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A potential superhard material m-BCN

We here propose a new superhard material m-BCN with comparable Vickers hardness to cBN by the use of first-principles calculations. The calculations show that the mentioned m-BCN is a thermodynamically and kinetically stable semiconductor. Hydrostatic calculation shows that it is anisotropic and its incompressibility is very close to c-BN. Structural analysis shows that its excellent mechanical property and thermodynamically stability are inherited from diamond and cBN. These results provide a new clue to find new superhard phase.

***Keywords**: m-BCN, mechanical properties, electronic structure, Vickers hardness, hydrostatic calculation*

INTRODUCTION

Superhard materials are generally thought of as the substances with Vickers hardness beyond 40 GPa [1, 2]. Diamond with Vickers hardness of 96 GPa is known to be the hardest materials in the world, however its utility is limited due to its high brittleness, low thermal and chemical stability. Thus, it is necessary and significant to find new superhard materials with hardness comparable to diamond but having other improved physical and/or chemical properties [3]. Because of its high hardness and unique bonding feature, diamond has been in practical use as a template to construct other superhard materials. Actually a series of carbon-based materials with diamond-like bonding [4–6] and binary substituted products have been theoretically predicted or experimentally proved to be superhard materials [7–11]. Among these materials, cubic boron nitride (cBN) is typical example which keeps the bonding feature and electrical configurations of diamond. Its Vickers hardness is as high as 64.5 GPa [3], although evidently lower than that of diamond, still far higher than the threshold of Vickers hardness of superhard materials; most importantly its oxidation resistance and thermal stability are even better than those of diamond.

Recently, ternary substituted materials have attracted extensive interests from chemists, physicists and materials scientists [12–15] since there are much more possibility to find new superhard materials due to structural diversity and bonding flexibility. Actually, some superhard B–C–N phase has been synthesized under high pressure and high temperature conditions. For example, a cubic structural BC_2N has been reported to have a Vickers hardness of 76 GPa [16], remarkably higher than the hardness of previously reported cBN.

It is established that a superhard material should have a small molar volume, short bond length and high covalent bond energy. Based on these rules, B and N atoms with atomic covalent radius of 0.84 and 0.71 Å [17] are most possible candidate atoms to replace C atom with covalent radius of 0.76 Å in a diamond to obtain a superhard material.

COMPUTATIONAL DETAILS

We screened a super-hardness phase of carbon by the use of CALYPSO software [18, 19]. But it is a metastable state with Vickers hardness of as high as 88 GPa, the corresponding pressure for phase conversion from graphite is calcu-lated to be as high as 100 GPa, much higher than ordinary conversion pressure of carbon allotropes required [20–24]. In other words, it is impossible to synthesize this kind of carbon-based superhard materials. Thus we substituted some of carbon atoms with B and N atoms to form ternary materials to improve its thermodynamic stability. The chemical formula of the system is BCN. The as-formed materials has a space group of P2, belonging to the category of monoclinic system, so we named it m-BCN.

The structural optimization and property predictions of the m-BCN phase were performed using density functional theory with both the Generalized Gradient Approximation (GGA) and Local Density Approximation (LDA) implemented in the Vienna Ab-initio Simulation Package (VASP) Code. As plane-wave basis set with cut-off energy of 500 eV is used. The k-point samplings are (5×5×5) in the Brillouin zone. The convergence has been thought to reach when the change in total energy is within 10^{-5} eV, and the force on each atom in the unit cell after optimization is less than 0.05 eV/Å. Hydrostatic calculations and shear stress-strain curves calculations are carried out with Cambridge Sequential Total Energy Package (CASTEP) Code. A plane-wave basis set with cut-off energy of 700 eV is used. The k-point samplings are (7×7×7) in the Brillouin zone.

RESULTS AND DISCUSSION

The crystal structure of proposed m-BCN is shown in Fig. 1. Its space group is P2, lattice parameters of *a*, *b*, *c* are 2.713, 2.903 and 2.696 Å, respectively, β = 124.37°. Atomic fractional coordinates of C, N, and B are (0, 0.3357, 0.5), (0.5, 0.6593, 0) and (0.5, 0.005, 0.5), respectively. The optimized bond length of C–N and C–B are 1.572 and 1.662 Å, respectively.

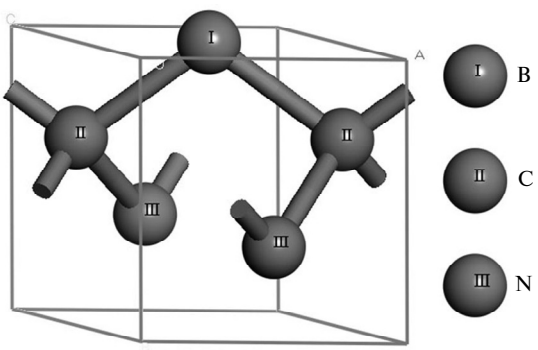

Fig. 1. The unit cell of m-BCN with carbon atom (I), boron atom (II), and nitrogen atom (III).

Elastic constant is a key parameter to characterize the resistance of the materials against the elastic deformation, and they should satisfy the stability condition for monoclinic crystals [25]:

$$C_{11} > 0,\ C_{22} > 0,\ \ C_{33} > 0,\ C_{44} > 0,\ \ C_{55} > 0,\ C_{66} > 0;$$

$$C_{33}C_{55} - C_{35}^2 > 0,\ \ C_{44}C_{66} - C_{46}^2 > 0,\ \ C_{22} + C_{33} - 2C_{23} > 0;$$

$$[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] > 0.$$

The calculated results shown in Table 1 demonstrate that elastic constants satisfy monoclinic crystal stability condition, thus m-BCN is mechanically stable.

Table 1. The calculated elastic constants (GPa) of m-BCN at the GGA and LDA level

Crystal	Method	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}	C_{15}	C_{25}	C_{35}	C_{46}
Diamond	GGA	1006.74			574.48			90.71						
	LDA	1100.63			589.99			149.92						
c-BN	GGA	782.63			441.78			168.80						
	LDA	825.08			479.02			189.22						
m-BCN	GGA	971.75	856.59	805.10	334.95	363.12	319.74	24.43	32.67	199.37	0	0	0	0
	LDA	1044.21	932.44	902.56	383.50	427.22	356.63	40.31	49.16	222.78	0	0	0	0

The bulk modulus, shear modulus, Young's modulus, and Poisson's ratio of the system can be calculated from elastic constants by Voigt-Reuss-Hill approximate [25] and the results are shown in Table 2. For comparison, diamond and cBN are also considered. It can be seen from Table 2 that the structure has a high bulk modulus and shear modulus, showing that it is difficult to be compressed and deformed. In addition, its Young's modulus is only slightly lower than that of cBN.

Table 2. The mechanical parameters of cBN, diamond, and m-BCN at the GGA and LDA levels

Crystal	Method	*a*, Å	*b*, Å	*c*, Å	*V*, Å^3	ρ/g, cm^3	*B*,GPa	*G*,GPa	*E*,GPa	ν
Diamond	GGA	3.560			45.12	3.534	396.1	524.7	1091.9	0.041
	LDA	3.536			44.21	3.606	466.8	541.1	1170.9	0.082
cBN	GGA	3.626			47.66	3.623	373.4	381.8	854.2	0.119
	LDA	3.582			45.98	3.756	401.2	406.4	911.5	0.121
m-BCN	GGA	2.713	2.903	2.696	17.51	3.490	349.5	357.8	800.3	0.105
	LDA	2.678	2.865	2.659	16.84	3.629	389.2	400.7	895.0	0.104

To estimate the hardness of a m-BCN, we used an empirical formula to calculate the Vickers hardness of m-BCN [26]:

$$HV = 2(G^3/B^2)^{0.585} - 3.$$

The calculations at LDA level show that the Vickers hardness of m-BCN is 65.9 GPa, although lower than that of diamond (91.5 GPa), is comparable to that of cBN (65.2 GPa). The GGA method provides the same conclusion. So it is a potential superhard material.

To further confirm the stability of the system under pressure, we performed hydrostatic calculations [27]. The ratio of the lattice constants as a function of pressure are plotted in Fig. 2, in which a_0, b_0, c_0 represent the lattice constants of the unit cell at equilibrium. It can be seen from Fig. 2 that all the ratios decrease with increasing pressure, however, the change rate of the three directions are different, suggesting that the structure is anisotropic. We further compared the incompressibility of m-BCN, cBN and diamond. The compression volume ratio V/V_0 were plotted in Fig. 3 (V_0 refers to a unit cell volume under equilibrium conditions). Figure 3 shows that m-BCN compression volume ratio V/V_0 changes from 1.00 to

0.82 with pressure from 0 to 100 GPa, evidently smaller than that of diamond under the same pressure, but very close to that of cBN. This indicates that the incompressibility of m-BCN is smaller than diamond, but very close to cBN.

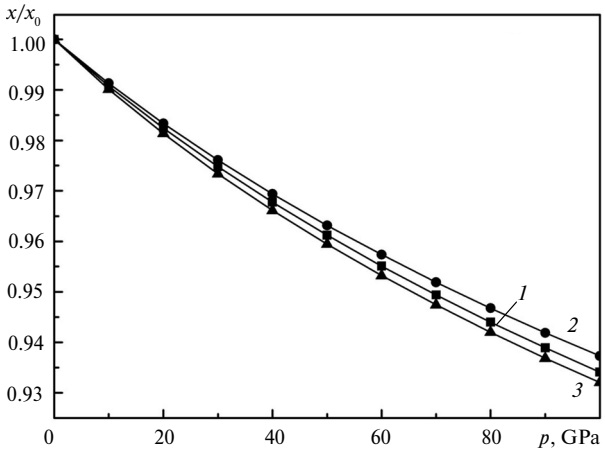

Fig. 2. The ratio of lattice constants a/a_0 (*1*), b/b_0 (*2*), c/c_0 (*3*) as functions of the pressure p for m-BCN.

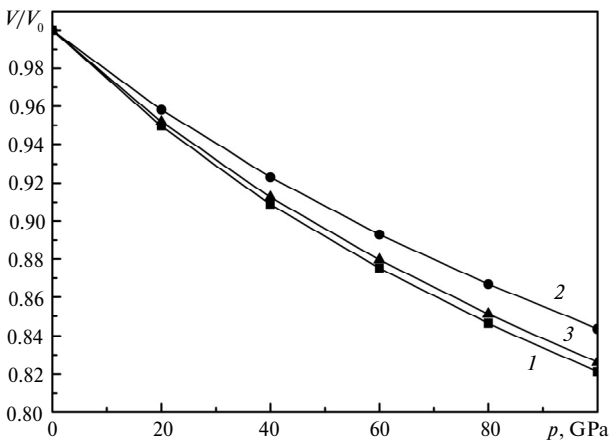

Fig. 3. The ratio of volume V/V_0 as function of the pressure for m-BCN (*1*), diamond (*2*), and cBN (*3*).

To further prove the mechanical stability of m-BCN, the shear stress-strain curve [28, 29] of the original cell in the (001) [100] direction was calculated. The shear stress-strain relations of m-BCN compared with cBN were plotted in Fig. 4. That is, by applying strain to obtain the stress changes from the elastic region to the unstable region to the final collapse. The turning point of the shear curve shown in Fig. 4 suggests a large deformation of the materials, the atoms will move from the original lattice position to a new lattice position. The stress-strain curve in this direction has a stress of 68.5 GPa when shear deformation is 10 %. In the range of 0–10 %, the stress values of m-BCN and cBN are very close. In the range of 10–20 %, the stress value of cBN is higher than that of m-BCN. As a whole, both the two materials have a high ability to resist deformation.

To study the electronic structure and understand the mechanical properties of the system, band structure and density of states (DOS) are calculated. Figure 5

shows that it is a semiconductor with energy gap of 0.8 eV. Figure 6 shows that the DOS are mainly from N-s, partly from C-s, C-p in the range of (–23)–(–17) eV; and are mainly from N-p, C-p, B-p, partly from C-s, B-s in the range of (–17)–0 eV; and are mainly from B-p, C-p, N-p, partly from B-s, C-s in the range of 0–18 eV. It is clearly shown that the hybridization between their atomic orbitals forms a strong sp^3-bonding structure and leads to a superhard material.

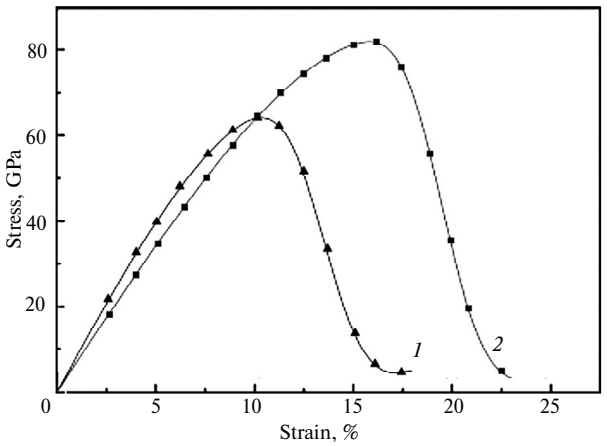

Fig. 4. The calculated shear stress–strain relations of m-BCN (001) [100] (*1*) compared with cBN (001) [100] (*2*).

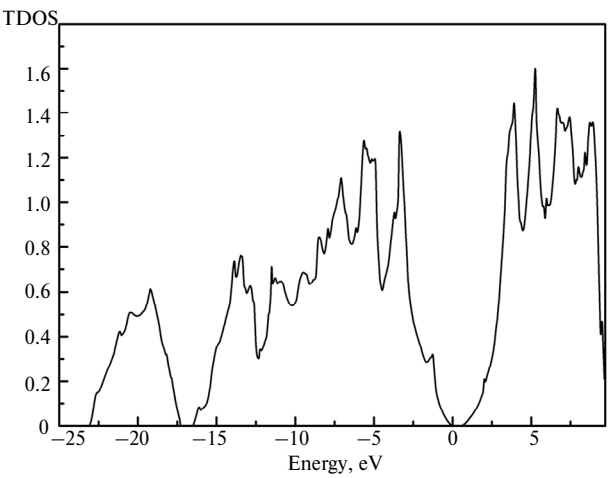

Fig. 5. TDOS of m-BCN.

To confirm the kinetic stability of this structure, we calculated phonon dispersion curves at the 0 GPa and 100 GPa, respectively. The curves are presented in Fig. 7. It is shown that there is no imaginary frequency in the Brillouin zone, suggesting that the structure is in the state of mechanical stability.

CONCLUSION

A potential superhard material m-BCN is proposed by the use of the first-principles calculations. The structural, mechanical, electronic properties of m-BCN are examined. The results show that the bulk modulus, shear modulus, Young's modulus are all high and its Vickers hardness is much higher than the threshold of

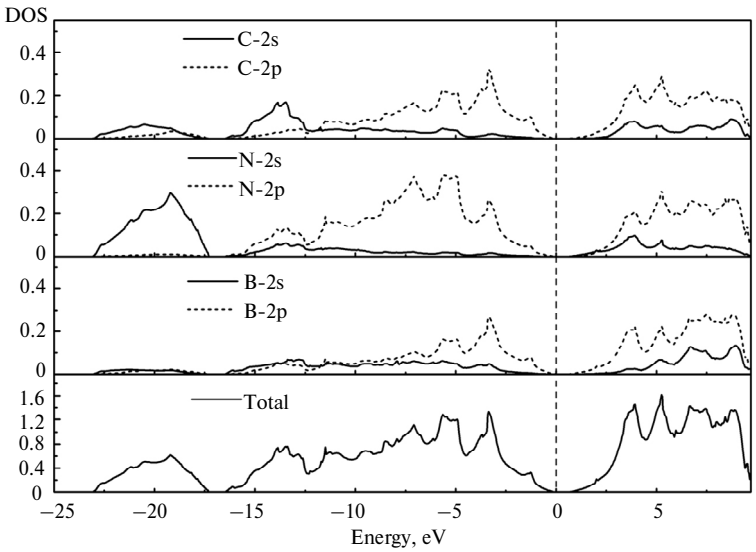

Fig. 6. DOS of m-BCN.

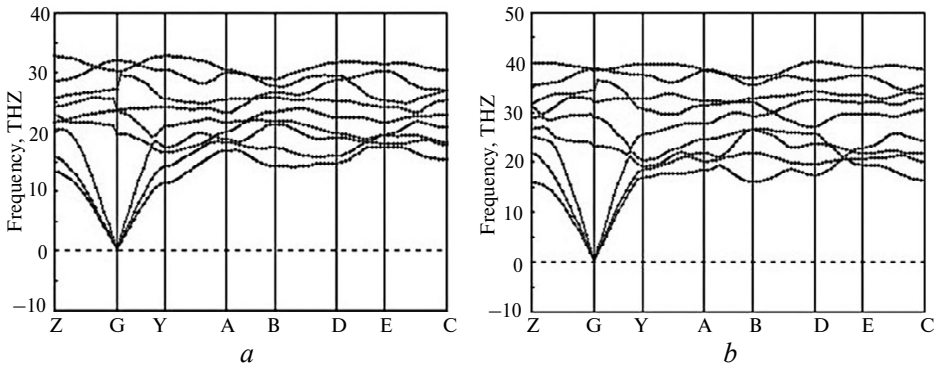

Fig. 7. Phonon dispersion curves in the Brillouin zone at the 0 (*a*) and 100 (*b*) GPa.

a superhard material 40 GPa. It is mechanical stable and its incompressibility is very close to that of cubic boron nitride. Electronic structure calculations show it is a semiconductor. Analysis on the geometrical and electronic structures shows the mentioned m-BCN inherits both the mechanical advantage of a superhard phase of carbon and electronic advantage of a B–N phase and leads it to be a superhard material.

Запропоновано новий надтвердий матеріал m-BCN, твердість за Віккерсом якого за розрахунками за першими принципами порівняна з твердістю cBN. Розрахунки показали, що згаданий m-BCN за термодинамічними і кінетичними показниками є стабільним напівпровідником. Гідростатичний розрахунок показав, що він є анізотропним і його нестисливість дуже близька до нестисливості cBN. Структурний аналіз показав, що його відмінні механічні властивості і термодинамічна стабільність успадковані від алмаза і cBN. Дані результати забезпечують нову схему пошуку нових надтвердих фаз.

***Ключові слова**: m-BCN, механічні властивості, електронна структура, твердість за Віккерсом, гідростатичний розрахунок.*

Предложен новый сверхтвердый материал m-BCN, твердость по Виккерсу которого по расчетам по первым принципам сравнима с твердостью cBN. Расчеты

показывают, что упомянутый m-BCN по термодинамическим и кинетическим показателям является стабильным полупроводником. Гидростатический расчет показал, что он анизотропный и его несжимаемость очень близка к несжимаемости cBN. Структурный анализ показал, что его отличные механические свойства и термодинамическая стабильность унаследованы от алмаза и cBN. Данные результаты обеспечивают новую схему поиска новых сверхтвердых фаз.

***Ключевые слова**: m-BCN, механические свойства, электронная структура, твердость по Викерсу, гидростатический расчет.*

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