Investigating the Hardness Properties of Superhard Materials (B-C-N)

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Abstract

We present the computational report with the first-principles calculations based on the DFT concepts, which were performed to solve the Kohn-Sham equations by the self-consistent field method. The crystal structures of BC_2N in the *Pmm2* and *C2/m* phases were initially observed. The energy-calculation result indicated that the *Pmm2* phase is a more stable phase due to the minimum free energy. Besides, the elastic constants were calculated so that the bulk modulus and hardness will be analyzed between the two phases. The elastic constants of both phases of BC_2N exhibited the brittle-material condition. We also proposed the positive value of Vickers hardness that the BC_2N in the *Pmm2* phase gave the hardest condition at 74.8 GPa, while it was just found at 32.2 GPa in the *C2/m* phase.

Keywords : Hardness, Structure, Boron-based compound, Physical properties

1. Introduction

Nowadays, technological innovations seek to find a new type of extremely hard material known as superhard material, Wentorf (1980). The condition of superhard material can be determined from an interesting material with the Vickers hardness value exceeding 40 gigapascals (GPa), Dubrovinskaia (2007). Superhard materials have widely interested in robot and vehicle industries that require strength and durability. Robotic materials require both soft material for skin or outside and hard material for bone or inside, Jing (2020). Steel is one of the most selected materials for use in robot builders. This metal is a smart choice if you're building a robot that needs to stand up to harsh conditions. It's possible to harden the steel to between 100,000 and 300,000 pound-force per square inch (psi) in many cases. The most widely used superhard material applications from cutting and polishing tools to wear-resistant coatings, while diamonds are still the hardest-known diamonds. This material is even synthetic for many years, and the theory of attempts to improve upon it. However, even diamonds have limitations, not effective for cutting ferrous metals.

In another way, iron is also included due to the chemical reaction that produces cubic iron carbide, Kaner (2005). Boron nitride (BN), the second hardest material with a structure similar to that of diamonds, can be used to cut ferrous metals, but it does not occur naturally and must be conditionally synthesized. The compressions under pressure and temperature conditions are so high that they are quite expensive. The new super-hard material is not only great science interesting, but also very useful to design a new superhard material. One has to understand what makes diamonds so special. In diamonds, tetrahedral-bound sp^3 carbon atoms form a three-dimensional covalent highly symmetrical network of other carbon-containing materials It has a shorter, stronger carbon bond. By studying the experiment report of Solozhenko (2001), a cubic phase of BC_2N was synthesized by direct conversion of graphite-like BN–C solid solutions at 25 GPa and 2100 K. The hardness, Young's modulus, fracture toughness, and structure of this phase were examined using micro-indentation and transmission electron microscopy. The hardness and elastic modulus values of the c-BC_2N are intermediate between diamond and cubic boron nitride, which made the hardest known solid after diamond. By the theoretical study of Li (2009), an ab initio evolutionary algorithm was employed to resolve the crystal structure of the observed

superhard BC_2N and uncovered two polymorphs with rhombohedral and orthorhombic symmetries, with which the experimental x-ray diffraction pattern was reproduced. Analysis of the total energy results and the simulated energy-loss near-edge spectroscopy suggested that the rhombohedral structure is the best candidate for the superhard BC_2N. They also demonstrated that earlier proposed high density and low-density forms are likely from this single rhombohedral phase. Later, hexagonal BC_2N was shown as a superhard material, reported by Sadeghi (2020), identified to be comparable to or even harder than cubic boron nitride (c-BN) due to the full sp^3 bonding character and the higher number of C–C and B–N bonds compared to C–N and B–C.

2. Objectives

Based on the literature review of BC_2N, structural, electronic, and elastic properties of the B-C-N compounds are the main points of interest in this research. Ab initio calculation based on the concepts of density functional theory (DFT) is mainly used as a theoretical instrument for evaluating the physical properties of these interesting materials. Besides, the calculated result will be compared and discussed in the next part of this report. Therefore, the objectives of this study would be specified to the investigating of structural, electronic, and elastic properties of the B-C-N compounds using ab initio calculation.

3. Calculation method

In this computational report, the first-principles calculations based on the DFT concepts are performed to solve the Kohn-Sham equations by self-consistent field method (SCF) as implemented in Cambridge Serial Total Energy Package (CASTEP) code. To study the DFT calculations in the ternary compound (B-C-N) systems, the generalized-gradient approximation functional of Perdew-Burke-Ernzerhof (GGA-PBE) is used in term of exchange-correlation functional term in the Kohn-Sham equations at the ambient-pressure condition for the suitable exchange-correlation functional term for the formation of lightweight compounds. The lattice parameters and bulk modulus of BC_2N are also calculated from the GGA-PBE results; which are mainly used as exchange-correlation functional for finding the high-pressure properties of the undoped and doped systems. The maximum energy of the plane-wave basis set is used at 500 eV, which is suitable cutoff energy to cooperate with ultrasoft-pseudopotential. Monkhorst-Pack grid sizes are used, while k point is initially finite as the condition of $k = 0.04$. The energy minimization with Brodyden-Fletcher-Goldfarb-Shanno (BFGS) scheme is used for the calculation of geometry optimization. External forces and pressure tensors on optimized structures are controlled through the Hellmann-Feynman theorem. The BFGS optimization was considered to be completed when the total energy difference was less than 2×10^{-6} eV/atom, Hellman–Feynman forces were less than 0.006 eV/Å, maximum atomic displacement within 0.0002 Å, and all of the stresses within 0.003 GPa. The average bulk modulus can be evaluated from elastic constants by Voigt-Reuss-Hill (VRH) method.

4. Results and discussion

First of all, the structural investigation of the crystal structures of BC_2N in the *Pmm2* and *C2/m* phases was initially observed as shown in Figure 1. The calculated lattice parameters (*a*, *b*, and *c*) in the *Pmm2* phase were found as (2.534, 2.562, 3.640), while it was found as (3.636, 3.636, 4.174) in the *C2/m* phase. Volumes of the unit cells are 23.66 and 52.94, respectively. This showed that the *Pmm2* phase exhibits a higher gravimetric density. For total energy consideration, it was found that the *Pmm2* phase gave lower free energy at -658.90 eV per a formula unit (f. u.), while the *C2/m* phase gave a higher energy value at -658.49 eV/f. u., indicating that the *Pmm2* phase is a more stable phase at ambient pressure

due to the minimum free energy. However, we considered the physical properties in both phases due to the minimal energy difference of 0.51 eV.

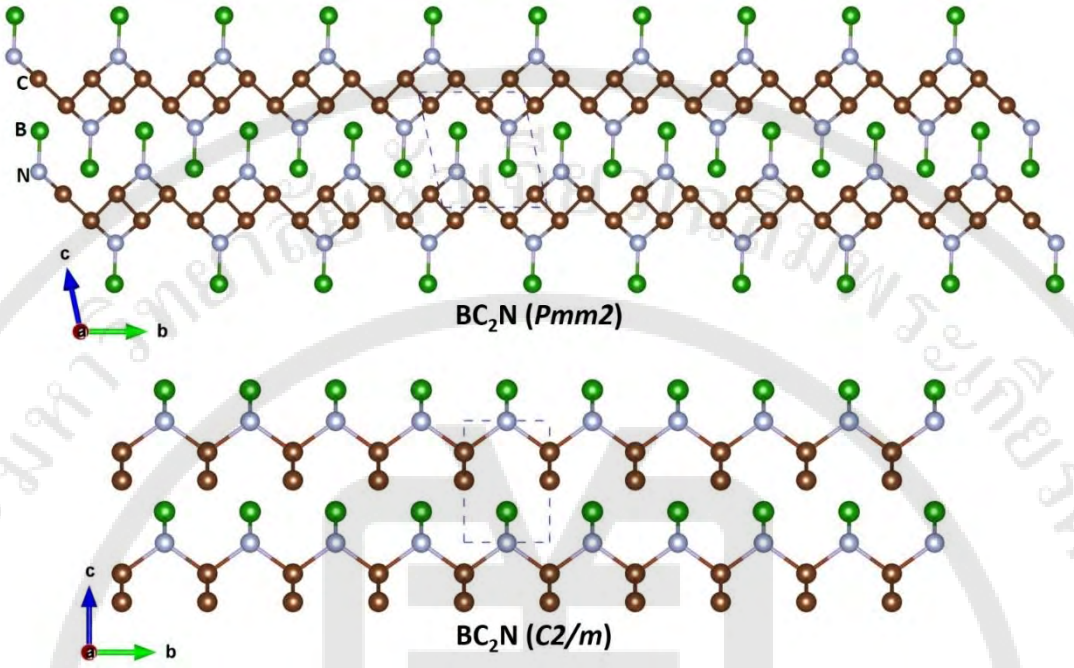

Figure 1 Structural virtualization of BC_2N in the *Pmm2* and *C2/m* phases.

Next, the elastic constants were calculated so that the bulk modulus and hardness will be analyzed between the two phases. We would like to obtain extensive detail on the elastic properties such as elastic constants (C_{ij}), bulk modulus (B), shear modulus (G), and Young's modulus (Y) were studied for determining the full physical properties of BC_2N in the *Pmm2* and *C2/m* phases. The elastic parameters at the ambient pressure phases were tested by using PBE functional as shown in Table 1. It was found that the PBE functional gave a good agreement with the previous experiments more than using the local-density approximation (LDA). The elastic properties of materials such as B and G can be estimated by using the Voigt–Reuss–Hill procedure. The Voigt and Reuss values are the upper and lower limits of crystalline constants, while the mean value from the Voigt (B_V, G_V) and Reuss (B_R, G_R) approximation is the Hill (B_H, G_H) modulus, which the Hill modulus is shown in Table 1. The type of material can be classified as brittle material if the ratio of B/G is less than 1.75, and it is a ductile material if the ratio is greater than 1.75. Considering the B/G ratio in Table 1, this indicates that both phases of BC_2N are the condition of the brittle material.

Table 1 The calculated elastic properties in a unit of gigapascal (GPa).

Phase	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}	B	G	B/G	H_V
BC_2N (Pmm2)	1009	892	873	420	478	369	17	138	122	370	414	0.89	74.8
BC_2N (C2/m)	463	995	842	395	209	188	47	172	135	289	225	1.28	32.2
BC_5 (P3m1)	870	870	1032	378	378	378	149	77	77	374	364	1.03	57.9

Tian (2012) proposed that the positive value of Vickers hardness (H_V) for the hardness materials can be corrected as

$$H_V = 0.92\left(\frac{G}{B}\right)^{1.137} G^{0.708} \qquad (1)$$

Using equation (1), the H_V values exhibit the property as the interior of the superhard material. When compared to the well-known compound (BC_5), it can be concluded that the

different space groups have a direct influence on the Vickers hardness of BC_2N. Our calculation results suggested that the BC_2N in the *Pmm2* phase gave the hardest material at 74.8 GPa, while it was just found at 32.2 GPa in the *C2/m* phase. These introduce us that the BC_2N in the *Pmm2* phase is one of the hardest materials; however, the usage of BC_2N for the robotic or mechanical devices has any question due to appearing the brittle-material property.

5. Conclusion

In summary, the present computational report with the first-principles calculations based on the DFT concepts has been performed to solve the Kohn-Sham equations by the self-consistent field method. The crystal structures of BC_2N in the *Pmm2* and *C2/m* phases were initially observed as shown in Figure 1. The energy-calculation result indicated that the *Pmm2* phase is a more stable phase due to the minimum free energy. However, we considered the physical properties in both phases due to the minimal energy difference of 0.51 eV. Then, the elastic constants were calculated so that the bulk modulus and hardness will be analyzed between the two phases. Both phases of BC_2N exhibited the condition of the brittle material. We also proposed the positive value of Vickers hardness that the BC_2N in the *Pmm2* phase gave the hardest material at 74.8 GPa, while it was just found at 32.2 GPa in the *C2/m* phase. Our calculation results introduce us that the BC_2N in the *Pmm2* phase is one of the hardest materials; however, the usage of BC_2N for the robotic or mechanical devices has any question due to appearing the brittle-material property.

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