First-principles study of a novel superhard boron nitride phase

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(Dated: February 20, 2022)

A superhard boron nitride phase dubbed as Z-BN is proposed as possible intermediate phase between h-BN and zinc blende BN (c-BN), and investigated using first-principles calculations within the framework of the density functional theory. Although the structure of Z-BN is similar to that of bct-BN containing four-eight BN rings, it is more energy favorable than bct-BN. Our study reveals that Z-BN, with a considerable structural stability and high density comparable to c-BN, is a transparent insulator with an indirect band gap about 5.27 eV. Amazingly, its Vickers hardness is 55.88 Gpa which is comparable to that of c-BN. This new BN phase may be produced in experiments through cold compressing AB stacking h-BN due to its low transition pressure point of 3.3 GPa.

In comparison with the efforts paid on new carbon allotropes, such as the monoclinic M-carbon [1, 2], cubic body center C4 carbon (bct-C4) [3, 4], orthorhombic W-carbon [6] and orthorhombic Z-carbon [7, 8], were proposed as the candidates for the superhard phase observed in cold compressing graphite [10]. These studies are significant for understanding the transformation between graphite and diamond and arouse many interests in searching for low energy superhard carbon phase [11–13]. Lots of theoretical efforts had been paid on searching for low energy superhard carbon allotropes, such as the particle-swarm optimization method [20, 21], graph theoretical methods [22], evolutionary algorithm USPEX [1], minima hopping method [23] (MHM) for crystal structure prediction [24] and fragment assembly method used by Niu [14], Zhou [15] and in our latest work [18]. Interestingly, the superhard bct-C4 [3] and M-carbon [20] were predicted before the cold compressing graphite experiment and later they are identified as the candidates [2, 3] for the superhard graphite.

Theoretical attentions are needed to search for the potential intermediate BN phases in cold compressing h-BN.

Recently, some superhard allotropes of carbon, such as the monoclinic M-carbon [1, 2], cubic body center C4 carbon (bct-C4) [3, 4], orthorhombic W-carbon [6] and orthorhombic Z-carbon [7, 8], were proposed as the candidates for the superhard phase observed in cold compressing graphite [10]. These studies are significant for understanding the transformation between graphite and diamond and arouse many interests in searching for low energy superhard carbon phase [11–13]. Lots of theoretical efforts had been paid on searching for low energy superhard carbon allotropes, such as the particle-swarm optimization method [20, 21], graph theoretical methods [22], evolutionary algorithm USPEX [1], minima hopping method [23] (MHM) for crystal structure prediction [24] and fragment assembly method used by Niu [14], Zhou [15] and in our latest work [18]. Interestingly, the superhard bct-C4 [3] and M-carbon [20] were predicted before the cold compressing graphite experiment and later they are identified as the candidates [2, 3] for the superhard graphite.

In this work, based on the first-principle calculations, we systematically investigate the stability, electronic and mechanical properties of new BN phases with the structure of M-carbon, bct-C4, W-carbon, Z-carbon and other proposed carbon structures due to the comparability between graphite and h-BN. The transforming path from h-BN to bct-BN has been studied by Wen et al. [39]. According to their results, M-BN is energy unstable due to the existence of the boron-boron (B-B) and nitrogen-nitrogen (N-N) bonds [39]. BN phases with the structure of M-carbon, W-carbon, S-carbon and H-carbon are expected to be unstable due to the existence of five-seven patterns in such structures. Similar to bct-C4, the recently theoretically proposed structure Z-carbon [7, 8] is an excellent template for new BN phase because its structure contains only even carbon rings (four-eight carbon rings). In our present work, based on the first-principle calculations, we systematically investigate the stability, electronic and mechanical properties of the BN allotrope with the structure of Z-carbon (named as Z-BN). The result is an interesting example of extending the previously predicted carbon allotropes to their corresponding BN counterpart. Such method is an effective approach to search for new superhard BN phases.
COMPUTATIONAL DETAILS

All calculations are carried out using the density functional theory with both local density approximation (LDA) and general gradient approximation (GGA) as implemented in Vienna ab initio simulation package (VASP). The interactions between nucleus and the valence electrons of boron and nitrogen are described by the projector augmented wave (PAW) method. A plane-wave basis with a cutoff energy of 500 eV is used to expand the wave functions of all systems considered in our present work. The Brillouin Zone (BZ) sample meshes for all systems are set to be denser enough (11×11×9 for h-BN, 9×9×9 for c-BN, 13×13×7 for w-BN, 7×7×13 for bct-BN and 5×9×11 for Z-BN) in our calculations. Crystal lattices and atoms positions of h-BN, w-BN, c-BN, bct-BN, and Z-BN are fully optimized (under different external pressure) up to the residual force on every atom less than 0.005 eV/Å through the conjugate-gradient algorithm. Vibration properties of all systems are studied by using the phonon package with the forces calculated from VASP.

To evaluate the transition pressure from h-BN to Z-BN, the exchange-correlation functional is describe by LDA. Although the LDA is a simple approximation of DFT, it can give reasonable interlayer distance, mechanical properties of h-BN sheets due to a delicate error cancelation between exchange and correlation in comparison with that of semi-local generalized gradient approximation (GGA). The detail comparison of the lattice parameters of h-BN derived from GGA and LDA can be found in our previous report.

Benchmark calculations are conducted for c-BN phase to validate our computational scheme. The calculated lattice parameter with GGA is 3.625 Å, the result agrees well with the experimental value of 3.620 Å. The computed elastic constants for the c-BN phase with GGA are C_{11} = 780 GPa, C_{44} = 444 GPa, and C_{12} = 173 GPa. They are also in reasonable agreement with the experimental values of C_{11} = 820 GPa, C_{44} = 480 GPa, and C_{12} = 190 GPa.

RESULTS AND DISCUSSIONS

The crystal structures of bct-BN and Z-BN are shown in Fig. 1. The lattice constants of c-BN, w-BN, bct-BN and Z-BN derived from GGA at zero pressure are listed in Tab. 1. Fig. 1(a) shows the [010] (top) and [001] (bottom) direction views of bct-BN. The crystal structure of bct-BN belongs to P42/mnm space group. At zero pressure, its equilibrium lattice constants are a=b=4.425 Å and c=2.555 Å. Z-BN belongs to Pbam space group. At zero pressure, its equilibrium lattice constants are a=b=4.444 Å and c=2.548 Å. One inequivalent B atom in its unit cell occupies the Wyckoff position at 4g (0.325, 0.3675, 0.0) and one inequivalent N atom locates at 4f (0.313, 0.313, 0.0). There are two inequivalent B-N bonds labeled as b_{1} and b_{2} with length of 1.601 Å and 1.541 Å in bct-BN. Their average length is 1.571 Å. Z-BN belongs to Pbam space group and its equilibrium lattice constants are a=8.891 Å, b=4.293 Å and c=2.555 Å. Two inequivalent N atoms in Z-BN occupy the Wyckoff positions at 4g (0.834, 0.301, 0.0) and 4h (0.589, 0.301, 0.5). Another two inequivalent B atoms in Z-BN occupy 4g (0.334, 0.827,
TABLE I: Space group, lattice information (LP), density (D: g/cm$^3$), band gap (Eg: eV), cohesive energy (Ecoh: eV/BN), bulk modulus (B$_0$: Gpa), shear modulus (G: Gpa) and Vickers hardness (H$_v$: Gpa) for the c-BN, w-BN, bct-BN and Z-BN.

| Systems     | Space group | LP          | D    | Eg  | Ecoh | B$_0$ | G    | H$_v$ | reference      |
|-------------|-------------|-------------|------|-----|------|-------|------|-------|----------------|
| c-BN        | F-43m       | a=b=c=3.625Å | 3.593 | 4.40 | -6.934 | 376.19 | 381.52 | 62.82 | this work      |
|             |             | a=b=c=3.620Å |      |     |       |       |       |       | experimental [27] |
|             |             | a=b=c=3.589Å |      |     |       |       |       |       | calculated [39] |
| w-BN        | P63mc       | a=b=2.555Å, c=4.225Å | 3.587 | 5.24 | -6.930 | 375.24 | 384.17 | 63.82 | this work      |
|             |             | a=b=2.550Å, c=4.200Å |      |     |       |       |       |       | experimental [27] |
|             |             | a=b=2.538Å, c=4.179Å |      |     |       |       |       |       | calculated [39] |
| bct-BN      | P42/mnm     | a=b=4.425Å, c=2.548Å | 3.431 | 4.83 | -6.845 | 348.35 | 309.44 | 46.86 | this work      |
|             |             | a=b=4.380Å, c=2.526Å |      |     |       |       |       |       | calculated [39] |
| Z-BN        | Pbam        | a=8.891Å, b=4.293Å, c=2.555Å | 3.520 | 5.27 | -6.872 | 359.61 | 347.45 | 55.88 | this work      |

0.0) and 4h (0.088, 0.827, 0.5) Wyckoff positions. The views from [010] (top) and [001] (bottom) direction of Z-BN are shown in Fig. 1(b). There are six inequivalent B-N bonds in Z-BN, labeled as b$_1$, b$_2$, b$_3$, b$_4$, b$_5$ and b$_6$, as shown in Fig. 1(b). Their bond length are 1.595 Å, 1.595 Å, 1.578 Å, 1.594 Å, 1.554 Å and 1.551 Å, respectively. The average length is 1.578 Å. The average bond lengths of both bct-BN and Z-BN are comparable to that of diamond (1.570 Å). We define the bond angles BNB and NBN in the parallelogram of both systems as $\theta_1$ and $\theta_2$, respectively. These two angles are $\theta_1=85.84$ and $\theta_2=94.16$ for bct-BN and $\theta_1=85.58$ and $\theta_2=94.42$ for Z-BN.

The apparent difference between these two new BN phases is the absence of hexagon pattern for bct-BN viewed from their [001] direction. The structures of both bct-BN and Z-BN are constructed with the four-eight patterns and without the five-seven patterns as those in M-carbon and W-carbon. From the structural point of view, both bct-BN and Z-BN can be regarded as the mutations of w-BN, as their corresponding counterpart systems bct-C4 and Z-carbon are the mutations of H-diamond [18]. Moreover, both bct-BN and Z-BN can be derived from reconstructing the AB stacking h-BN with different manners, as the potential intermediate products in cold compressing AB stacking h-BN.

The relative stability of c-BN, w-BN, bct-BN and Z-BN is evaluated through comparing their cohesive energy per BN pair. Bct-BN has been predicted more favorable than M-type BN phase [33]. According to our GGA results, we find that Z-BN (-6.872 eV/BN) is more favorable than bct-BN (-6.845 eV/BN), and its cohesive energy is only 62 meV per BN above c-BN (-6.934 eV/BN). The enthalpy per BN pair for c-BN, w-BN, bct-BN as well as Z-BN as functions of pressure relative to AB stacking h-BN derived from LDA calculation is shown in Fig. 2. The results indicate that when the pressure is larger than 3.3 GPa (5.5 Gpa), Z-BN (bct-BN) is more stable than h-BN. Namely, the transition pressure point of Z-BN (bct-BN) from h-BN under external pressure is 3.3 GPa (5.5 Gpa). Moreover, Z-BN is always more favorable than bct-BN as the external pressure ranging from 0 to 30 GPa. To further confirm the dynamic stability of bct-BN and Z-BN, we calculated their phonon band structures and phonon density of states. The results derived form GGA are shown in Fig. 3 (a) and (b) for bct-BN and Z-BN, respectively. For both systems, there is no negative frequency and states in phonon band structure and phonon density of states, confirming the dynamic stability of bct-BN and Z-BN.

The space group, density, band gap, cohesive energy, bulk modulus, shear modulus and Vicker’s hardness of c-BN, w-BN, bct-BN and Z-BN are summarized in Tab. 1. The results of density reveal that Z-BN (3.520 g/cm$^3$) is denser than bct-BN ( 3.431 g/cm$^3$), and its density is comparable to those of w-BN (3.587 g/cm$^3$) and c-BN (3.593 g/cm$^3$). The values of bulk modulus of bct-BN (348.35 GPa) and Z-BN (359.61 Gpa ) are comparable to those of c-BN (376.19 Gpa) and w-BN (375.24 Gpa). To further analyze the hardness of Z-BN, we adopt the recently introduced empirical scheme [52] to evaluate the Vickers hardness (H$_v$) determined by the bulk modulus (B$_0$) and shear modulus (G), where: $H_v=2(G^3/B_0^2)^{0.5885}$. The values of Vickers hardness

![FIG. 3: Phonon band structure and phonon density of states of bct-BN (a) and Z-BN (b) at Zero pressure.](image-url)
for bct-BN, Z-BN, w-BN and c-BN are 46.86 GPa, 55.88 GPa, 63.82 GPa and 62.82 GPa, respectively. The results indicate that Z-BN is a superhard material comparable to c-BN.

To investigate the electronic properties of bct-BN and Z-BN, their band structures and density of states are calculated and shown in Fig. 3(a) and (b), respectively. The results indicate that the valence band maximum (VBM) and conduction band minimum (CBM) of Z-BN (bct-BN) are mainly derived from the N atoms and B atoms, respectively. Moreover, both systems are indirect-wide-band-gap insulators. The band gap of bct-BN is 4.83 eV which is in good agreement with previous first-principles calculation [39]. The band gap of Z-BN is 5.27 eV which is bigger than those of c-BN, w-BN and bct-BN. Namely, both Z-BN and bct-BN are transparent superhard materials.

Finally, we provide the simulated X-ray diffraction (XRD) patterns for C-BN, w-BN, bct-BN and Z-BN at 10 Gpa (above all the phase transition pressures) to identify their potential products. Each phase have their characteristic peaks. C-BN has a characteristic peak located at 1.77 Å. w-BN holds characteristic peaks at d-spacing of 1.17 Å and 2.07 Å, both of them are absent in bct-BN and Z-BN. There are two characteristic peaks for bct-BN located at d-spacing of 1.37 Å and 3.06 Å, respectively. Five characteristic peaks of Z-BN are located at d-spacing of 1.60 Å, 1.73 Å, 2.10 Å, 2.39 Å and 3.78 Å. These peaks are absent in the other three BN phases. One can identify Z-BN from other three phases according to these characteristic peaks.

CONCLUSION

The structural, vibrational, mechanical and electronic properties of a new BN allotrope (Z-BN) with the structure of Z-carbon has been systematically investigated using first-principles calculations. Our results indicate that Z-BN is dynamically stable. The value of hardness of Z-BN is larger than that of bct-BN and comparable with those of w-BN and c-BN. Z-BN is a transparent insulator with an indirect band gap about 5.27 eV. Under external pressure up to 3.3 Gpa, Z-BN is energy more stable than h-BN. Our results indicate that Z-BN phase with remarkable stability may be the potential intermediate product in cold compressing AB stacking h-BN.

ACKNOWLEDGEMENTS

This work is supported by the National Natural Science Foundation of China (Grant Nos. 10874143 and 10774127), the Cultivation Fund of the Key Scientific and Technical Innovation Project, the Ministry of Education of China (Grant No. 708068), the Program for New Century Excellent Talents in University (Grant No. NCET-10-0169), the Scientific Research Fund of Hunan Provincial Education Department (Grant No. 10K065) and the Hunan Provincial Innovation Foundation for Postgraduate (Grant No. CX2010B250).

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