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Structural, mechanical, and electronic properties of P3m1-BCN



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ABSTRACT

The mechanical and electronic properties of P3m1-BCN have been studied by using first principles calculations. The anisotropy studies of Young's modulus, shear modulus and Poisson's ratio show that P3m1-BCN exhibits a large anisotropy. Electronic structure study shows that P3m1-BCN is an indirect semiconductor with band gap of 4.10 eV. Unusually, the band gap of P3m1-BCN increase with increasing pressure.

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1. Introductions

The ternary boron-carbon-nitride systems, which are isoelectronic with diamond and c-BN, have attracted much attention because of the theoretical prediction that β -C₃N₄ compound should have a hardness comparable to diamond [1]. However, most of the synthesized B-C-N compounds have the amorphous structures so far. A large number of the previous experimental studies on this topic are originally from the view that isoelectronic carbon and c-BN should have the similar crystal structures with diamond and c-BN. The theoretically studied structures are all focused on high dense phases, such as hexagonal BC_2N [2–6], chalcopyrite BC₂N [7], and cubic BC₂N [8–15]. The structural form of c-BC₂N [15] is studied with the ab initio pseudopotential density functional method for all the possible c-BC₂N structures starting from an eight-atom zincblende-structured cubic unit cell. The c-BC₂N structures are expected to be metastable. The hardest phases of c-BC₂N are studied to have bulk and shear moduli comparable to or slightly higher than those of c-BN, which is opposite to the experimental result that the hardness of this c-BC₂N phase is only slightly smaller than diamond. The calculated bulk

http://dx.doi.org/10.1016/j.jpcs.2014.12.008 0022-3697/© 2014 Elsevier Ltd. All rights reserved. modulus and shear modulus indicate that this phase should be softer than c-BN. Their results provide an explanation for recent experimental observations as well as a possible path to synthesis of the materials. Using the particle swarm optimization algorithm, Li et al. [16] report five competitive structures with clear tetrahedrally sp³ hybridization, among which two metallic orthorhombic structures (Pmm2 and Pmma) with the maximal stable bonds (C-C and B-N) is energetically more favorable than earlier proposed structures. Further first principles calculations suggest that the predicted five structures possess simultaneously superhard and superconducting properties. The five structures have the similar calculated hardness (56-58 GPa), but show distinct difference in superconducting critical temperature, ranging from 2 to 53 K. Based on the ab initio plane-wave pseudopotential density functional theory (DFT) and quasi-harmonic Debye model, J. Chang [17] have investigated the structure and thermodynamic properties of the potential superhard boron–carbon–nitride β -BC₂N. They found that the bulk modulus value of β -BC₂N is between the diamond and c-BN, and they also obtained the Debye temperature $\Theta_D = 1745$ K, which is consistent with the theoretical values 1700 K, as reported by Cheng et al. [18]. Using a developed methodology of designing superhard materials for given chemical systems under external conditions, a new P3m1 phase of BCN was proposed by Zhang et. al [19]. Till now, there is no detailed mechanical and electronic properties studies on this new phase of

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BCN. In the present work, we have performed detailed first principles calculations of the equilibrium crystal structure, mechanical properties, and electronic properties of P3m1-BCN based on DFT.

2. Theoretical method

In our calculations, the structural optimization and property predictions of the BCN polymorphs were performed using DFT [20,21] with the generalized gradient approximation (GGA) parameterized by Perdew, Burke and Ernzerrof (PBE) [22] and the local density approximation (LDA) [23,24] as implemented in the Cambridge Serial Total Energy Package (CASTEP) code [25]. In the structure calculation, a plane-wave basis set with energy cut-off 540 eV is used. The Vanderbilt ultrasoft pseudopotential was used in present work. For the Brillouin-zone sampling, the $10 \times 10 \times 4$ Monkhorst-Pack mesh [26] is adopted. The Broyden–Fletcher–Goldfarb–Shanno (BFGS) [27] minimization scheme was used in geometry optimization. The self-consistent convergence of the total energy is 5×10^{-6} eV/atom; the maximum force on the atom is 0.01 eV/Å, the maximum ionic displacement within 5×10^{-4} Å and the maximum stress within 0.02 GPa.

3. Results and discussion

P3m1-BCN has a trigonal symmetry that belongs to the P3m1 space group. The crystal structure of P3m1-BCN is shown in Fig. 1. Table 1 lists the calculated equilibrium lattice parameters within GGA and LDA method for P3m1-BCN, c-BN, and diamond, together with previous results. From Table 1, we can see that our calculated lattice parameters for P3m1-BCN are reasonable compared with previous study [19]. The predicted lattice constants and bond lengths within LDA method are smaller than those within GGA method, as the usual cases. In Fig. 2, we illustrate the hydrostatic pressure dependence of the equilibrium lattice parameters a/a_0 , and c/c_0 (where a_0 , and c_0 are the equilibrium conventional lattice constants at zero pressure and temperature, respectively). For P3m1-BCN, it can be easily seen that the compressibility along *c*axis is less than that along *a*-axis (*b*-axis). To compare the incompressibility of P3m1-BCN, c-BN and diamond under pressure, the volume compressions V/V_0 (where V_0 is at the zero pressure and temperature equilibrium primitive cell volume) as a function of pressure are also plotted in Fig. 2. With the applied pressure increasing from 10 to 100 GPa, the volume V/V_0 of P3m1-BCN changes from 0.976 to 0.830 in GGA calculations, and the volume V/V_0 of diamond (c-BN) changes from 0.978 (0.975) to 0.843 (0.826) in GGA calculations when the applied pressure increases from 10 to 100 GPa, respectively. It shows that the incompressibility of P3m1-BCN is little smaller than that of diamond, whereas slightly larger than that of c-BN. So we predict the bulk modulus of P3m1-BCN is slightly larger than c-BN, while it is slightly smaller than diamond.

The elastic properties give important information concerning the nature of the forces operating in solids. Particularly, they provide information about the stability and stiffness of materials. In this paper, we calculated the elastic constants and elastic modulus of P3m1-BCN, c-BN, and diamond, together with previous results, which are shown in Table 2. The criteria for mechanical stability of trigonal symmetry group are given by:

$$C_{ij} > 0, \quad i = j = 1 \sim 6,$$
 (1)

$$C_{11} - C_{12} > 0, (2)$$



Fig. 1. Crystal structures of P3m1-BCN ($2 \times 2 \times 1$ supercell), the red, blue, and black spheres represent B, C and N atoms, respectively.

Table 1

Lattice constants *a*, *c* (Å), and cell volume per formula unit V_0 (Å³) for P3m1-BCN, c-BN, and diamond.

Crystal	Method	а	С	V				
P3m1-BCN	GGA	2.546 ^a , 2.550 ^b	6.294 ^a , 6.301 ^b	17.671 ^a , 17.742 ^b				
	LDA ^a	2.515	6.215	17.020				
c-BN	GGA ^a	3.622		11.884				
	LDA	3.576^{a} , 3.581^{c} ,		11.436 ^a , 11.480 ^c ,				
		3.616 ^f		11.558 , 11.860 , 11.820 ^f				
	Experiment ^g	3.620		11.8595				
Diamond	GGA	3.566 ^{a,h}		11.341 ^a , 11.337 ^h				
	LDA	3.526 ^a , 3.525 ^h		10.961 ^a , 10.950 ^h				
	Experiment ^g	3.567		11.3462				
^a This work								

- ^b Ref [19].
- ^c Ref [36].

^d Ref [37].

^e Ref [38].

^f Ref [39].

^g Ref [40].

^h Ref [41].



Fig. 2. The ratio a/a_0 , c/c_0 for P3m1-BCN as functions of pressure, and V/V_0 for P3m1-BCN, c-BN and diamond.

		C ₁₁	C ₁₂	<i>C</i> ₁₃	<i>C</i> ₁₄	C ₃₃	C ₄₄	C ₆₆	В	G	Ε	v
P3m1	GGA ^a LDA ^a	982 1050	106 119	64 70	-55 -64	1003 1079	385 405	438 466	381 411	419 444	920 979	0.10 0.10
c-BN	GGA ^a LDA ^a LDA ^b	779 823	165 185				446 479		370 397 391	384 407 411	856 910 913	0.12 0.12 0.11
	LDA ^c Experiment ^d	819 820	195 190				475 480		403 400			
Diamond	GGA ^a GGA ^e LDA ^a LDA ^e Experiment ^d	1053 1053 1104 1106 1076	120 120 140 141 125				563 569 598 607 577		431 431 461 462 442	522 518 549 545	1116 1109 1179 1174	0.07 0.07 0.08 0.08

 Table 2

 Calculated elastic constant C_{ij}, bulk modulus B (GPa), shear modulus G (GPa), Young's modulus E (GPa), Poisson's ratio v and hardness of P3m1-BCN, c-BN, and diamond

^a This work.

^b Ref. [36].

^c Ref. [42]. ^d Ref. [43].

^e Ref [41].

$$C_{11}C_{33}C_{44} - C_{14}^2C_{33} - C_{13}^2C_{44} > 0, (3)$$

 $C_{11}C_{33} + C_{12}C_{33} - 2C_{13}^2 > 0, (4)$

$$C_{44}(C_{11} - C_{12}) - 2C_{14}^2 > 0, (5)$$

The calculated results show that the P3m1-BCN is mechanically stable under ambient conditions. To ensure the stability of P3m1-BCN, the phonon spectra are calculated at 0 GPa and 100 GPa (see Fig. 3). There is no imaginary frequency, which means P3m1-BCN can be stable up to 100 GPa. For a trigonal crystal, there are six independent components, i.e. C_{11} , C_{12} , C_{13} , C_{14} , C_{33} , and C_{44} . From Table 2, one can see that the elastic constants of P3m1-BCN are smaller than diamond, but slightly larger than c-BN. The elastic constants versus pressure for P3m1-BCN are displayed in Fig. 4. All the elastic constants C_{ij} (except for C_{14}) increase with different rates under increasing pressure. C_{33} of P3m1-BCN increases faster than others, and C_{44} grows the slowest.



Fig. 4. Elastic constants and elastic moduli of P3m1-BCN as a function of pressure.



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The elastic modulus is defined as the slope of its stress-strain curve in the elastic deformation region [28]: $\lambda = stress/strain$, where λ is the elastic modulus. The bulk modulus (*B*) describes volumetric elasticity. The shear modulus (G) describes an object's tendency to shear when acted upon by opposing forces, and Young's modulus (E) describes tensile elasticity. It is a measure of the stiffness of an elastic isotropic material and is a quantity used to characterize materials. It is defined as the ratio of the stress along an axis over the strain along that axis in the range of stress in which Hooke's law holds [29]. In anisotropic materials, Young's modulus may have different values depending on the direction of the applied force with respect to the structure. Young's modulus E and Poisson's ratio v are taken as: E = 9BG/(3B+G), v = (3B-2G)/[2(3B+G)]. The elastic modulus versus pressure for P3m1-BCN is also plotted in Fig. 4. It is clear that all the elastic modulus increase but with different rates under increasing pressure. E increases faster than B, and the increasing rate of G is the slowest. From Table 2, we noted that the elastic modulus of P3m1-BCN is smaller than diamond, but larger than c-BN. This agrees with our previous forecast. The Poisson's ratio v of P3m1-BCN is 0.10 within GGA, slightly larger than diamond (0.07) and slightly smaller than c-BN (0.12), respectively.

Pugh [30] proposed the ratio of bulk to shear modulus (B/G) as an indication of ductile verses brittle characters. The bulk modulus B represents the resistance to fracture, while shear modulus Grepresents the resistance to plastic deformation. A high B/G ratio is concerned with ductility, whereas a low value according with brittle nature. If B/G > 1.75, the material behaves in a ductile manner [31]; otherwise, the material behaves in a brittle manner. For the P3m1-BCN at 0 K and 0 GPa, the calculated value is 0.91 (0.93) within the GGA (LDA) calculations, which suggests that BCN in P3m1 phase is prone to brittle. When the applied pressures changes from 0 to 100 GPa, the B/G ratio changes from 0.91 to 1.26, that it to say, P3m1-BCN still keeps brittle in this pressure range.

It is well known that the anisotropy of elasticity is an important implication in engineering science and crystal physics. The stiffness tensor expresses the stress tensor in terms of the strain tensor: $\sigma_{ij} = C_{ijkl} \varepsilon_{kl}$. C_{ijkl} is elastic stiffness constant. The compliance tensor is the inverse of the stress tensor and interprets the strain tensor in terms of the stress tensor: $\varepsilon_{ij} = S_{ijkl} \sigma_{kl}$. The S_{ijkl} is the elastic compliance constant. Young's modulus is defined as the ratio of normal stress to linear normal strain (both in the direction of applied load). The shear modulus is defined as the ratio of shear stress to linear strain. Poisson's ratio is defined as the ratio of transverse strain (normal to the applied load), to axial strain (in the direction of the applied load).

A fourth order tensor transforms in a new basis set following the rule:

$$S'_{\alpha\beta\gamma\delta} = r_{ai}r_{aj}r_{ak}r_{al}S_{ijkl},\tag{6}$$

where Einstein's summation rule is adopted and r_{cd} is the component of the rotation matrix (or direction cosines). The transformation can be substantially simplified in calculation of specific modulus. The uniaxial stress can be represented as a unit vector, and advantageously described by two angles (θ , φ), we choose it to be the first unit vector in the new basis set *a*. The determination of some elastic properties (shear modulus, Poisson's ratio) requires another unit vector *b*, perpendicular to unit vector *a*, and characterized by the angle χ . It is fully characterized by the angles θ (0, π), φ (0, 2π) and χ (0, 2π), as illustrated in Fig. 5. The coordinates of two vectors are [32]:

$$a = \begin{pmatrix} \sin\theta\cos\phi\\ \sin\theta\sin\phi\\ \cos\theta \end{pmatrix}, \quad \text{and } b = \begin{pmatrix} \cos\theta\cos\phi\cos\chi - \sin\phi\sin\chi\\ \cos\theta\sin\phi\cos\chi + \cos\phi\sin\chi\\ -\sin\theta\cos\chi \end{pmatrix}.$$
(7)



Fig. 5. Definitions of angles used to describe directions in calculations.

Young's modulus can be obtained by using a purely normal stress in $\varepsilon_{ij} = S_{ijkl} \sigma_{kl}$ in its vectors form and it is given by

$$E(\theta, \varphi) = \frac{1}{S'_{11}(\theta, \varphi)} = \frac{1}{r_{1i}r_{1j}r_{1k}r_{1l}S_{ijkl}} = \frac{1}{a_i a_j a_k a_l S_{ijkl}}.$$
(8)

Other properties depending on two directions (if perpendicular this corresponds to 3 angles) make them difficult to represent graphically. The shear modulus is obtained by applying a pure shear stress in the vector form and results in

$$G(\theta, \varphi, \chi) = \frac{1}{4S_{66}(\theta, \varphi, \chi)} = \frac{1}{4r_{1i}r_{2j}r_{1k}r_{2l}S_{ijkl}} = \frac{1}{4a_ib_ja_kb_lS_{ijkl}},$$
(9)

Poisson's ratio can be expressed as

$$v(\theta, \varphi, \chi) = -\frac{S_{12}(\theta, \varphi, \chi)}{S_{11}(\theta, \varphi)} = -\frac{r_{1i}r_{1j}r_{2k}r_{2l}S_{ijkl}}{r_{1i}r_{1j}r_{1k}r_{1l}S_{ijkl}} = -\frac{a_ia_jb_kb_lS_{ijkl}}{a_ia_ja_ka_lS_{ijkl}}.$$
 (10)

Using above formulas, the calculated Poisson's ratio, shear modulus and Young's modulus along different directions as well as the projections in different planes can be obtained. We first focus on Poisson's ratio, Fig. 6(a), (b), and (c) displays the 2D representation of Poisson's ratio in the *xy*, *xz*, and *yz* planes for P3m1-BCN, respectively. We found that $0 \le v \le 0.18$, showing that v remains positive.

In order to quantify the anisotropy, we calculated the shear modulus for all possible directions of shear strain, the 2D representation of shear modulus in the *xy*, *xz*, and *yz* planes for P3m1-BCN are shown in Fig. 6(d), (e), and (f), respectively. We observed that shear modulus varies between 350 and 473 GPa, the average value of all directions is 411 GPa, this value is close to previous calculated value (419 GPa, see Table 2). The directional dependence of the Young's modulus and the projection in *xy*, *xz*, and *yz* planes for P3m1-BCN are illustrated in Fig. 7. The minimal value of $E_{max}/E_{min}=1.25$ shows P3m1-BCN exhibits a large elastic anisotropy.

3.1. Electronic properties

The calculated band structure, total and partial density of states (DOS) of P3m1-BCN are plotted in Fig. 8. The dashed line represents the Fermi level (E_F). The electronic energy band structure of P3m1-BCN shows that it is an indirect semiconductor and its band gap is 4.10 (4.06) eV within GGA (LDA). The valence band maximum and conduction band minimum are at Γ point and M point, respectively. It is known that the calculated band gap with DFT are usually underestimated by 30–50%, the true band gap must be larger than the calculated results. The total DOS and the partial wave DOS projected onto different atoms at 0 GPa are also shown in Fig. 8. The main















Fig. 6. 2D representation of Poisson's ratio in the *xy* plane (a), *xz* plane (b) and *yz* plane (c) for P3m1-BCN. 2D representation of shear modulus in the *xy* plane (d), *xz* plane (e), and *yz* plane (f) for P3m1-BCN. The black solid line represents the maximum and red dashed line represents the minimum.



Fig. 7. The directional dependence of the Young's modulus for P3m1-BCN (a), 2D representation of Young's modulus in the xy plane (b), xz plane (c), and yz plane (d).

features of P3m1-BCN can be summarized as follows: (i) the peak present in the lower energy part (-19 to -12 eV) of the DOS is mainly due to contributions from the s electrons of N, the contribution from B atom is very small; (ii) the states from -12 eV to Fermi energy (0 eV) mainly originate from B-s and C-p orbitals with slight contributions from B-p, the contribution of the C atom s orbital and N atom s orbital are very small. (iii) The part present in the energy part (4 to 18 eV) of the DOS is mainly due to contributions from the pelectrons of B atom, the contribution of the N atom s orbital is the smallest, Fig. 9 shows the band gap of P3m1-BCN as a function of pressure. The band gap of diamond and c-BN as a function of pressure are also shown for comparison. It can be seen that, the band gap increases approximately 5.6%, 9.9% and 4.3% with the increase of pressure from 0 to 100 GPa for P3m1-BCN, diamond and c-BN, respectively. This similar trend is also observed for PtAs₂ [33] and FeS₂ [34] under pressure. The relationships of band gap and pressure are $E_{g}(P3m1-BCN) = -9.0210 \times 10^{-6}P^{2} + 0.0031P + 4.1064, E_{g}(Diamond) =$ $8.8578 \times 10^{-6}P^2 + 0.0050P + 4.1598$, E_g (c-BN) = $-7.8904 \times 10^{-6}P^2$ +0.0027P+4.4556. In the pressure range from 0 to 100 GPa, P3m1-BCN keeps an indirect semiconductor. We found through Mulliken atomic population analysis that the $B \rightarrow C$ charge transfers slightly increases from 0.55 e to 0.56 e with pressure up to 100 GPa, leads to a relative enhanced ionicity between B and C atoms at high pressure. This trend has been explained by Oliver Tschauner et al. [35] using the Bader charge analysis.

4. Conclusions

This study reports a detailed investigation of the structural, and electronic properties of P3m1-BCN using the DFT within the ultrasoft psedopotential scheme in the frame of LDA and GGA. The most relevant results are summarized as follows: (1) The elastic constants and phonon calculations reveal P3m1-BCN is mechanically and dynamically stable and it has large bulk modulus 381 GPa, shear modulus 419 GPa, Young's modulus 920 GPa, and small Poisson's ratio 0.10 at ambient condition. The elastic anisotropy properties show that P3m1-BCN exhibits a large anisotropy in its Poisson's ratio, shear modulus and Young's modulus. (2) P3m1-BCN is an indirect semiconductor and its band gap is 4.10 (4.06) eV within GGA (LDA) at zero pressure. We also calculated the relationship between band gap and the pressure. Unusually, it is found that the band gap energy increases with the pressure increases.



Fig. 8. Electronic band structure (a), density of state and (b) for the P3m1-BCN at 0 GPa.



Fig. 9. Energy band gap for P3m1-BCN and diamond as a function of pressures.

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