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Hard three-dimensional BN framework with one-dimensional metallicity

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ABSTRACT

Carbon can be metal, semiconductor or insulator depending on its structures, and its conductivity can be one-dimensional (1D), 2D, and 3D correspondingly. Boron Nitride (BN) is isoelectronic to carbon, but one prominent difference between the two systems is their electronic properties. For many years, the synthesized and predicted BN allotropes were always insulators, irrespective of their structures. In this paper, with the help of structures searching based on first-principles calculations, a sp^2/sp^3-hybridized metallic monoclinic 3D BN (*M*-BN) structure is proposed. *M*-BN can be viewed as puckered hexagonal-BN (h-BN) layers bucked by partial sp^3 B–N bonds. The electronic property analysis revealed that the metallicity of *M*-BN is attributed to the delocalized 2*p* electrons of the sp^2 B and N atoms. The metallic B atoms and N atoms are aligns in two arrays along a 1D axial direction, resulting in the unusual 1D dual-threaded conduction in 3D *M*-BN structure. The enthalpy calculation have revealed that *M*-BN is the most energetically favorable structure among the predicted metallic BN structures so far, and it might be obtained via compressing layered h-BN precursor theoretically. Due to the 3D strong framework, *M*-BN has an estimated Vickers Hardness of 33.7 GPa, indicating it is a potential hard material with novel 1D conduction.

1. Introduction

Boron nitride is considered an intriguing compound, and has thus been studied for many years. There are four basic experimentally BN frameworks, including hexagonal BN (h-BN), rhombohedral BN (r-BN), wurtzite BN (w-BN), and cubic BN (c-BN). Since h-BN has been successfully synthesized, one of the topics in BN system is the exploration of novel BN structures. In the early years, studies were focused on high-pressure phase transitions between layered sp^2-hybridized (h-BN/r-BN) and sp^3-hybridized (w-BN/c-BN) phases [1–6]. In the past two decades, researchers have attempted to synthesize novel BN polymorphs via chemical methods and explore their potential applications. Some examples are the synthesized 1D BN nanotubes (BNNTs) for biomedicine applications, 2D BN nanosheets and BN nanoribbons for optoelectronics, or 3D porous BN architectures with high thermal conductivity [7–10]. In terms of their electronic applications, these synthesized BN compounds are always considered semiconductors/insulators, while reports on BN compounds used as conductive materials are scarce. However, it has been reported that BNNRs can be transformed into metallic by an external electric field [11]. Thus, searching for BN phases with intrinsic metallicity is still attracting the attention of researchers. Owing to the mechanical stability of 3D frameworks, 3D metallic BN has been highly anticipated and would have exciting applications in electronic devices.

Due to the ability of B and N atoms to form *sp*-, sp^2-, and sp^3-hybridizations, BN compounds can theoretically exhibit a variety of frameworks. In recent years, with the aid of first-principles calculations, a series of novel BN structures have been proposed [12–32]. Most of them are wide band gap semiconductors, including some superhard structures [15,20–23], 3D BN nanotubes and nanoribbon polymers [16,18], and 3D fully sp^2-hybridized structures [23,24]. This situation changed since 2013 when 3D metallic BN structures were predicted in three studies [29–31]. Unfortunately, one of the four structures, i.e. T-B_3N_3, was proven to be mechanically unstable in a subsequently study [33], and the four structures had also relatively high ground-state energies. These results prompt us to

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further explore metallic BN allotropes with high thermodynamical and mechanical stabilities, which may possibly be synthesized in the future, as was the case of the theoretically predicted BNNTs in 1994 that were later prepared by experimental scientists in 1995 [34,35]. Moreover, the metallicity in different dimensions (1D, 2D, and 3D) would potentially result in a wide variety of electronic properties and applications. Particularly, the unusual 1D or 2D conduction in 3D frameworks would be worth pursuing, due to its advantageous combination of both novel electronic properties and robust mechanical stability.

In this study, a 3D sp^2/sp^3-hybridized BN allotrope with novel 1D metallicity is theoretically proposed. This BN form has a monoclinic structure, and thereby has been denoted as *M*-BN. *M*-BN is mechanically and dynamically stable at zero pressure. It is the most energetically stable allotrope among the proposed metallic BN structures so far, and its energy is comparable to some pure sp^3 BN structures previously proposed. Due to the structural similarity, *M*-BN may be obtained by compressing layered BN precursor through partial sp^3 buckle, like the transition from graphite to diamond. Furthermore, we also study the origin of unusual 1D metallicity and excellent mechanical performance for this hybridized BN structure.

2. Computational methods

The BN structural searching was executed through the well-developed CALYPSO code [36], which is based on *ab inito* particle-swarm optimization. It was conducted up to 12 BN formulas per unit cell. Further structural optimizations, electron orbits and elastic properties of the pre-screened structures were performed using the CASTEP code based on density functional theory (DFT) [37]. The plane wave energy-cutoff is set as 330 eV with ultra-soft pseudopotential, which was chosen to achieve the accuracy of total energy convergence of 1–2 meV per atom [38]. The local density approximation (LDA) functional of Ceperley and Alder parameterized by Perdw and Zunger (CA-PZ) was used for describe the electron-electron exchange interaction [39,40]. The Monkhorst-Pack grids for Brillouin zone sampling [41] was generated by $2\pi \times 0.04$ Å^{-1} *k*-point separation. Phonon dispersion spectra were calculated by finite displacement method in the CASTEP code by using primitive cell, and the unit cell was used to calculate elastic constants, bulk and shear modulus, and 0.003 was chosen as the applied maximum strain amplitude during process. The band structure was calculated by the HSE06 hybrid functional [42] as implemented in VASP code [43]. The used convergence plane wave cutoff energy was 550 eV, and the Monkhorst-Pack *k* mesh of $13 \times 13 \times 9$ for electronic property calculations.

3. Results and discussion

3.1. Structural configuration

The configuration of the predicted crystal structure is shown in Fig. 1 with different views. The structure has a monoclinic symmetry (*Cm* space group, No. 8), and thus has been denoted as *M*-BN hereafter. The fully relaxed lattice constants of *M*-BN structure are $a = 8.18$ Å, $b = 2.58$ Å, $c = 6.45$ Å, and $\beta = 133.3°$ at zero pressure. As shown in Fig. 1a and b, there are four inequivalent B and four inequivalent N atoms in per unit cell. The B atoms are colored in dark yellow, occupies the B1 (−0.495, −0.5, −0.728), B2 (−0.202, −0.5, −0.185), B3 (−0.133, 0, 0.53), B4 (−0.836, 0, −0.944), respectively. The N atoms are colored in blue, occupies the N1 (−0.895, 0, −0.215), N2 (−0.686, −0.5, −0.751), N3 (−0.255, −0.5, −0.467), N4 (−0.048, 0, 0.0026), respectively. In Fig. 1a, one can identify that B1 and N1 atoms are sp^2-hybridized, the other atoms are sp^3-hybridized. Fig. 1c shows, the *M*-BN can be viewed as puckered h-BN layers interlinked via sp^3 B–N bonds, the layered blocks are colored as rectangles in different colors. Due to the partial sp^3 bonding, *M*-BN has a density of 3.32 g/cm^3, lower than that of pure sp^3 hybridized c-BN (3.46 g/cm^3).

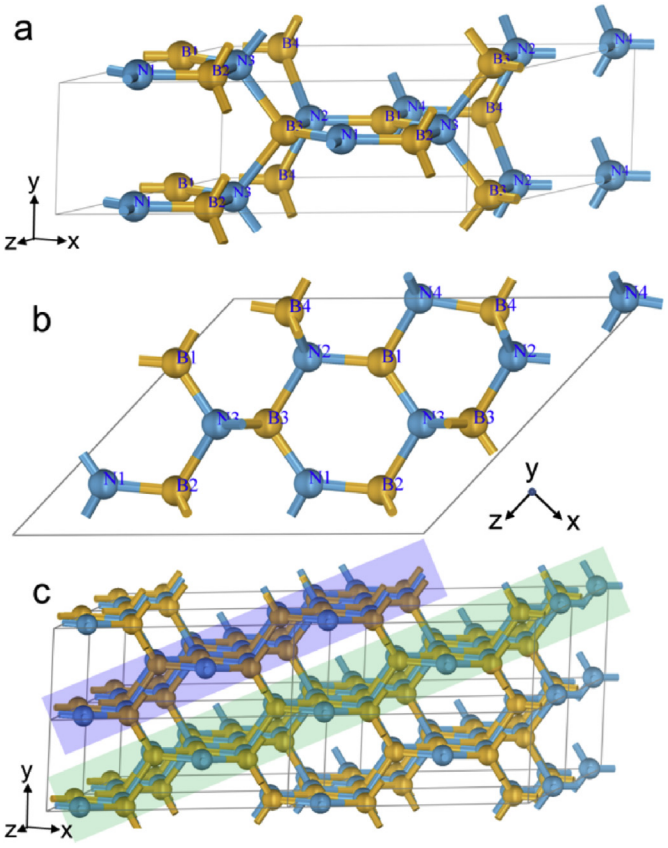

Fig. 1. Configurations of *M*-BN. The blocks marked with blue and green rectangles stand for the puckered h-BN layers. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.2. Dynamical stability

The phonon spectra were calculated to study the dynamical stability of *M*-BN. We plotted the phonon dispersion curves of *M*-BN at 0 GPa and 40 GPa in Fig. 2, the sequence of high-symmetry

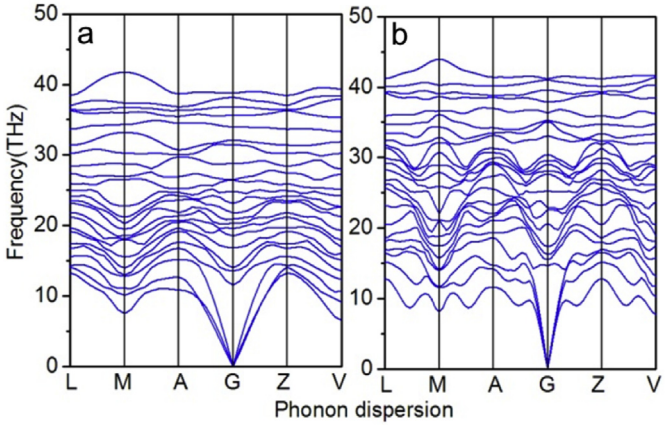

Fig. 2. Phonon dispersion curves of *M*-BN at (a) 0 GPa and (b) 40 GPa.