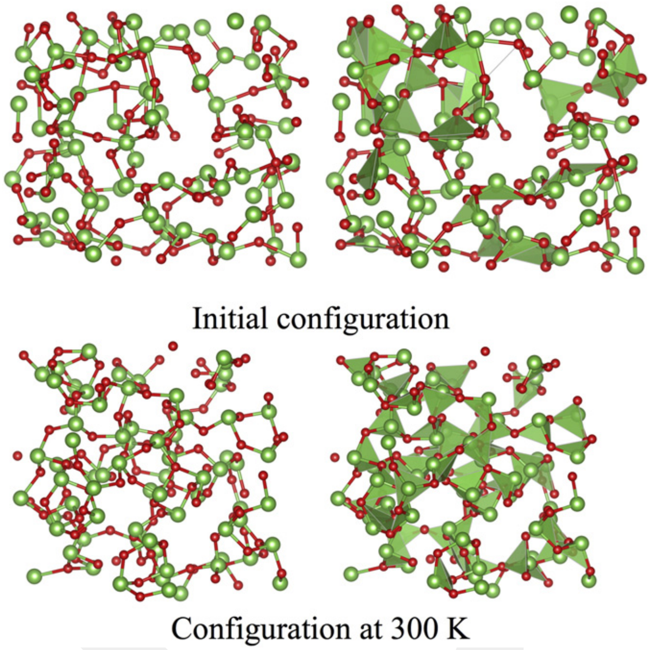

Fig. 2. Ball and stick and polyhedral representation of the initial and glass models.

atoms were substituted by As and O atoms respectively (see Fig. 2). The initial system had 180 atoms (72 As atoms and 108 O atoms) with the lattice parameters of 15.17 Å 12.74 Å and 11.98 Å and presented some O–O homopolar bonds as shown in Fig. 3. The supercell was subjected to a high temperature of 3500 K for 4.0 ps and then the system was cooled to 1000 K in 5.0 ps. At this temperature, it was thermalized for 10.0 ps. The liquid structure was quenched to 300 K in a period of 35.0 ps. The lattice parameters of the supercell at 300 K were 15.604953 Å, 14.698795 Å and 15.455896 Å. The ISAACS [15] and VESTA [16] programs were used to analyze the glass structure.

3. Results and discussion

Fig. 3 shows the computed partial pair distribution functions (PPDFs) at selected pressure, an important parameter to partly reveal the structural features of the system.

The most visible modification of the PPDFs is the sharpening of the first peaks with decreasing temperature, indicating a more ordered structure. The position of these peaks is not significantly changed by temperature. At 300 K the first neighbor separation of As–O is located at 1.88 Å, which is somehow larger than the experimental values of 1.79 Å [17,18] and 1.775 Å [10] reported for g-As_2O_3 and 1.79 Å As–O bond distance in the arsenolite crystal and 1.72–1.81 Å bond distances in the claudetite phases [3–5]. The main peak As–As correlation is placed at 3.27 Å, again slightly larger than the experimental value of 3.19 Å [17,18]. The feeble peak around 2.54 Å in the As–As distribution implies the existence of As–As homopolar bonds. A careful evaluation of the system validates that only two As atoms involve homopolar bonds (~2.8%). The O–O correlation is located at 2.80 Å. The slight disagreement between experiments and the present simulation can be attributed to the GGA calculation in which the bond distances are slightly

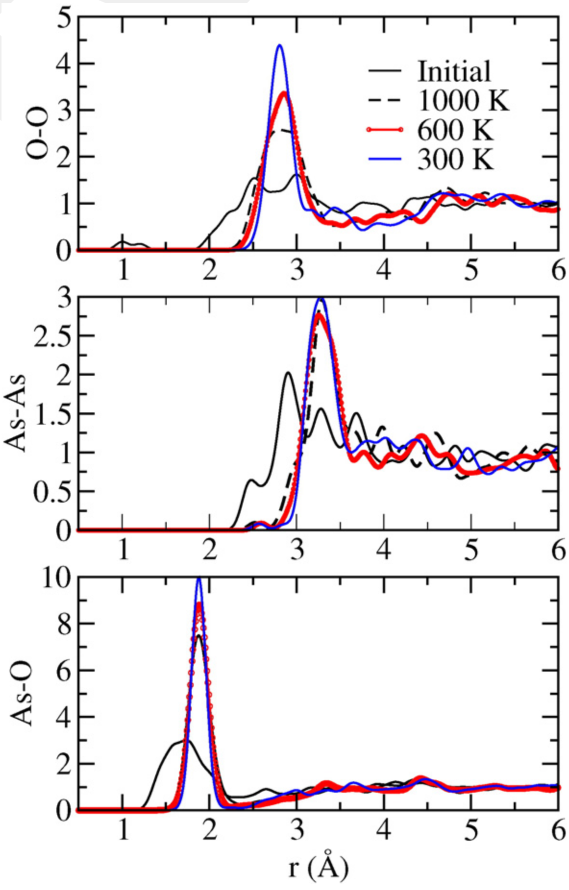

Fig. 3. Partial pair distribution functions.

overestimated [19]. In order to see whether the glass state is locally similar to any known crystalline phase of As_2O_3, we plot the total PDF of the glass and crystalline phases in Fig. 4. The lattice parameters and the atomic positions in Refs [3–5] are used to calculate the PDFs and the total PDF of the glass model was shifted by an amount of 0.1 Å to lower distances for a clear evaluation. Reasonable resemblance in the PDF of the glass and claudetite phases up to around 3.5 Å and the lack of a pronounced peak around 3.2 Å in the PDF of the glass phase as in arsenolite might offer some evidence that the local structural arrangements of the glass state can be represented by distorted layer-like monoclinic phases as pointed out in Ref. [6].

In order to describe the short-range order in details, we also estimate the coordination number (CN) as a function of temperature using the cutoff distances of 2.43–2.23 Å for As–O correlations and 2.66–2.71 Å for As–As correlations depending on temperature. The system at all temperature range has predominantly threefold coordinated As atoms (~88–97%) and twofold coordinated O atoms (~89–96%). The average coordination of the liquid state at 1000 K and the glass state is estimated to be 2.42 and 2.38, respectively. This finding means that the average CN is not very sensitive to temperature. The fraction of defects (fourfold and twofold for As atoms and onefold and threefold for O atoms) during the quenching from 1000 K is provided in Fig. 5. Noted that the glassy As_2O_3 system presents a small amount of coordination defects (~1.4-2.8%) and chemical defect (~2.8 As–As) compared to As-based chalcogenides such as As_2Se_3 or As_2S_3 [20–27]. Such a different behavior can be attributed to the iconicity of these materials because it seems that the defects, in particular, the fourfold As, correlate with the number of homopolar bonds [20]. The oxide glassy systems are more ionic and thus chemical disorder is much unfavorable while the formation of wrong bonds is likely, with a small penalty, in some non-oxide glasses though they are not energetically favorable.

The bond angle distribution functions (BADFs) given in Fig. 6 might deliver additional suggestions regarding the short-range order of g-As_2O_3. For the comparison purpose, we also calculated the BADFs of the crystal forms of As_2O_3 using the lattice parameters and the atomic positions of Refs [3–5]. The O–As–O distribution has a main peak around 96°, close to experimental prediction of 97.3° [10] for g-As_2O_3. Note that this value is also rather comparable with the O–As–O angles of about 96° produced in both claudetite-I and claudetite-II and of 98° formed in arsenolite. On the other hand, the As–O–As distribution has two strong peaks at 114° and 123°, two subpeaks at 95° and 133° and a shoulder at 126°. The angles at 95° is due to the edge-sharing units (fourfold rings, see below), which do not exist in the crystalline phases. Claudetite-I has peaks at 123°, 126° and 133° in the As–O–As distribution while claudetite-II has the angles of 124° and 128°. The As–O–As peak for arsenolite is located at 128°. The angles of the crystalline phases are relatively close to each other and thus a small distortion in these crystalline phases can easily produce any of these angles. Consequently, the BADFs appear to be not a good parameter to undoubtedly categorize the local structural arrangements of g-As_2O_3.

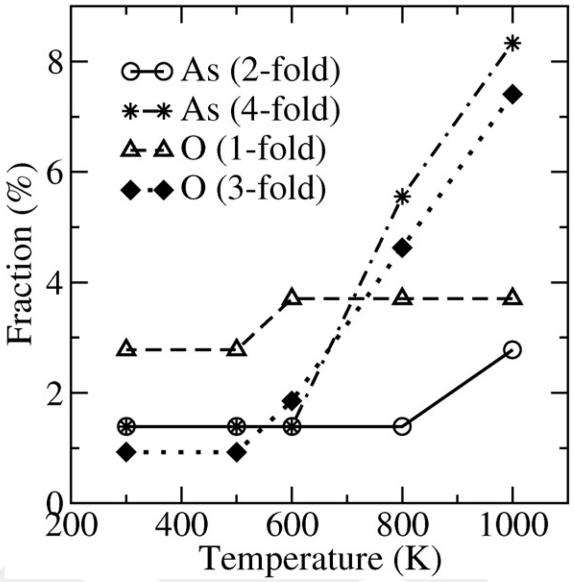

Fig. 5. Fraction of coordination defects as a function of temperature.

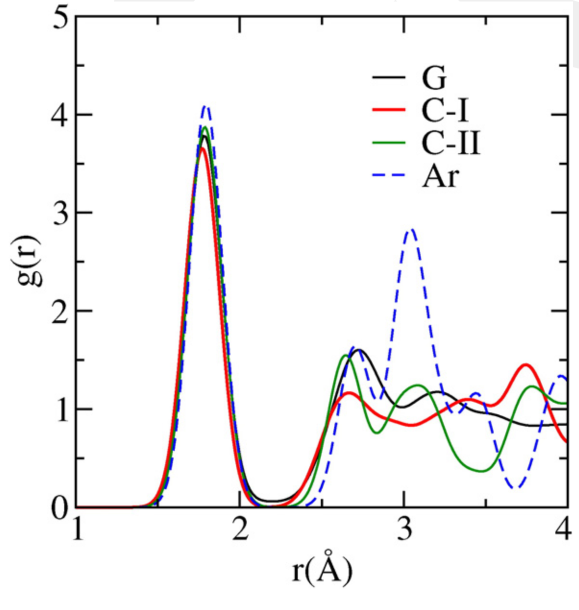

Fig. 4. Total pair distribution function of the glass and crystalline phases. G = glass, C-I = claudetite-I, C-II = claudetite-II, and Ar = arsenolite.

So far all structural analysis techniques do not allow us to have a perfect atomic level description of the glass state, in particular the linkage of AsO_3 pyramids. The major difference between the claudetite phases and the arsenolite crystal is the ring distribution. Namely, the claudetite phases have twelve membered rings while arsenolite has six membered rings. Consequently the rings statistics analysis of the glass configuration might be helpful in determining the connectivity of AsO_3 pyramids. The primitive ring distribution is illustrated in Fig. 7. As can be seen from the figure, both six and twelve membered rings exist in the glass state but the fraction of hexagonal rings is a factor of about five larger than

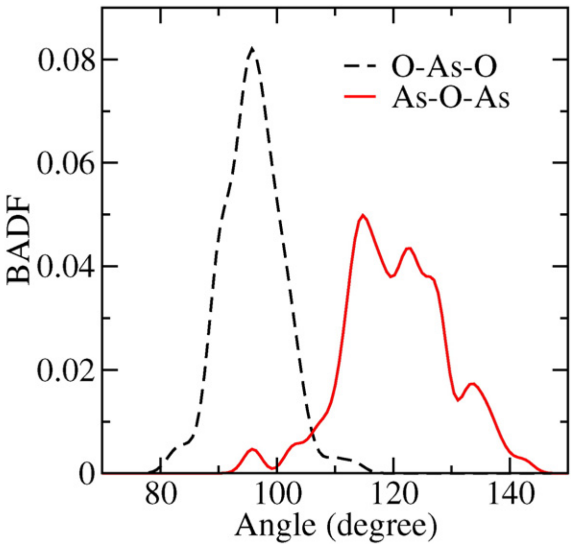

Fig. 6. The bond angle distribution functions.

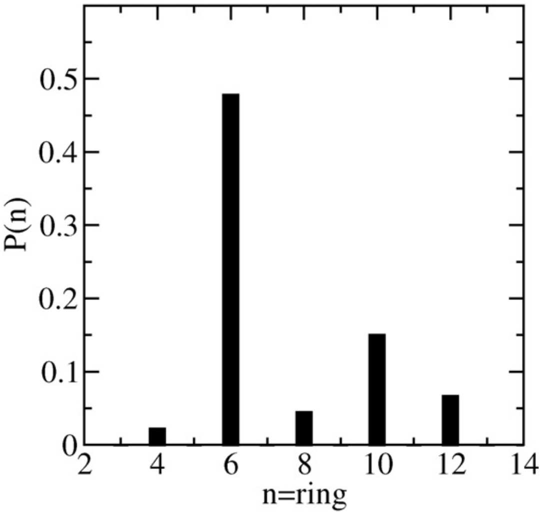

Fig. 7. Ring distribution of the glass state.

that of twelve membered rings. In addition to these rings, there exist four and ten membered rings with small frequencies in the model and none of them is presented in the crystalline phases. The six membered rings are similar to what has been formed in the As_4O_6 molecules. This finding supports experimental studies. It should be noted here that the isolated or complete As_4O_6 molecules do not survive in the glass state. The fourfold ring refers the presence of the edge-sharing units in the glass state. The ring static analysis reveals that the glass state carries *partially* the signature of both layer-like monoclinic phases and incomplete As_4O_6 molecules.

One of the advantages of simulations is that the computer-generated models can be easily visualized and some supportive information/evidence at the atomistic level including the connectivity of atoms/clusters can be visibly obtainable. The ball and stick and polyhedral representations of the glass model are given in Fig. 2. As can be understood from the figure, the AsO_3 pyramids are randomly connected *via* corner sharing as suggested in the experiments and the *g*-As_2O_3 has layer-like configurations.

4. Conclusions

A glass model of As_2O_3 has been generated from its liquid state using an *ab initio* MD technique. The model exhibits a negligible amount of coordination and chemical defects. The AsO_3 pyramids are randomly corner connected to structure the glass state. The six membered hexagonal-like rings similar to those shaped in the As_4O_6 molecules are also presented in the model but complete As_4O_6 molecules do not survive. Consequently the glass state carries *partially* the trace of both layer-like monoclinic phases and incomplete As_4O_6-like molecules. It should be noted here that all conclusions are based on a 216-atom model generated using a fast quench rate relative to experiments. The small amount of topological and chemical defects and the formation of incomplete As_4O_6-like molecules might be related to both the size of the supercell and/or the short simulation time. For a larger system and a long simulation time, different amount of structural and chemical disorders can be anticipated. In order to eliminate these ambiguities, it is, of course, necessary to repeat this type of study on a larger system for a longer simulation time.

Acknowledgments

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