Densification of amorphous boron under pressure

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The densification mechanism of amorphous boron under pressure is investigated using a constant pressure *ab initio* technique and found to be associated with two consecutive amorphous-to-amorphous phase transformations. Amorphous boron gradually transforms into a high density amorphous phase, followed by a first order phase transformation into another high density amorphous state. The high density amorphous phases of boron are not quenchable to ambient pressure. Most quasimolecular B_{12} icosahedra in the model are found to be stable at the highest the theoretical pressure of 280 GPa reached in the present work and thus the phase transformations are principally due to the re-structural arrangements in the parts of the model connecting B_{12} icosahedra.

1. Introduction

Boron is an important element because of its superior physical properties and numerous technological applications. Even though it was discovered > 200 years ago, it still stays as the most puzzling element [1,2]. Due to its complex structure, its ground state is still not well established yet. Initially β-rhombohedral (B_{106}) was assigned as the ground state structure because it was frequently perceived in experiments [3–7]. Recent investigations proposed two different phases as a candidate for its ground state structure. The first one is the well-known form of boron, α-rhombohedral (B_{12}) [2]. The second one is a new crystal structure called as τ-B (an orthorhombic structure with the space group of *Cmcm*) having 210 atoms in the unitcell [8]. The quantum mechanical simulations suggest that the τ-B phase is more stable than β-rhombohedral by 13.8 meV/atom and more stable than α-rhombohedral by 9.5 meV/atom [8]. Yet this new crystalline structure has been questioned in later studies [9,10].

Researchers have made considerable efforts to uncover the pressure-temperature phase diagram of boron [11–17]. According to the experimental phase diagram, α-rhombohedral (B_{12}), β-rhombohedral, γ-orthorhombic (B_{28}), δ-tetragonal (B_{50}, T-50 or T52), ε-rhombohedral (B_{15}, isostructural to boron carbide $B_{13}C_2$) can form at ambient and high pressure and temperature conditions. An α-Ga type structure was considered as a candidate for boron above 90 GPa [17]. In addition to these crystalline phases, a pressure-induced amorphization of β-rhombohedral at a high pressure of 100 GPa was reported in an experiment [18]. This amorphous phase was quenchable to ambient pressure.

Amorphous boron (*a*-B) also exists and can be synthesized using different experimental procedures [19–28]. Although the microstructure of *a*-B is assumed to be comparable with that of the crystalline

phases, its local structure still remains controversy as well. The β-rhombohedral-like structure [25–27], α-tetrahedral-like configuration [28] and a transition state between α- and β-rhombohedral [24] were suggested for *a*-B. In a recent *ab initio* simulation, a structure comparable to the α-rhombohedral-like phase was projected for *a*-B [29].

An experiment work focused on the high-pressure behavior of *a*-B [11] and *a*-B → α-rhombohedral, *a*-B → β-rhombohedral and *a*-B → δ-tetragonal phase transformations were observed depending on the temperature (1400–1500 K) and pressure (11–15 GPa) conditions applied. To our knowledge, no other research has been performed to better understand its response to high pressure so far. Limited information regarding *a*-B under pressure inspires us to execute this simulation. Here using a constant pressure *ab initio* method, we compress an *a*-B model and find two amorphous to amorphous phase transformations: Amorphous boron transforms progressively to a high-density amorphous (HDA) phase up to 230 GPa at which point it presents a first order phase transformation into another high-density amorphous phase having a mean coordination number of 7.35.

2. Methodology

A density functional theory (DFT) code, SIESTA [30], was used in the present work to investigate the high-pressure behavior of *a*-B. We used the Troullier and Martins scheme to contract pseudopotentials [31] and a generalized gradient approximation (GGA) [32,33] to evaluate the exchange correlation energy. The double zeta basis set was used. The Brillouin zone integration was done at Γ point. The iso-enthalpic-isobaric ensemble using the Parrinello-Rahman method [34] and power quenching technique was selected to perform the present simulations. At high-pressures, the model was relaxed using the force
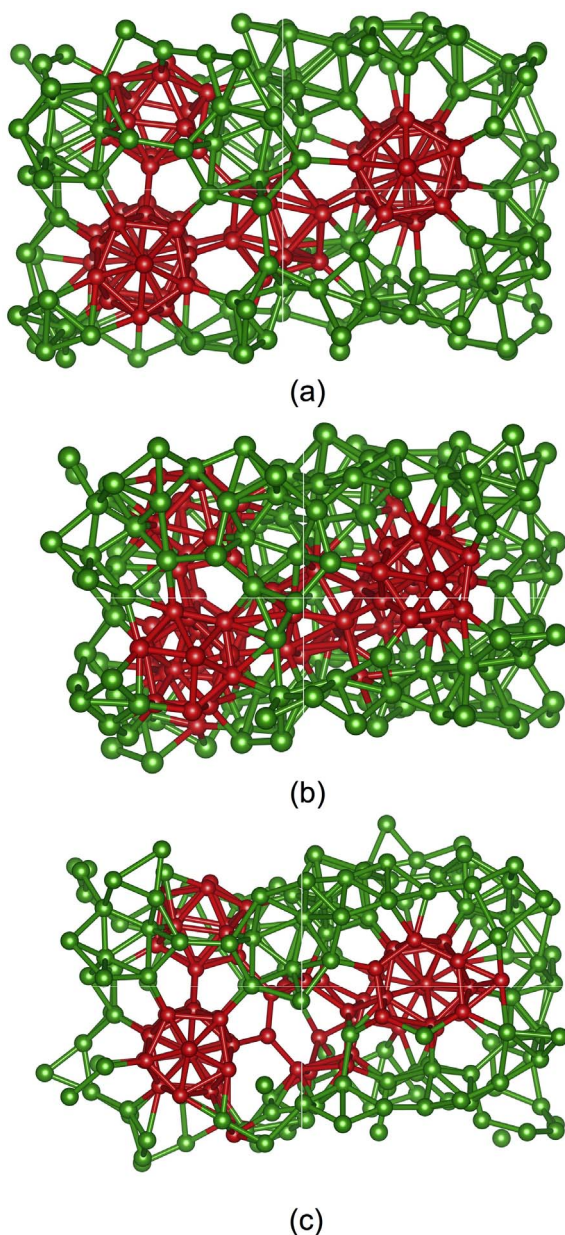
Fig. 1. (a) Uncompressed model (b) VHDA model at 230 GPa (c) Decompressed model. For clarity and to see how the B_{12} icosahedra change under pressure, the atoms of some ideal B_{12} icosahedra in the uncompressed model are represented by a different color.

criteria of 0.01 eV/Å. Some of structural analyses were carried out using the ISAACS [35] and VESTA [36] programs. The amorphous network having 224 atoms was created using the same DFT code and the same simulation parameters in our previous investigation [29] in which the melt and quench method and the isothermal-isobaric ensemble were used. The model mainly consisted of B_{12} icosahedra as shown in Fig. 1 In contrast to the earlier predictions [24–28], however, it was found to be structurally close to the α-rhombohedral boron (see Ref. 29 for more information). The origin of the contradictory observations between the present and previous investigations was attributed to impurities. Namely our model was 100% pure whist the samples used in experiments were not. Note that boron is very sensitive to contaminations and hence it is not easy to have boron samples with negligible amount of impurities in experiments. Consequently we believe that our model represents the local structure of pure *a*-B. Yet careful investigations on the influences of impurities on the local structure of *a*-B will be necessary to clarify this issue.
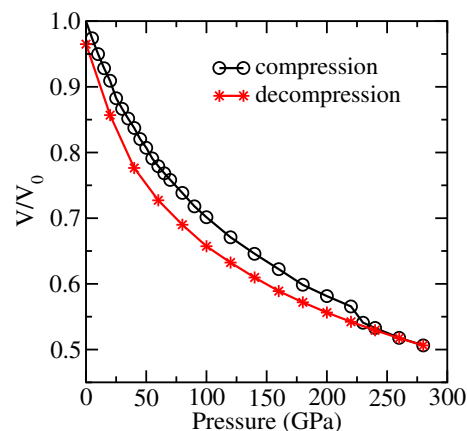

Fig. 2. Variation of volume under pressure.

3. Results

Fig. 2 illustrates the modification of the normalized volume with the application of pressure. The change in the volume is mostly smooth at pressures of up to 230 GPa at which point it shows a small discontinuity. The volume collapse at this pressure is about 5% and might imply a first order-like phase transformation in *a*-B. On pressure release from 280 GPa, a hysteretic behavior is observed but a structure slightly denser than the original one is attained at zero-pressure, demonstrating that a pressure-induced permanent densification in *a*-B is trivially small.

In order to uncover the pressure-induced restructurings in the model, we next probe real space pair correlation functions (PCFs), one of the most commonly used techniques to resolve the structural features of materials at ambient and high pressure and temperature conditions, and present them in Fig. 3. The PCFs exhibit an obvious short-range order and the absence of a long-range order during the entire compression process. This finding reflects the fact that *a*-B still retains its disorder nature at the highest-pressure explored at the present work and experiences amorphous-to-amorphous phase transformation(s).

From the PCFs analysis, we also perceive that the first neighbor separation gradually decreases with increasing pressure and accompanied by the volume collapse at 230 GPa it sharply increases to a larger value as shown in Fig. 4. A sudden enlargement in the mean bond distance is related to the substantial structural rearrangements in the model. Upon decompression, the first neighbor distance continuously increases and reaches the value of the initial model, indicating that the recovered amorphous arrangement is structurally close to the
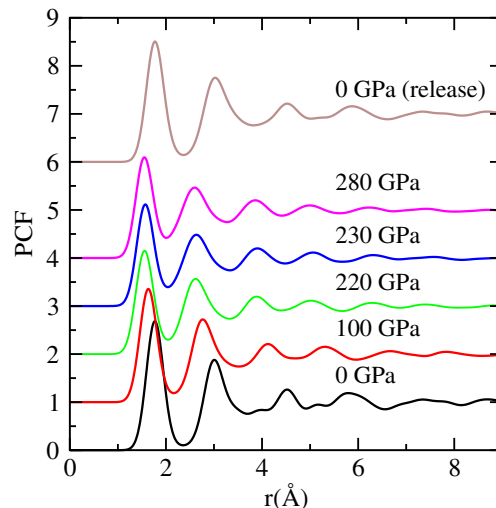

Fig. 3. Pair correlation function (PCF).