Predicting the structural, electronic and mechanical properties of three-dimensional boron nitride foam containing $sp$, $sp^2$ and $sp^3$ hybridized bonds

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Abstract. A first-principles approach is utilized to systematically investigate the structural, electronic and mechanical properties from a new BN phase (denoted super-(BN)$_{16}$). Super-(BN)$_{16}$ contains $sp$, $sp^2$ and $sp^3$ hybridized bonds. It is mechanically stable, even though it is energetically unfavorable than c-BN, w-BN, yne-BN, and so on. Due to the different hybridization type and the B-N covalent bonds with ionic characteristics, super-(BN)$_{16}$ has unequal bonds and bond angles in these equal space positions. The calculated electronic structure showed it is a semiconductor with a direct band gap of 1.94 eV. The electronic states in the region near Fermi level mainly come from the 2p orbitals of the $sp$ hybridized B and N atoms. The elastic constants and moduli of this phase exhibit clear anisotropy and super-(BN)$_{16}$ should have a low hardness and high ductility. Additionally, it can be obtained from nanosheets, nanotubes and nanoribbons of yne-BN family under pressure.

1. Introduction

Because B and N atoms can form chemical bonds by means of $sp$, $sp^2$ and $sp^3$ hybridizations or combining them together, boron nitride (BN) has many different phases. The common c-BN and h-BN have many excellent properties and play an important role in machining, functional component and all aspects of daily life. As a simple and typical III-V compound, numerous BN structures have been theoretical predicted or experimental synthesized in the past decades. Such as $sp$ and $sp^2$ graphyne-BN (yne-BN) and graphdiyne-BN (diyne-BN) [1-2], $sp^3$ hybridized nanocages [3], nanotubes [4], nanoribbons [5] and nanosheets [6], $sp^2$ and $sp^3$ M-BN [7], HBNFs [8], $sp^3$ hybridized c-BN, bct-BN, Z-BN [9], etc. They usually have high chemical stability, thermal conductivity, excellent mechanical properties and unique electronic properties, exhibiting practical application potentials in the many fields about advanced abrasives [10], hydrogen energy [11], nanoscale spintronic devices [12] and flexible resistive memory [13].

Meanwhile, it is worth noting these BN phases exhibit unique physical and chemical properties. For example, they have many forms of crystal structure, from zero-dimension to one-dimension, two-dimension and three-dimension. The mechanical properties of these reported BN phases are different from each other. Well-known c-BN and w-BN with $sp^3$ hybridized bonds are typical superhard materials, the recent proposed M-BN with $sp^2$ and $sp^3$ hybridized bonds is hard, while h-BN formed by $sp^2$ hybridized atoms is more ductile and is a widely used lubricant. Furthermore, with the same fundamental
hybridization type, their electronic structures are different, too. For example, with the same \( sp^2 \) and \( sp^3 \) hybridized bonds, T-B3N3 is metal coming from the \( sp^2 \) hybridized B atoms \[14\], while M-BN with a one-dimensional metalliclicity comes from \( sp^2 \) hybridized B and N atoms \[7\]. However, the l22-BN, dz2-BN, 3D(n,0)-I (n=6, 8, 10, 12) and Na-HBNFs are all semiconductors \[8, 11, 15\]. All these characters indicate BN properties highly dependent on the crystalline structure including hybridization type. However, a few studies have been performed for the influences from \( sp, sp^2 \) and \( sp^3 \) hybridized bonds in 3D multi-porous BN polymorphs. Moreover, the role of \( sp, sp^2 \) and \( sp^3 \) hybridization in the stability, hardness and electronic property is an interesting issue and worth studying for understanding the basic nature of BN materials and the elements of B and N.

In this work, we present a 3D BN skeleton consisting of \( sp, sp^2 \) and \( sp^3 \) hybridized bonds. This BN phase has an orthorhombic structure, and 16 pairs of BN in a conventional unit cell. Thereby, we have denoted it as super-(BN)\(_{16}\). Super-(BN)\(_{16}\) is mechanically stable, even though it is energetically meta-stable. There is a direct band gap of 1.94 eV at the Brillouin zone from GGA. We performed a systematic first-principles study the effect of \( sp, sp^2 \) and \( sp^3 \) hybridizations on the structural, electronic and mechanical properties.

2. Methods and computational details

In this work, first-principles calculations were performed with the density functional theory (DFT) approach implemented in the Vienna ab initio simulation package known as VASP \[16\]. The electron–electron interactions were treated using a generalized gradient approximation (GGA) \[17\]. The energy cut off for the plane-wave basis was set at 420 eV. The k-point separation in the Brillouin zone of the reciprocal space was sampled 8×4×7. The elastic constants (\( C_{ij} \)) were theoretically calculated using Hooke's law \( \sigma_i = C_{ij} e_j \) for small stresses (\( \sigma \)) and strains (\( e \)) \[18\]. Young’s bulk, and shear moduli were estimated using the Voigt–Reuss–Hill approximation \[19\] and Vickers hardness was calculated using Chen’s \[20\], Teter’s \[21\] and Gao’s \[22\] hardness models.

3. Results and discussion

3.1. Structural configuration

The structure of the predicted BN phase is shown in Figure 1 with different views. The phase has an orthorhombic symmetry with I4mm space group (\( D_{2h}^{25} \), No.71). It contains all three \( sp, sp^2 \) and \( sp^3 \) hybridizations and 16 BN pairs per primitive cell, and thus has been denoted as super-(BN)\(_{16}\) hereafter. The fully relaxed lattice constants are \( a=16.960 \) Å, \( b=7.084 \) Å and \( c=14.087 \) Å. There are five inequivalent B and five inequivalent N atoms in per primitive cell. B atoms occupy the 16o (0.323, 0.270, 0.594), 16o (1.417, 1.291, 0.874), 16o (1.144, -1.214, 1.070), 8n (1.303, 1.303, 1) and 8l (1, 0.823, 0.823) Wyckoff positions, and N atoms occupy the 16o (0.825, 0.769, 1.593), 16o (1.202, 1.202, 1) and 8l (0.5,0.320, 0.820) Wyckoff positions.

The density of Super-(BN)\(_{16}\) is 0.78 g/cm\(^3\) as the ratio of \( sp \), \( sp^2 \) BN pairs to \( sp^3 \) BN pairs is 12/2/2. This density value is well below the values of pure \( sp^2 \) hybridized h-BN (2.27 g/cm\(^3\)) and pure \( sp^3 \) hybridized c-BN (3.47 g/cm\(^3\)).

The values of bond lengths are shown in Figure 2. There exist ten distinct bonds. The length of two distinct \( sp-sp \) bonds in the two \( sp \) B and N atoms component are 1.254, 1.248 and 1.239 Å; these values are slightly shorter than in yne-BN (1.265 Å) \[24\]. The length of the \( sp-sp^2 \) bonds are 1.434 and 1.438 Å. The length of the \( sp^2-sp^2 \) bonds is 1.423 Å, which is shorter than in h-BN (1.451 Å) and in a pristine BN sheet (1.452 Å) \[47\]. The length of the \( sp-sp^3 \) bonds are 1.548, 1.508, 1.496 and 1.487 Å. The bond angles deviate from the standard values in c-BN (109.5°), in h-BN monolayer (120°) and the corresponding values in yne-BN (180°).
Figure 1. Atomic structure of super-(BN)$_{16}$. (a) primitive cell, (b) Top view, (c) side view, (d) perspective view and (e) schematic representation of $sp$, $sp^2$ and $sp^3$ hybridizations.

The different bond lengths and angles can be attributed to two reasons. 1) different hybrid orbitals in B and N atoms have an important influence to the bond lengths and angles. 2) although B-N bonds in this phase are covalent in nature, they have ionic characteristics, which lead to B and N atoms are unequivalent. Mulliken analysis further verifies the polarity of these B-N bonds. Which are in reasonable agreement with results published in the literature [1]. We contribute the significant differences in bond structure to the former, while small differences to the latter.
3.2. Energetical and mechanical stability

To evaluate the relative stability of the porous super-(BN)\textsubscript{16}, we calculated the cohesive energy and compared it with several known BN phases. The cohesive energy determined using the following equation:

$$E_{coh} = (nE_B + nE_N - nE_{(BN)n})/n,$$

where $E_B$, $E_N$ and $E_{(BN)n}$ are the energies of a B atom, N atom, and (BN)\textsubscript{h} molecule at zero pressure, respectively. The cohesive energy is lower to those of bct BN, c-BN, w-BN, h-BN and yne-BN. From the cohesive energy of c-BN, h-BN and yne-BN, we can deduce $sp^2$ hybridization is the energetically most favorable hybridization for B and N atoms, followed by $sp^3$ hybridization and $sp$ hybridization. Super-(BN)\textsubscript{16} contains a large number of $sp$ hybridized B/N atoms. Therefore, it is not surprising that super-(BN)\textsubscript{16} is energetically inferior to c-BN, h-BN and yne-BN. Moreover, the unequal bond lengths and bond angles in these hybrid-orbitals (as mentioned in previous paragraph) imply that super-(BN)\textsubscript{16} contains state, which probably increases the total energy. This is one reason why the relative energetic stability of super-(BN)\textsubscript{16} with $sp$, $sp^2$ and $sp^3$ hybridizations is lower than that of c-BN, h-BN and yne-BN.

| Stru     | Sys  | $R_{sp}$ | $R_{sp}^2$ | $R_{sp}^3$ | $\rho$   | $E_{coh}$ | $E_g$  |
|----------|------|----------|------------|------------|----------|-----------|--------|
| super-(BN)\textsubscript{16} | Orth | 75       | 12.5       | 12.5       | 0.78     | 15.05     | 2.36   |
| h-BN     | Hex  | 0        | 100        | 0          | 2.27/2.270\textsuperscript{[8]} | 17.33     | 4.68/4.778\textsuperscript{[8]} |
| lz2-BN   | Orth | 0        | 80         | 20         | 1.917    | 17.09     | 2.04/1.53\textsuperscript{[17]} |
| c-BN     | Cub  | 0        | 0          | 100        | 3.47/3.48\textsuperscript{[25]} | 17.18     | 4.45/4.440\textsuperscript{[8]} |
| bct BN   | Tetra | 0     | 0          | 100        | 3.31/3.688\textsuperscript{[8]} | 16.98     | 4.77/4.782\textsuperscript{[8]} |
| w-BN     | Hex  | 0        | 0          | 100        | 3.46/3.49\textsuperscript{[25]} | 17.15     | 5.20/5.207\textsuperscript{[8]} |
| yne-BN   | Hex  | 50       | 50         | 0          | --       | 16.26     | 4.21   |
Then, we calculated the elastic constants of super-(BN)\textsubscript{16} in order to test the mechanical stability. The orthorhombic Immm super-(BN)\textsubscript{16} have 9 independent elastic constants: $C_{11}$, $C_{22}$, $C_{33}$, $C_{44}$, $C_{55}$, $C_{66}$, $C_{12}$, $C_{13}$, and $C_{23}$ are 61.734, 94.859, 40.946, 3.091, 0.780, 13.727, 63.146, 34.536 and 53.969 GPa, respectively. The mechanical stability criteria have been adapted from Born criteria for an orthorhombic crystal [24]:

$$C_{11}>0, C_{22}>0, C_{33}>0, C_{44}>0, C_{55}>0, C_{66}>0, (C_{11}+C_{22}-2C_{12})>0, (C_{22}+C_{33}-2C_{13})>0, \frac{[C_{11}+C_{22}+C_{33}+2(C_{12}+C_{13}+C_{23})]}{3}>0.$$ 

Obviously, these calculated elastic constants satisfy the mechanical stability, confirming the plausibility of forming super-(BN)\textsubscript{16} from another point.

### 3.3. electronic properties

The electronic band lines of super-(BN)\textsubscript{16} obtained with the GGA functional are shown in Figure 3a. Obviously, this BN phase is a semiconductor with an indirect band gap of 1.94 eV at equilibrium. Using the same strategy, the band gaps of some known BN phases are consistent with previous results listed in Table 1, which validate the computational methods used in this work.

In order to explain the origins of the electronic band structure, the electron density was calculated as shown in Figure 3b. Figure 3b shows the electron density of states (PDOS) projected onto s- and p-orbitals of B and N atoms. It is evident the electronic states in the region near the Fermi level mainly arise from the 2p orbitals of B and N atoms, whereas the contribution from the $sp^2$ and $sp^3$ hybridized atoms is very small. This suggests that the electron band lines near the Fermi level are dominated by the stronger interactions between two adjacent $sp$ hybridized B and N atom. We contribute the significant differences to $sp$ hybrid-orbital has stronger interactions than $sp^2$ and $sp^3$ hybrid orbitals. This result is reasonable agreement with the strength of $sp$, $sp^2$ and $sp^3$ hybridized bonds.

![Figure 3. (a) Electronic band structures of super-(BN)\textsubscript{16} along the high symmetry direction in the Brillouin zone. (b) Electron density of states (PDOS) projected on the s- and p-orbitals in B and N atoms with different hybridization as labelled in Figure 1c. The energy at the Fermi level was set to zero.](image-url)

### 3.4. mechanical properties

For further understanding the mechanical properties of super-(BN)\textsubscript{16}, Young’s modulus was obtained along the three axes ($Y_x$, $Y_y$ and $Y_z$) and the net Young’s modulus ($E$) were obtained from the following equation [19]:

$$E = \frac{9BG}{3B+G},$$

where bulk modulus ($B$) and shear modulus ($G$) were calculated using Voigt-Reuss-Hill (VRH) approximations [19]. The elastic constants and modulus of this phase exhibit clear anisotropy. It is worth noting that all the Young’s moduli as listed in Table 2 are far below the
corresponding values from c-BN, w-BN, and so on. These is basically correlated with the calculated elastic constants.

Table 2. Calculated Young’s modulus along the three axes ($Y_x$, $Y_y$, and $Y_z$), Young’s modulus ($E$), bulk modulus ($B$), shear modulus ($G$), Pugh modulus ($k$), hardness ($H_v$), and the behavior ($Beha$) for brittle (Bri) or ductility (Duc) of super-(BN)$_{16}$, lz2-BN, c-BN, bet-BN and w-BN at zero pressure. All parameters (except Pugh modulus and behavior) are in GPa.

| Stru     | super-(BN)$_{16}$ | lz2-BN | c-BN   | bet-BN | w-BN   | Ref.       |
|----------|------------------|--------|--------|--------|--------|------------|
| $Y_x$    | 19.51            | 687.13 | 719.25 | 711.97 | 910.27 | our work   |
| $Y_y$    | 14.20            | 90.48  | --     | --     | --     | our work   |
| $Y_z$    | 10.14            | 50.61  | --     | 934.74 | 1004.92| our work   |
| $E$      | 12.98            | 259.07 | 854.40 | 730.25 | 858.49 | our work   |
| $B$      | 41.48            | 168.10 | 368.06 | 345.54 | 368.05 | our work   |
| $G$      | 4.48             | 104.19 | 383.61 | 318.12 | 386.27 | our work   |
| $k$      | 0.11             | 0.62   | 1.04   | 0.92   | 1.05   | our work   |
| $H_v$    | -2.64            | 14.32  | 65.18  | 49.85  | 66.01  | Chen’s result |
|          | 0.68             | 15.73  | 57.93  | 48.04  | 58.32  | Teter’s result |
|          | 31.14            | 49.14  | 64.25  | 61.36  | 63.62  | Gao’s result |
|          | --               | 46-80  | 58.77  | 50-60  |        | [15, 28, 29] |

$Beha$  duc Bri Bri Bri Bri our work

Modulus and hardness are often discussed together, though they are different in nature [20, 21, 30, 31]. Because super-(BN)$_{16}$ is highly anisotropic and porous structure, we estimated the theoretical Vickers hardness ($H_v$) using three different semi-empirical models. In Chen et al. model [20], the hardness is correlated with $G$ and $B$ from the formula: $H_v=2(k^2G)^{0.585}-3$, where $k = G/B$ is the Pugh’s modulus ratio [19]. The hardness of Hex-(BN)$_{12}$ given by Chen’s model is below zero, suggesting the ductility. In Teter model [21], the hardness has a linear relationship with shear modulus: $H_v=0.151G$. The hardness of super-(BN)$_{16}$ was estimated to be 0.68 GPa. In Gao et al. model [22], the hardness is calculated through: $H_v=350\times N_e^{4.1916/d^{3.7}}$, where $N_e$ is the electron density of valence electrons per Å$^3$, $d$ is the bond length (Å). Here, $d$ is averaged bond lengths. $f_i$ is the Phillips iconicity and we used 0.256 for all the B-N bonds [7]. Using this model, the $H_v$ values of super-(BN)$_{16}$ is calculated to be 31.14 GPa, which is about half values of c-BN. It is amazing that there are notable differences between the results of the three semi-empirical models.

The factors affecting $H_v$ are complex, such as elastic modulus, bond length, bond density, etc. We attribute the notable differences major to that there are large void network in the covalent bond skeleton. Even though the covalent bonds with $sp$ hybridization in this phase are strong, the large void reduces its mechanical properties, which is similar to previous research results of highly anisotropic and large porous compound [32, 33]. We therefore deduce that super-(BN)$_{16}$ should have a low hardness, suggesting the ductility. It is well known that c-BN, w-BN and bet-BN composed of tetrahedral $sp^3$ hybridized B and N atoms cannot tolerate large deformations and are extremely brittle, while h-BN formed by $sp^2$ hybridized atoms can sustain large distortions and is more ductile. Then, how about the ductility of super-(BN)$_{16}$ consisting of $sp$, $sp^2$ and $sp^3$ hybridized B/N atoms? Here, the Pugh modulus ratio ($k$) is adopted to divide brittle (above 0.57) and ductile (below 0.57) [34]. Our calculations show
the $k$ value of super-(BN)$_{16}$ is 0.11, indicating that it is brittle. This high ductility is related to the large voids in the skeleton of super-(BN)$_{16}$. It endows super-(BN)$_{16}$ with capability of resisting large deformation without fracturing.

3.5. Synthesis methods
A lot of results of experiments and theoretical calculations demonstrate that using precursors to seek new BN phases to be a feasible method. Dai et al. predict two types of porous BN networks which can be obtained with BNNRs [11]. Xiong et al. reported phase transitions of BNNT bundles under pressure [15]. Here, we assumed one way to synthesize this new material based on this background. Super-(BN)$_{16}$ can be obtained from nanosheets, nanotubes and nanoribbons of yne-BN family under pressure as the literatures of Ref. [11, 14, 15]. Note that the major obstacle in obtain of new BN materials is the limitation of high-quality BN precursor. Today, the successful preparation of BN nanosheet, single-walled BN nanotubes [35], and nanoribbons [36] provides the fundamental building blocks for 3D BN polymorphs. There are reasons to believe the special properties of super-(BN)$_{16}$ will arouse further experimental efforts in achieving this novel BN family.

4. Conclusions
From first-principles calculations, we have reported a new, ductility and porous BN phase, named as super-(BN)$_{16}$. The super-(BN)$_{16}$ has $sp$, $sp^2$ and $sp^3$ hybridized B and N atoms. It’s mechanically stable, even though it is energetically unfavorable than c-BN, w-BN, and so on. It can be obtained from nanosheets, nanotubes and nanoribbons of yne-BN family under pressure. Due to the special structural characteristics, super-(BN)$_{16}$ has unequal bond and bond angle in these equal space positions. The electronic states in the region near Fermi level mainly arise from the 2p orbitals of the $sp$ hybridized atoms. The elastic constants and moduli of super-(BN)$_{16}$ exhibit clear anisotropy and super-(BN)$_{16}$ should have a low hardness and high ductility. We expect this work provides a new understanding of the structural, mechanical and electronical properties of BN materials containing $sp$, $sp^2$ and $sp^3$ hybridized B and N atoms.

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