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Superhard phases of B_2O: An isoelectronic compound of diamond[☆]

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ABSTRACT

Using *ab initio* crystal structure prediction, we have predicted several polytypic structures for B_2O under high pressure. The structural parameters, total energies, electronic properties and hardness of the obtained structures have been studied using pseudopotential density functional theory within the local density approximation. We find that a monoclinic *C*2/*m* phase is the most energetically favorable structure; however, its X-ray diffraction pattern could not fit into the experimental data [J. Mater. Sci. Lett. 6 (1987) 683]. Instead, X-ray diffraction patterns of the energetically less stable tetragonal $P4_2mc$ and designed *P*-4*m*2 structures are in overall agreement with the experimental data. The simulated hardness of $P4_2mc$ and *P*-4*m*2 are 40.5 and 44.8 GPa, respectively, in accordance with the experimental values of 33.5~40.5 GPa.

1. Introduction

Experimentally, (nano)diamond remains the hardest known substance with the hardness reaching 100–160 GPa. The experimental and theoretical efforts are focused on the synthesizing and designing of new superhard material due to its importance in fundamental science and technological applications. Several sp^3 bonded B—C—N compounds have recently been synthesized by high temperature and high pressure method, and labeled as “diamond-like” or “cubic (*c*-),” such as symmetrical and isoelectronic compounds: *c*-BN [1], and *c*-BC_xN ($x = 1$–6) [2–6], and asymmetrical and non-isoelectronic compounds BC_3 [7], BC_5 [8], and B_2CN [9]. These densely packed, three-dimensional and strongly covalent bonded compounds have short bond length, low ionicity, high bulk modulus and high hardness.

Furthermore, an isoelectronic and asymmetrical compound of diamond, B_2O, was experimentally synthesized by Endo et al. through the reaction of BP with oxygen [10] under conditions of 2.0–6.0 GPa and 800–1350 °C, which was supplied by the thermal decomposition of CrO_3 into CrO_2. The Vickers' microhardness of the sintered sample is in the range of 33.5 to 40.5 GPa. From the measured X-ray diffraction data (XRD), Endo et al. proposed a possible crystal structure consisting of diamond lattice sites with planes of O alternating with two planes of B along the [111] crystallographic direction (named as 111 structure). Subsequently, Grumbach et al. [11] theoretically found that as the 111 structure relaxes, it segregates into layers of BO and B and then proposed a 100 structure with stacking of the B and O planes in the [100] direction which is energetically more stable than the 111 structure. However, the XRD peaks of the 111 and 100 structures could not match the experimental data. Thus, the crystal structure of synthesized B_2O remains still unknown.

Using *ab initio* genetic algorithm for crystal structure prediction, we have obtained several polytypic structures for B_2O under high pressure. A monoclinic *C*2/*m* phase of B_2O was uncovered to have the lowest enthalpy among earlier and currently predicted structures, however, its simulated XRD data could not fit into the experimental data [10]. Instead, the XRD patterns of metastable tetragonal $P4_2mc$ and *P*-4*m*2 structures are in good agreement with the experimental data. Moreover, the simulated hardness values of $P4_2mc$ and *P*-4*m*2 structures are 40.5 and 44.8 GPa, respectively, indicating their super hardness.

2. Computational details

Evolutionary search of high-pressure structures (10, 50 and 100 GPa) for B_2O was performed with the genetic algorithm [12] in conjunction with *ab initio* structure relaxations within the framework of density-functional theory and the projector augmented wave (PAW) method [13,14] as implemented in the VASP code [15]. 1–4 formula units are constrained in the simulation cell. The genetic algorithm employed here was designed to search for the structure possessing the lowest free energy at given P/T conditions. The first generation of structure is produced randomly. Discarding the worst (i.e., highest-enthalpy) structures, we produced the new generation from the best 65% of the structures in a given generation. New structures are created

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by (1) heredity (70% structures, combining spatially coherent slabs cut from two parent structures in a random direction at random positions and with random thicknesses), (2) permutation (20% structures, i.e. switching identities of two or more atoms in a structure) and (3) lattice mutation (random change of the cell vectors and/or atomic positions). In addition, the best structure of a generation is carried over into the next generation. The methodology has been successful to explore the stable crystal structures with only the knowledge of chemical composition [16–28]. The PAW potentials used here were derived using the local density approximation (LDA) [29] functional and have [He] core radius of 1.70 and 1.52 a.u. for B and O. The use of a plane-wave kinetic-energy cutoff of 600 eV was shown to give excellent convergence on the total energies and structural parameters.

Table 1
Calculated equilibrium lattice parameters (Å and degree), hardness (GPa), bulk modulus B_0 (GPa), and density (g/cm^3).

Structure	a	b	c	α	β	γ	H_v	B_0	ρ
P-3m1	2.560	2.560	6.958	90	90	120	41.8	231	3.16
$I4_1/amd$	2.688	2.688	11.116	90	90	90	51.7	236	3.11
$P4_2mc$	2.459	2.459	6.902	90	90	90	40.5	187	2.99
P-4m2	2.498	2.498	6.842	90	90	90	44.8	196	2.93
P-62m	4.159	4.159	2.627	90	90	120	57.2	268	3.18
$C2/m$	9.753	2.678	8.435	90	134.9	90	66.7	281	3.20

3. Results and discussion

Evolutionary variable-cell simulations with 1–4 formula units (f.u.) in the simulation cell were performed at 10, 50 and 100 GPa, respectively. As shown in Fig. 1(a) and (b), earlier proposed 111 (hexagonal P-3m1) and 110 (tetragonal $I4_1/amd$) structures with tetrahedrally bonding (sp^3 hybridization) have been successfully reproduced in the current simulation. Moreover, we obtain an intriguing monoclinic $C2/m$ (Fig. 1e) structure which is most energetically favorable. The $C2/m$ structure contains four B_2O formula units in one unit cell, in which both B and O atoms occupy the Wyckoff 4i (z1, 0, z2) sites. Interestingly, B atoms possess coordination numbers ranging from 4 to 7. As shown in the Fig. 1c, a novel tetragonal $P4_2mc$ contains both sp^3- and sp^2-hybridized boron atoms, in which vertical flat 6-fold rings are linked together by sp^3-hybridized B atoms along the c axis. Note that similar metastable structures for pure carbon and c-BC_2N were also reported [12,17]. Inspection of the crystal structure of hexagonal P-62m (Fig. 1f) along c axis revealed that it can be viewed as distorted graphite with one B atom shifting to the middle of the two flat layers and forming six-coordinated bonds. All O atoms in $C2/m$, $P4_2mc$ and P-62m structures are three-coordinated (sp^2). Except for the 111 and 110 structures, the other three structures of B_2O are reported here for the first time. Table 1 lists the optimized structure parameters at ambient pressure.

The enthalpy curves for different structures relative to P-3m1 structure were plotted in Fig. 2. One observes that the current predicted $C2/m$, $P4_2mc$ and P-62m structures are energetically much more favorable than the previous 110 and 111 structures, and in the whole pressure region studied $C2/m$ is the most stable structure. As shown in Fig. 3, we have simulated XRD patterns of these five structures to compare with the experimental data of the synthesized B_2O. Such simulations have been widely used in the literatures to aid the identification of unknown crystal structures [17,18]. It is found that the simulated XRD for $C2/m$ phase could not fit into the experimental data [10]. Also $I4_1/amd$ and P-62m can be ruled out by evidence of the mismatching XRD pattern with experimental data. P-3m1 structure can only reproduce two strong peaks at 25.240° and 38.254°. Interestingly, except for the first peak at 12.54°, the XRD pattern of the metastable tetragonal $P4_2mc$ structure matches the experimental observation very well. It is thus reasonable to propose that the synthesized B_2O is not a pseudo-diamond structure, but a structure with similar characteristic of our predicated $P4_2mc$. Based on this idea, through exchanging the atom positions of B (0.5, 0, 0.2257) with O (0.5, 0, 0.0205), a tetragonal structure with space group of P-4m2 [Fig. 1d] can be derived, whose enthalpy is only 0.093 eV/atom higher than that of $P4_2mc$ but 0.271 eV/atom lower than that of P-3m1 at 0 GPa. Remarkably, the peak at 12.54° appears in P-4m2 after structural relaxation; meanwhile,

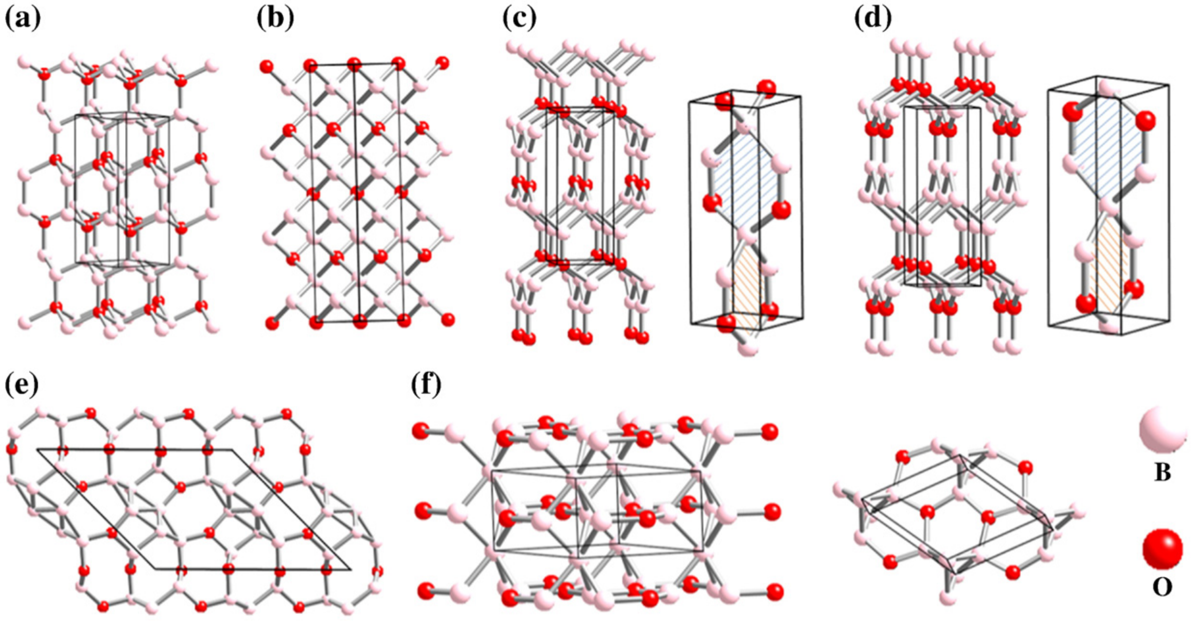

Fig. 1. Polyhedral views of the P-3m1 (a), $I4_1/amd$ (b), $P4_2mc$ (c), P-4m2 (d), $C2/m$ (e), and P-62m (f) structures. The dark solid lines denote the unit cells, and the light pink and deep red spheres represent B and O atoms, respectively. At zero pressure, for P-3m1, atomic positions of B at 2d (0.66667, 0.33333, 0.04933) and 2c (0, 0, 0.38194), and O at 2d (0.33333, 0.66667, 0.27570); for $I4_1/amd$, atomic positions of B at 8e (0, 0, 0.83354), and O at 4b (0, 0, 0.5); for $P4_2mc$, atomic positions of B at 2b (0.5, 0.5, 0.89111) and 2c (0, 0.5, 0.72639), and O at 2c (0, 0.5, 0.52046); for P-4m2, B at 1b (0.5, 0.5, 0), 1c (0.5, 0.5, 0.5) and 2 g (0.5, 0, 0.33796), and O at 2 g (0, 0.5, 0.88172); for $C2/m$, atomic positions of B at 4i (0.03147, 0, 0.85820), (0.23003, 0, 0.75689), (0.78220, 0, 0.67879), and (0.17617, 0, 0.49678), and O at 4i (0.37364, 0, 0.00810) and (0.04105, 0, 0.69226); for P-62m, atomic positions of B at 3 g (0, 0.71314, 0.5) and 1a (0, 0, 0), and O at 2d (0.33333, 0.66667, 0.5).