



Liquid boron and amorphous boron: An ab initio molecular dynamics study



Murat Durandurdu

Department of Materials Science & Nanotechnology Engineering, Abdullah Gül University, Kayseri 38080, Turkey

ARTICLE INFO

Article history:

Received 23 January 2015

Received in revised form 24 February 2015

Accepted 8 March 2015

Available online 14 March 2015

Keywords:

Boron;

Amorphous;

Liquid;

B_{12} icosahedra

ABSTRACT

The atomic structure of liquid and amorphous boron is investigated using an ab initio molecular dynamics technique. Liquid and amorphous states are found to have notably different microstructures and an average coordination number. Ideal and defective pentagonal pyramidal polyhedrons are the primary building unit of liquid boron but B_{12} icosahedra do not exist in the liquid state. During the rapid solidification, more ideal pentagonal pyramids develop progressively, resulting into a gradual formation of B_{12} icosahedra. On the basis of our findings, the atomic packing of pure amorphous boron is proposed to be somewhat close to that of the α -rhombohedral phase in contrast to the previous suggestions.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Boron is one of the most fascinating and complex elements exhibiting different varieties of novel and unusual properties such as having many physical forms (called allotropes), neutron absorption, hardness, resistivity to heat, and changing bonding character by small impurities [1,2]. Considerable efforts have been made to understand pure boron but it still remains as a mystery element [3,4]. Because of its unique physical and mechanical properties, it has a wide range of technological applications [5–7].

Several different crystalline phases have been proposed for boron but so far experimental and theoretical studies revealed a few crystalline forms at ambient and high temperature and pressure conditions for pure boron. They are α -rhombohedral (B_{12}) [8], β -rhombohedral (B_{106}) [9], γ -orthorhombic (B_{28}) [10], tetragonal (B_{192}) [11], tetragonal (B_{52}) [12], α -Ga crystal structure (B_2) [10], and ϵ -rhombohedral (B_{15} , isostructural to boron carbide $B_{13}C_2$ if carbon atoms are substituted by boron ones) [13]. These crystalline polymorphous commonly have a very complex structure but all have one thing in common: their principal building blocks are dominated by the quasimolecular B_{12} icosahedra.

In addition to the crystalline modifications, amorphous form of boron also exists and can be prepared using a variety of experimental techniques such as physical vapor deposition [14], chemical vapor deposition [15], pyrolysis [16], or rapid cooling [17]. The atomic packing of amorphous boron is believed to be similar to the crystalline phases, that is, the key local structural units are due to the randomly packed the B_{12} icosahedra without a long-range order [18,19].

The short-range order of liquid boron remains unspecified as well because of some difficulties to handle it experimentally [20,21]. Liquid boron is indeed very reactive with any container and hence limited experimental investigations can be found in the literature. Regrettably the microstructure of liquid boron could not be unambiguously determined in these experiments but it was argued that its short-range structural arrangement is essentially similar to that of crystalline and amorphous phases [21]. To our knowledge only two theoretical investigations [20, 22] based upon ab initio molecular dynamics (MD) simulations were employed to uncover the microstructure of the liquid state. Both studies found that the B_{12} icosahedrons do not persist in liquid boron but they reported a contradictory finding about the survival of pentagonal pyramids. Therefore additional reliable simulations are unquestionably desirable to clear the inconsistent predictions and to reveal the true atomic structure of the liquid state of this important element.

Here we perform ab initio MD simulations to systematically explore the atomistic arrangement of not only liquid boron but also amorphous boron. Our simulations provide substantial and novel information regarding their microstructures. Ideal and incomplete pentagonal pyramids are the central building unit of the liquid state. However, the B_{12} icosahedra do not survive in it but they form gradually during the rapid solidification process. Amorphous boron is proposed to be locally similar with the α -rhombohedral phase.

2. Methodology

To investigate the atomic structure of the liquid boron and amorphous boron, we used the SIESTA ab initio code [23] within the frame of the density functional theory. The method adopts a localized linear combination of numerical atomic orbitals. Norm-conserving nonlocal

E-mail address: murat.durandurdu@agu.edu.tr

pseudopotential was generated by Troullier and Martins scheme [24]. To calculate the exchange correlation energy we used the generalized gradient approximation that implemented Becke gradient exchange functional [25] and Lee, Yang, and Parr correlation functional [26]. A double- ξ basis set was employed for the valence electrons. A real space grid equivalent to a cut-off of 120 Ry was adopted to compute the electron density, the local part of the pseudopotential, and the Hartree and the exchange–correlation potential. The MD simulations were done using the NPT (constant number of atoms, constant pressure, and constant temperature) ensemble. We had a supercell having 224 atoms and periodic boundary conditions. Only Γ point was applied for the Brillouin zone integration. The orthorhombic boron with the simulation box lengths $A = 10.108 \text{ \AA}$, $B = 11.24 \text{ \AA}$ and $C = 13.974 \text{ \AA}$ was melted at 4500 K for 10.0 ps. The liquid state was quickly cooled to 2500 K in 3.5 ps. At this temperature, the liquid state was thermalized for 20 ps and then it was gradually annealed to 300 K using the cooling rate of 0.05 K/fs. A time step of 1 fs was used. The total simulation time was more than 85.0 ps. Temperature was controlled using the velocity rescaling method. The volume of the supercell at zero pressure was equilibrated via the Parrinello Rahman technique [27] without allowing shear deformation. The final dimensions of the supercell at 300 K were $A = 10.278418 \text{ \AA}$, $B = 16.590147 \text{ \AA}$ and $C = 10.649009 \text{ \AA}$. The last 1000 MD steps of the liquid state were gathered for the structural analyses. During the cooling process, a few configurations around some specific temperatures were used for the analyses.

3. Results and discussion

In order to confirm that the simulation time is long enough to capture the dynamics of the liquid state at 2500 K, the mean square displacement (MSD) shown in Fig. 1 is studied for the last 1000 MD steps using the isaacs program [28]. The MSD is proportional to t^2 up to 75 fs, representing a ballistic motion. Beyond that point, it displays a linear behavior, specifying a diffuse state. The linear functioning of the MSD additionally implies a state of equilibrium. Fitting the diffusive part with a straight line and using the Einstein relation, $\langle (r(t) - r(0))^2 \rangle = 6tD$, the diffusion constant D is computed to be about $1.3 \times 10^{-4} \text{ cm}^2/\text{s}$.

The temperature dependence of pair distribution function (PDF) is presented in Fig. 2. The most noticeable change in the PDF is the sharpening of the peaks with decreasing temperature, demonstrating more order in the structure. On the other hand, the position of all peaks is found to be not too sensitive to temperature. The first, second and third peaks of the liquid phase at 2500 K are located at 1.75 \AA , 3.14 \AA and 4.65 \AA , respectively, which are in good agreement with the experimental results of 1.76(8) \AA , 3.15(6) \AA and 4.7 \AA found for the liquid boron at 2600 K (2400 K) (Ref. 21). At 300 K, that is, for amorphous boron, the first three peaks are placed at 1.78 \AA , 3.02 \AA and 4.54 \AA , respectively, which are again sensibly in accordance with the experimental values of 1.80 \AA , 2.93 \AA , and 4.38 \AA [29]. It can be seen that the

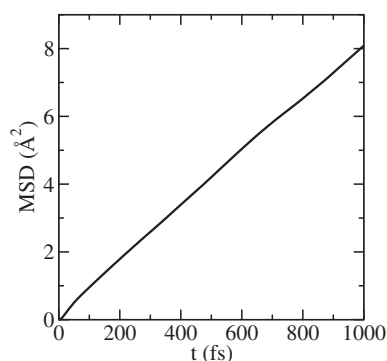


Fig. 1. The mean square displacement (MSD).

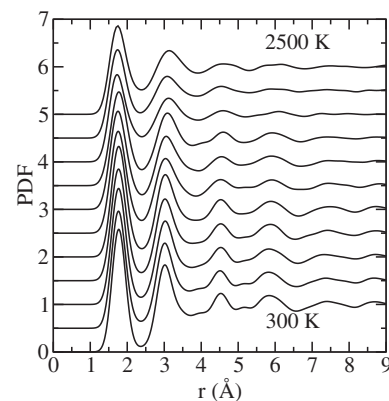


Fig. 2. Pair distribution function as a function of temperature.

model lacks long-range order since there is no clear peak beyond 7.0 \AA and the PDF approaches to one. Yet the slightly pronounced peaks around 3.0 \AA , 4.5 \AA and 6.0 \AA might be interpreted as the existence of medium-range order in the amorphous boron. A careful analysis suggests that the peaks start to be noticeable when B_{12} icosahedra form in the system near 1900 K and they become more pronounced as more ideal B_{12} icosahedra develop. Therefore it can be concluded that the medium-range order correlates with B_{12} icosahedra in the amorphous boron.

To have more complete information about the short-range order of liquid boron and amorphous boron, another critical parameter, average coordination number (CN), is studied as a function of temperature (Fig. 3). The CN gradually increases with decreasing temperature and reaches approximately a constant value of 6.1 around 1200 K. The CN of liquid boron at 2500 K is calculated to be 5.5, which is somehow lower than the experimental results of 5.8 ± 1 at 2600 K or 6.0 at 2400 K (Ref. 21) and the previous theoretical predictions of 6.0 [20, 22]. On the other hand, the CN of amorphous morphology at 300 K is 6.1, fairly close to the experimental value of 6.3 [29]. The distribution of CN is also evaluated and presented in Fig. 4. At 2500 K, the five- and sixfold coordinated atoms are dominated with a frequency of about 30%. With decreasing temperature, the fraction of sixfold coordination increases monotonically and touches the maximum value of about 65% around 1200 K. The parallel to the increase in the sixfold coordination, the fraction of fivefold and fourfold (12% at 2500 K) coordination declines during the solidification. Surprisingly, the sevenfold-coordinated atoms are found to be less responsive to temperature. About 16% and 15% of atoms are sevenfold coordinated at 2500 K and 300 K, respectively.

Voronoi polyhedral method [30] is used to further explore the structure at different temperatures. This technique is a practical approach to differentiate the short-range order in disordered systems. A Voronoi

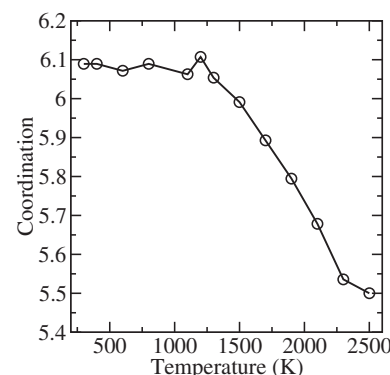


Fig. 3. Temperature dependence of coordination number (CN).

Download English Version:

<https://daneshyari.com/en/article/7900940>

Download Persian Version:

<https://daneshyari.com/article/7900940>

[Daneshyari.com](https://daneshyari.com)