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Elastic and electronic properties of Pbca-BN: First-principles calculations

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ABSTRACT

A fully tetrahedrally bonded boron nitride (BN) allotrope with an orthorhombic structure (Pbca-BN, space group: Pbca) was investigated by first-principles calculations. In this work, we have investigated the structural, elastic, electronic properties and elastic anisotropy of Pbca-BN by density functional theory method with the ultrasoft pseudopotential scheme in the frame of the local density approximation (LDA) and the generalized gradient approximation (GGA). From our calculations, we found that Pbca-BN has a bulk modulus of 344 GPa, a shear modulus of 316 GPa, a large Debye temperature 1734 K, a small Poisson's ratio 0.14, and the hardness of 60.1 GPa, thereby making it a superhard material with potential technological and industrial applications. Our calculations predict that Pbca-BN is mechanically stable and it is an insulator with wide band gap of 5.399 eV.

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1. Introduction

Since the announcement in 1957 of the discovery of the cubic form of boron nitride [1], BN has been studied widely. Being one of the most interesting solids, the III–V compounds, boron nitride has motivated tremendous amount of theoretical and experimental investigations of its fundamental properties for a long time. BN can exist in various crystalline forms, such as hexagonal BN (h-BN) [2], BN nanotubes (BNNTs) [3], wurtzite BN (w-BN), and cubic zinc-blende structured BN (c-BN) [4], etc., because of its specific sp^2 or sp^3 atomic bonding. h-BN is an analog of graphite; however, it is a wide bandgap semiconductor, and thus is distinct from semi-metallic graphite. c-BN is isoelectronic with diamond [5] and has a hardness that is only second to diamond. In addition, c-BN exhibits a chemical inertness far superior than that of diamond, such as a high melting temperature, high thermal conductivity, wide band gap and low dielectric constant. A primitive-centered tetragonal BN (Pct-BN) [6–8] has recently been reported as an analog of the Bct-BN structure [9,10]. The calculation indicated that Pct-BN is a superhard material with a hardness of 65.2 GPa and its shear strength along the (001) [001] direction is stronger than that of c-BN along the (111) [112] [6].

To understand the transition from h-BN to w-BN, a new transformation mechanism has been suggested recently based on

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accurate inelastic X-ray scattering experiments and recent first-principles calculations [11,12]. They argued that h-BN layers get close together; each N atom in a hexagonal layer buckles down in the *c*-axis direction and forms bond with a B atom directly below it in an adjacent layer. A fully tetrahedrally bonded boron nitride (BN) allotrope with an orthorhombic structure (O-BN) was investigated through first-principles calculations [13]. O-BN has a bulk modulus of 371.8 GPa and a hardness of 66.4 GPa, thereby making it a superhard material with potential technological and industrial applications. O-BN becomes thermodynamically more stable than layered hexagonal BN (h-BN) at pressure above 1.5 GPa and more favorable than the recently reported Pct-BN at any pressure. Using first-principles calculations, Jiang et al. [14] identify a new orthorhombic boron nitride (BN) phase (space group: Pmn21), which has similar topological structure to Bct-BN and Z-BN, but without the six-membered ring. This Pmn21-BN allotrope is energetically more favorable than previously reported Pnma-BN, Bct-BN and Z-BN phases. With only 0.06 eV/atom less stable than h-BN at ambient pressure, it can be formed from h-BN under cold compression at a low pressure of 4 GPa and the theoretical hardness and bulk modulus of the Pmn21-BN crystal are 403 GPa and 60.5 GPa, respectively, comparable to those of c-BN. Effects of stacking behavior of hexagonal basal layers to the structural stability and electronic properties of five possible h-BN structures were investigated thoroughly using first-principles calculations based on the density-functional theory (DFT) by Liu et al. [15]. They found that these structures with “bad” stacking of BN layers have a longer

lattice constant c compared to structures with “good” stacking sequences and the electronic properties of h-BN were found to be strongly dependent on the stacking of the hexagonal BN layers.

Using a developed methodology of designing superhard materials for given chemical systems under external conditions, a new Pbcn phase of BN was proposed by Zhang et al. [16]. But the detailed properties are not studied so far. In the present work, the mechanical, electronic and thermodynamic properties of Pbcn-BN are studied systematically.

2. Theoretical method

In our calculations, the structural optimization and property predictions of the BN polymorphs were performed using the DFT [17,18] with the local density approximation (LDA) [19,20] and the generalized gradient approximation (GGA) parameterized by Perdew, Burke and Ernzerhof (PBE) [21] as implemented in the Cambridge Serial Total Energy Package (CASTEP) code [22]. For Pbcn-BN, we used a plane-wave basis set with energy cut-off 500 eV (700 eV) is used with GGA (LDA). The $8 \times 8 \times 8$ ($4 \times 4 \times 4$) Monkhorst–Pack mesh [23] is adopted with GGA (LDA). The Broyden–Fletcher–Goldfarb–Shanno (BFGS) [24] minimization scheme was used in geometry optimization. The structural relaxation is stopped when the total energy, the maximum ionic displacement, the maximum stress, and the maximum ionic Hellmann–Feynman force are less than 5.0×10^{-6} eV/atom, 5.0×10^{-4} Å, 0.02 GPa and 0.01 Å, respectively. For c-BN and diamond, energy cut-off was used with 520 eV and 400 eV, respectively. The k -points of $9 \times 9 \times 9$ for c-BN, and $8 \times 8 \times 8$ for diamond are generated using Monkhorst–Pack mesh scheme, respectively, other parameters are set as the same as Pbcn-BN.

3. Results and discussion

3.1. Structural properties

The calculated lattice parameters for Pbcn-BN, c-BN and diamond, together with previous results are presented in Table 1. From Table 1, we can find that the calculated equilibrium volume are 4.84% (4.82%) and 9.86% (9.37%) larger than c-BN and diamond with GGA (LDA), respectively. Pbcn-BN has an orthorhombic symmetry that belongs to the Pbcn space group. For c-BN, the calculated lattice parameters are in excellent agreement with the reported calculated results [6,13,25,26]. For diamond, the

calculated lattice parameters are in excellent agreement with the reported calculated results [27], Pbcn-BN has four different bond lengths, namely, 1.583 Å, 1.526 Å, 1.522 Å and 1.568 Å. The average bond length 1.550 Å is comparable with that of diamond 1.527 Å (1.540 Å [9]) within LDA. The results imply that Pbcn-BN should have the similar bond strengths to that of diamond [28,29].

The lattice constants ratios a/a_0 , b/b_0 , c/c_0 and V/V_0 of Pbcn-BN (where a_0 , b_0 , c_0 and V_0 are the zero pressure and temperatures equilibrium lattice constants and volume, respectively) as a function of applied pressure are plotted in Fig. 1. The volume V/V_0 changes from 0.973 to 0.816 in GGA calculations when the applied pressure increases from 10 to 100 GPa. We noted that, when the pressure increases, the compression along the c -axis is much larger than those along the a -axis and b -axis in the basal plane. From Fig. 1, we can also easily see that the compression of c -axis is the most difficult. The lattice parameters volume V/V_0 as a function of applied pressure of Pbcn-BN, c-BN and diamond are also shown in Fig. 1. It can be easily seen that the compression of diamond is the most difficult. The calculated B–N bond distances are 1.5878 Å (1.5686 Å), 1.5268 Å (1.5119 Å) and 1.4843 Å (1.4718 Å) of Pbcn-BN (c-BN) at $P = 0, 50$ and 100 GPa, respectively. As the calculated values shown, all the B–N bond lengths decrease with pressure.

3.2. Elastic properties and anisotropy

The elastic properties of a solid are important. They are not only closely related to various fundamental solid-state phenomena, such as interatomic bonding, equations of state, and phonon spectra, but also linked thermodynamically with specific heat, thermal expansion, Debye temperature, and Grüneisen parameter. Most importantly, knowledge of the elastic constants is essential for many practical applications related to the mechanical properties of a solid. The criteria for mechanical stability of orthorhombic phase are given by [30]:

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

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

$$(C_{11} + C_{22} - 2C_{12}) > 0, \quad (3)$$

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

$$(C_{22} + C_{33} - 2C_{23}) > 0. \quad (5)$$

The calculated elastic constants of Pbcn-BN indicated that it is mechanically stable due to the satisfaction of the mechanical stability criteria. To ensure the stability of Pbcn-BN, the phonon

Table 1
Lattice constants a , b , c (in Å), and cell volume per formula unit V_0 (in Å³).

		a	b	c	V_0
Pbcn-BN	GGA ^a	5.1103	4.4336	4.3992	12.4591
	LDA ^a	5.0458	4.3800	4.3392	11.9873
c-BN	GGA ^a	3.6224	3.6224	3.6224	11.8835
	LDA ^a	3.5764	3.5764	3.5764	11.4364
	LDA ^b	3.5810	3.5810	3.5810	11.4803
	LDA ^c	3.5890	3.5890	3.5890	11.5574
Diamond	LDA ^d	3.6200	3.6200	3.6200	11.8595
	LDA ^e	3.6160	3.6160	3.6160	11.8202
	GGA ^f	3.5664	3.5664	3.5664	11.3408
	LDA ^f	3.5261	3.5261	3.5261	10.9606
		3.5660	3.5660	3.5660	11.3366
		3.5250	3.5250	3.5250	10.9501

^a This work.

^b Ref. [13].

^c Ref. [6].

^d Ref. [25].

^e Ref. [26].

^f Ref. [27].

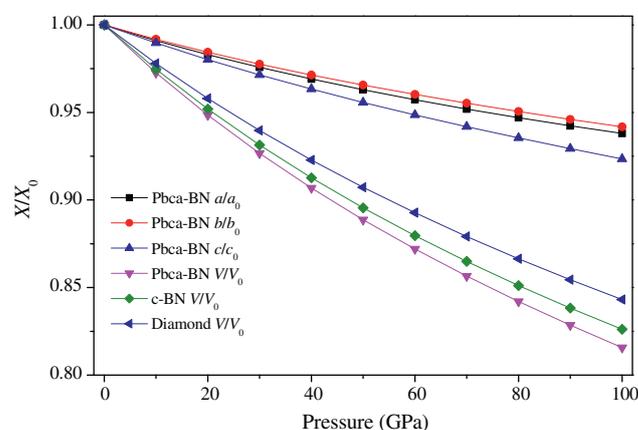


Fig. 1. The lattice constants a/a_0 , b/b_0 , c/c_0 compression as functions of pressure P for Pbcn-BN, and primitive cell volume V/V_0 for Pbcn-BN, c-BN and diamond.

spectra are calculated at 0 GPa and 100 GPa (see Fig. 2). There are no imaginary frequencies, indicating Pbca-BN can be stable up to 100 GPa. The calculated bulk modulus B and shear modulus G were calculated by the Voigt–Reuss–Hill approximations [31–33]. Calculated single crystal elastic constants C_{ij} , bulk modulus B , shear modulus G , Young's modulus E and Poisson's ratio ν of Pbca-BN, c-BN and diamond within both GGA and LDA, together with previous results are showed in Table 2. The elastic constants of Pbca-BN, c-BN, w-BN, O-BN, P-BN and diamond are also listed for comparison. It is evident that, the elastic constants of Pbca-BN, C_{11} and C_{33} are slightly smaller than those of c-BN, O-BN and P-BN, C_{22} is slightly larger than that of c-BN, O-BN, and P-BN. The calculated bulk modulus of Pbca-BN is 344 (370) GPa using GGA (LDA), slightly smaller than that of c-BN (370 GPa (397 GPa)). This suggests that Pbca-BN has the similar ability to resist uniform compression as c-BN. In other words, Pbca-BN will present a high uniaxial compressive strength, competing with that of c-BN. The calculated bulk modulus of Pbca-BN is 344 (370) GPa within GGA (LDA), 7.0% (6.8%) smaller than that of c-BN and 20.2% (19.7%) smaller than that of diamond, respectively. And the bulk modulus of Pbca-BN is 4.6% smaller than that of w-BN, 0.5% smaller than that of O-BN, and 8.2% smaller than that of P-BN within LDA. In view of the large bulk and shear moduli of Pbca-BN, the hardness calculations are of great interest. According to the Šimůnek model [34], the estimated values of hardness are listed in Table 2. The calculated results of Pbca-BN in GGA (52.2 GPa) and LDA (54.9 GPa) are larger than 40 GPa, indicating Pbca-BN is a potential superhard material. The hardness of Pbca-BN is comparable to that of c-BN, w-BN, O-BN, p-BN, and less than diamond (see Table 2), this is in accordance of the less bulk and shear modulus of Pbca-BN.

From Table 2, we can obtain more information about the mechanical properties. The Young's modulus E is important for technological and engineering applications. It is defined as the ratio between stress and strain, and is used to provide a measure of the stiffness in solid, The Young's modulus E is obtained from the following equations [33]:

$$E = \frac{9BG}{3B + G}. \quad (6)$$

The Young's modulus of Pbca-BN is less than that of c-BN by about 16% and less than that of diamond by about 35%. The other important property is the Poisson's ratio ν . The Poisson's ratio ν

provides more information about the characteristics of the bonding forces than any of the other elastic constants. The Poisson's ratio ν is obtained from the following equations [33]:

$$\nu = \frac{3B - 2G}{2(3B + G)}. \quad (7)$$

The Poisson's ratio ν of Pbca-BN is 0.14 within GGA, slightly larger than c-BN (0.12), w-BN (0.11), O-BN (0.13), and diamond (0.07), respectively, but slightly smaller than P-BN (0.15).

From Table 2, the B (G) of c-BN is calculated to be 397 GPa (407 GPa) with LDA in our series of calculations and it is in good agreement with previous calculations results (391 GPa (411 GPa) [13], 387 GPa [6], 400 GPa [35]). The E (ν) of c-BN is calculated to be 910 GPa (0.12) with LDA, almost equal to 913 GPa (0.11) in Ref. [13]. For diamond, according to the Voigt approximation, we obtain the isotropic bulk modulus B_V and shear modulus G_V of a polycrystalline aggregate from the single-crystal elastic constants C_{ij} [36].

$$B_V = \frac{1}{9}[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})], \quad (8)$$

$$G_V = \frac{1}{15}[C_{11} + C_{22} + C_{33} + 3(C_{44} + C_{55} + C_{66}) - (C_{12} + C_{13} + C_{23})], \quad (9)$$

Reuss [32] indicated that the isotropic bulk modulus B_R and shear modulus G_R of a polycrystalline aggregate can be rewritten in the following form in terms of the corresponding elastic constants C_{ij} :

$$B_R = \Delta[C_{11}(C_{22} + C_{33} - 2C_{23}) + C_{22}(C_{33} - 2C_{13}) - 2C_{33}C_{12} + C_{12}(2C_{23} - C_{12}) + C_{13}(2C_{12} - C_{13}) + C_{23}(2C_{13} - C_{23})]^{-1}, \quad (10)$$

$$G_R = 15\{4[C_{11}(C_{22} + C_{33} + C_{23}) + C_{22}(C_{33} + C_{13}) + C_{33}C_{12} - C_{12}(C_{23} + C_{12}) - C_{13}(C_{12} + C_{13}) - C_{23}(C_{13} + C_{23})]/\Delta + 3(\frac{1}{C_{44}} + \frac{1}{C_{55}} + \frac{1}{C_{66}})\}^{-1}, \quad (11)$$

with

$$\Delta = C_{13}(C_{12}C_{23} - C_{13}C_{22}) + C_{23}(C_{12}C_{13} - C_{23}C_{11}) + C_{33}(C_{11}C_{22} - C_{12}^2), \quad (12)$$

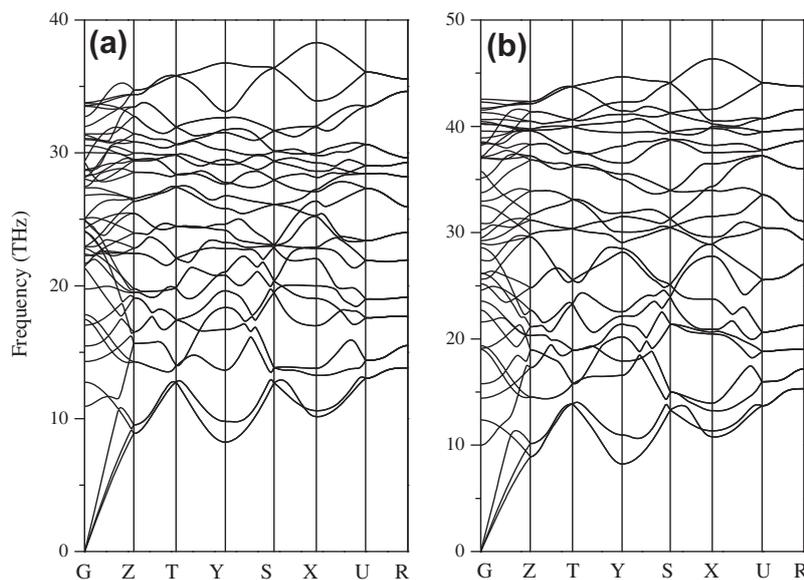


Fig. 2. The phonon spectra of Pbca-BN at 0 GPa (a) and 100 GPa (b).

Table 2

Calculated elastic constant C_{ij} , bulk modulus B (GPa), shear modulus G (GPa), Young's modulus E (GPa), Poisson's ratio ν and hardness of Pbca-BN, c-BN, w-BN, O-BN, P-BN and diamond.

		C_{11}	C_{12}	C_{13}	C_{22}	C_{23}	C_{33}	C_{44}	C_{55}	C_{66}	B	G	E	ν	H_v
Pbca-BN	GGA ^a	772	135	139	885	92	716	312	257	357	344	316	718	0.14	60.1
	LDA ^a	825	152	151	945	101	764	327	261	376	370	331	765	0.16	63.3
c-BN	GGA ^a	779	165					446			370	384	856	0.12	63.1
	LDA ^a	823	185					479			397	407	910	0.12	66.4
	LDA ^b										391	411	913	0.11	63.5
	LDA ^c	819	195					475			403				
w-BN	LDA ^b										388	409	908	0.11	67.7
O-BN	LDA ^b	890	82	129	910	70	986	344	393	279	372	370	834	0.13	66.4
P-BN	LDA ^d	1032	153	90	934	114	953	386	284	340	403	368	846	0.15	60.5
Diamond	GGA ^a	1052	120					563			431	522	1116	0.07	90.0
	GGA ^e	1053	120					569			431	518	1109	0.07	94.2
	LDA ^a	1104	140					598			461	549	1179	0.07	
	LDA ^e	1106	141					607			462	545	1174	0.08	

^a This work.

^b Ref. [13].

^c Ref. [45].

^d Ref. [14].

^e Ref. [27].

Hill [33] proved that the Voigt and Reuss equations represent upper and lower limits of the true polycrystalline constants. He showed that the polycrystalline modulus are the arithmetic mean values of the Voigt and Reuss modulus and thus given by

$$G_H = \frac{1}{2}(G_R + G_V), \quad (13)$$

$$B_H = \frac{1}{2}(B_R + B_V), \quad (14)$$

The obtained bulk modulus (B_H) and shear modulus (G_H) at different pressures are also presented in Table 3. In general, C_{44} and G are the two important parameters related to hardness of a material. For Pbca-BN at 0 K and 0 GPa, $C_{44} = 327$ GPa and $G = 331$ GPa in the LDA calculations.

Pugh [37] proposed the ratio of B/G as an indication of ductile or brittle characters. The bulk modulus B represents the resistance to fracture, while the shear modulus G represents the resistance to plastic deformation. A higher B/G ratio is associated with ductility, whereas a lower value corresponds to brittle nature. If $B/G > 1.75$,

the material behaves in a ductile manner; otherwise, the material behaves in a brittle manner. In the case of Pbca-BN at 0 K and 0 GPa, our calculated value of B/G is 1.118 within LDA calculations, which suggests that Pbca-BN is brittle. For the c-BN at 0 K and 0 GPa, the B/G value is 0.975, which also suggests that c-BN be prone to brittle. For diamond at 0 K and 0 GPa, the experimental B/G value is 0.826 [38] and our calculated value of B/G is 0.840 within LDA calculations. When the applied pressure changes from 0 GPa to 100 GPa, the ratio B/G value changes from 1.118 to 1.670, that is to say, Pbca-BN become less brittle with increasing pressure.

It is well known that the anisotropy of elasticity is an important implication in engineering science and crystal physics. So we go on investigating anisotropy at different pressures. The shear anisotropic factors provide a measure of the degree of anisotropy in the bonding between atoms in different planes. The shear anisotropic factor for the {100} shear plane between (011) and (010) directions is [39]:

$$A_1 = \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}}, \quad (15)$$

Table 3

Zero temperature elastic constants C_{ij} (GPa), bulk modulus B_H (GPa), shear modulus G_H (GPa) and Debye temperature θ_D (K) of Pbca-BN under P (GPa) from GGA and LDA calculations.

	P	C_{11}	C_{12}	C_{13}	C_{22}	C_{23}	C_{33}	C_{44}	C_{55}	C_{66}	B_H	G_H
GGA	0	772	135	139	885	92	716	312	257	357	344	316
	10	830	165	162	949	113	770	323	261	372	380	328
	20	886	194	183	1009	134	820	334	264	386	414	340
	30	939	225	206	1066	154	867	343	266	399	447	350
	40	990	254	231	1122	175	911	351	268	412	481	358
	50	1040	284	255	1176	195	952	358	270	422	513	367
	60	1088	315	278	1227	214	991	365	271	433	544	374
	70	1136	343	300	1278	234	1029	371	273	442	575	381
	80	1183	374	323	1327	252	1066	377	274	451	605	388
	90	1230	403	345	1375	270	1101	382	276	460	634	394
	100	1276	433	367	1422	288	1136	387	278	468	663	401
LDA	0	825	152	151	945	101	764	327	261	376	370	331
	10	882	181	171	1008	124	818	337	263	391	405	343
	20	936	212	196	1066	144	865	347	268	404	439	353
	30	987	241	219	1124	165	910	355	269	416	473	362
	40	1039	273	244	1176	184	951	362	270	428	505	371
	50	1089	302	265	1228	205	994	369	272	438	537	378
	60	1137	331	289	1281	224	1033	375	274	449	568	386
	70	1185	361	313	1331	242	1068	381	275	458	598	393
	80	1230	391	336	1381	261	1107	387	276	467	629	399
	90	1277	421	354	1427	280	1142	391	277	475	658	405
	100	1323	449	377	1476	299	1178	396	279	485	688	412

for the {010} shear plane between $\langle 101 \rangle$ and $\langle 001 \rangle$ directions it is [39]:

$$A_2 = \frac{4C_{55}}{C_{22} + C_{33} - 2C_{23}}, \quad (16)$$

for the {001} shear plane between $\langle 110 \rangle$ and $\langle 010 \rangle$ directions it is [39]:

$$A_3 = \frac{4C_{66}}{C_{11} + C_{22} - 2C_{12}}. \quad (17)$$

For an isotropic crystal the factors A_1 , A_2 , and A_3 must be 1.0, while any value smaller or larger than 1.0 is a measure of the elastic anisotropy possessed by the crystal. The anisotropy factors of Pbca-BN at 0 K as a function of pressure are shown in Fig. 3. When the applied pressure increases from 0 to 100 GPa, the anisotropy factor A_1 , A_2 , and A_3 decrease 11.7%, 29.4% and 0.78%, respectively. A_1 decreases sharply with pressure (due to the fact that the elastic constants C_{11} , C_{33} , C_{44} and C_{13} are affected by pressure). The anisotropy is only dependent on the symmetry of the crystal. The structure of the crystal has been changed under applied pressures due to the variations of a , b and c at various pressures. Therefore, the elastic anisotropy is different because of the variations of the elastic constants with pressure. Furthermore, since the compound is orthorhombic, the shear anisotropy factors are not enough to describe the elastic anisotropy. Therefore, the anisotropy of the linear bulk modulus should also be considered. The anisotropy of the bulk modulus along the a -axis and c -axis with respect to b -axis can be estimated by:

$$A_{B_a} = \frac{B_a}{B_b}, \quad (18)$$

$$A_{B_c} = \frac{B_c}{B_b}. \quad (19)$$

Noting that a value of 1.0 indicates elastic isotropy and any departure from one represents elastic anisotropy. B_a , B_b , and B_c are the bulk moduli along a , b and c axes, which can be calculated by [40]:

$$B_a = a \frac{dP}{da} = \frac{\Lambda}{1 + \alpha + \beta}, \quad (20)$$

$$B_b = b \frac{dP}{db} = \frac{B_a}{\alpha}, \quad (21)$$

$$B_c = c \frac{dP}{dc} = \frac{B_a}{\beta}, \quad (22)$$

with

$$\Lambda = C_{11} + 2C_{12}\alpha + C_{22}\alpha^2 + 2C_{13}\beta + C_{33}\beta^2 + 2C_{23}\alpha\beta, \quad (23)$$

$$\alpha = \frac{(C_{11} - C_{12})(C_{33} - C_{13}) - (C_{23} - C_{13})(C_{11} - C_{13})}{(C_{33} - C_{13})(C_{22} - C_{12}) - (C_{13} - C_{23})(C_{12} - C_{23})}, \quad (24)$$

$$\beta = \frac{(C_{22} - C_{12})(C_{11} - C_{13}) - (C_{11} - C_{12})(C_{23} - C_{12})}{(C_{22} - C_{12})(C_{33} - C_{13}) - (C_{12} - C_{23})(C_{13} - C_{23})}, \quad (25)$$

Our calculated B_a , B_b and B_c of Pbca-BN at different pressures are shown in Fig. 4. The results suggested that Pbca-BN is elastic anisotropic. The calculated directional bulk moduli suggest that it is the largest along b -axis; the smallest along c -axis, indicating that the compressibility along b -axis is the smallest, while along c -axis is the largest. Clearly, B_a , B_b and B_c increase with pressure. It is in accordance with the relationships between the ratio X/X_0 and pressure P as shown in Fig. 1. The variations in elastic constants and the

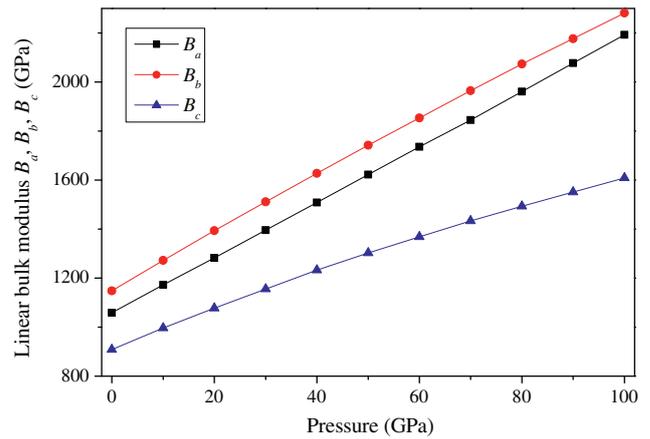


Fig. 4. Linear bulk modulus B_a , B_b and B_c of Pbca-BN at 0 K as a function of pressure.

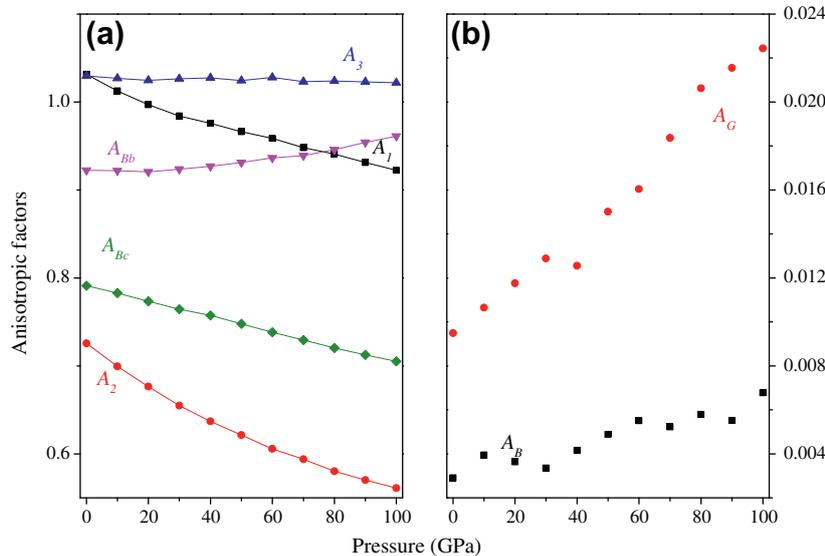


Fig. 3. Anisotropy factors of Pbca-BN at 0 K as a function of pressure, (a) A_1 , A_2 , A_3 , A_{Bb} , and A_{Bc} ; (b) A_G and A_B .

directional bulk moduli can also be understood in terms of the crystal structure. In the c -axis, the B and the N atoms are offset from each other; therefore, the electrostatic repulsion did not push each other directly, and then could not maximize incompressibility. On the contrary, along the a -axis and b -axis, the B and the N atoms are almost directly aligned, leading to highly directional repulsive electronic interactions, and then the least compressibility. As the pressure increases, the anisotropy of the linear bulk modulus A_{Bb} increase by 4.06% and A_{Bc} decrease 12.2%, respectively (Fig. 3).

In addition, the percentage of elastic anisotropy for bulk modulus A_B and shear modulus A_C in polycrystalline materials can also be estimated in the form of:

$$A_B = \frac{B_V - B_R}{B_V + B_R}, \quad (26)$$

$$A_C = \frac{G_V - G_R}{G_V + G_R}, \quad (27)$$

where B and G denote the bulk and shear modulus, and the subscripts V and R represent the Voigt and Reuss approximations. A value of zero represents elastic isotropy and a value of 100% is the largest possible anisotropy. The percentage of bulk and shear anisotropies are illustrated in Fig. 3. It shows that the value of bulk modulus anisotropy is smaller than the value of shear modulus anisotropy, suggesting that Pbca-BN is slightly anisotropic in compressibility.

The Debye temperature (Θ_D) is a fundamental physical property and correlates with many physical properties of solids, such as specific heat and the thermal coefficient [41]. It is used to distinguish between high and low temperature regions for a solid. If the temperature $T > \Theta_D$, we expect all modes to have the energy of $k_B T$, and if $T < \Theta_D$, one expects the high-frequency modes to be frozen, i.e. the vibrational excitations arise solely from the acoustic vibrations. We estimated the Debye temperature Θ_D of the studied compounds Pbca-BN from the average sound velocity, v_m , by the following equation [42]:

$$\Theta_D = \frac{h}{k_B} \left[\frac{3n}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{\frac{1}{3}} v_m, \quad (28)$$

where h is Planck's constant, k_B is Boltzmann's constant, N_A is Avogadro's number, n is the number of atoms in the molecule, M is

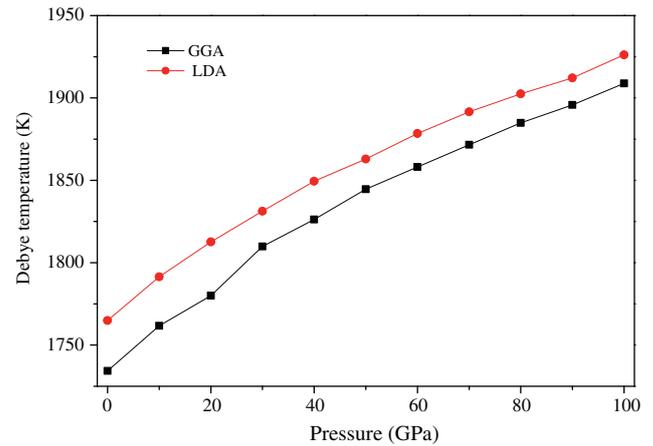


Fig. 5. Debye temperature of Pbca-BN as a function of pressure.

molecular weight, and ρ is the density. The average sound velocity v_m is approximately calculated from

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_s^3} + \frac{1}{v_p^3} \right) \right]^{-\frac{1}{3}}, \quad (29)$$

where v_p and v_s are the compressional and shear sound velocities, respectively, which can be obtained from Navier's equation [43]:

$$v_p = \sqrt{\left(B + \frac{4}{3}G \right) \frac{1}{\rho}}, \quad (30)$$

$$v_s = \sqrt{\frac{G}{\rho}}, \quad (31)$$

The calculated results of density, the compressional, shear and mean elastic sound velocity, and the Debye temperature for Pbca-BN are listed in Table 4. It is shown that the ρ , v_p , v_s , v_m and Θ_D increase with pressure and the calculated values are slightly larger.

The obtained Debye temperatures of Pbca-BN under pressure are shown in Fig. 5. At zero pressure and zero temperature, we obtain $\Theta_D = 1734$ K (1764 K) with GGA (LDA). It releases that for the

Table 4

The calculated density (ρ in g/cm^3), the longitudinal, transverse and mean elastic wave velocity (v_s , v_p , v_m in m/s), and the Debye temperature (Θ_D in K) for Pbca-BN.

	P	ρ	v_s	v_p	v_m	Θ_D
GGA	0	3.3076	9774	15,211	10,733	1734
	10	3.4005	9821	15,504	10,803	1762
	20	3.4874	9874	15,770	10,823	1780
	30	3.5693	9902	15,999	10,920	1810
	40	3.6475	9907	16,209	10,939	1826
	50	3.7219	9930	16,410	10,976	1845
	60	3.7932	9930	16,579	10,987	1858
	70	3.8618	9933	16,746	11,000	1872
	80	3.9282	9938	16,903	11,015	1885
	90	3.9224	9934	17,040	11,019	1896
	100	4.0548	9945	17,186	11,038	1909
LDA	0	3.4378	9812	15,363	10,783	1765
	10	3.5279	9860	15,634	10,851	1791
	20	3.6127	9885	15,868	10,893	1813
	30	3.6930	9901	16,087	10,924	1831
	40	3.7694	9921	16,285	10,958	1849
	50	3.8427	9918	16,459	10,967	1863
	60	3.9132	9932	16,634	10,992	1878
	70	3.9810	9936	16,788	11,006	1892
	80	4.0468	9930	16,938	11,009	1902
	90	4.1106	9926	17,072	11,013	1913
	100	4.1724	9937	17,221	11,032	1926

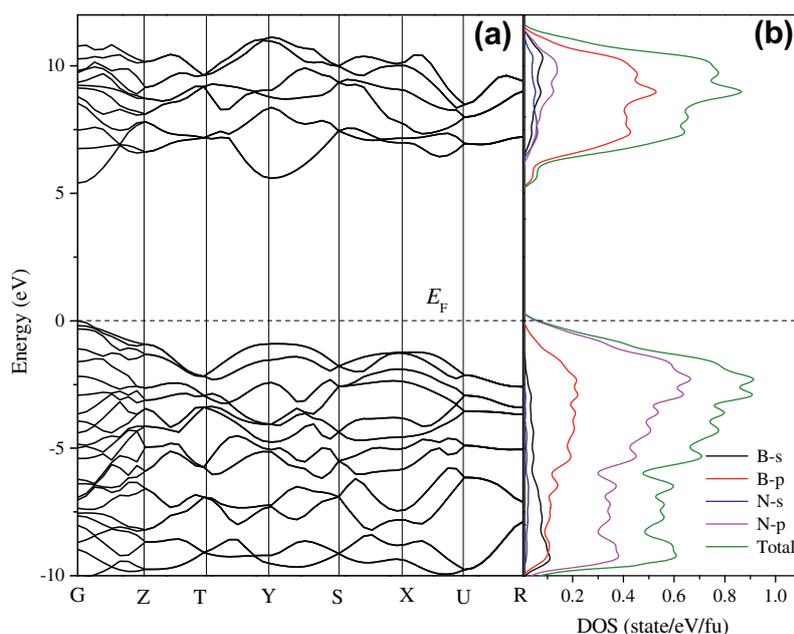


Fig. 6. Electronic band structure (a) and density of state (b) for the Pbca-BN at 0 GPa within GGA.

Pbca-BN, as pressure increases, the Debye temperature increases with pressure. For materials, usually, the higher Debye temperature, the larger microhardness. Therefore, although there is no other theoretical or experimental data available for comparison, but we believe that our predicated Θ_D for Pbca-BN is reasonable and can be used as reference for experiments.

3.3. Electronic properties

We analyzed the structural and electronic properties of the Pbca-BN structure in more detail. The Electronic band structure of the Pbca-BN is shown in Fig. 6(a). It is an insulator with direct band gap of 5.399 eV within GGA. The gap is larger than diamond (4.158 eV) and c-BN (4.454 eV) within GGA. For Pbca-BN, the valence band maximum and the conduction band minimum both are at G point. While LDA tends to underestimate the band gap slightly less than GGA, the band gap of Pbca-BN, diamond and c-BN are 5.207 eV, 4.236 eV and 4.496 eV, respectively. The band gap of Pbca-BN is slightly larger than that of O-BN (4.977 eV), Bct-BN (4.676 eV) within LDA. The value calculated within LDA of c-BN is in good agreement with that in Ref. [7] (4.4 eV) (the experimental value for c-BN is 6.1 eV [44]). The calculated total and partial density of states (DOS) of Pbca-BN with the equilibrium lattice parameters are plotted in Fig. 6(b). The dashed line represents the Fermi level (E_F). We can find that in the energy region from -20 to -12.5 eV, the contribution from B 2s and N 2p orbitals are small. From -12.5 to 0 eV, the contribution from N 2s orbitals is small and the main contribution comes from N 2p orbitals. The DOS at energy region from 5 to 17.5 eV is contributed mainly from the B 2p orbitals. One can see from partial DOS that, there is a strong hybrid between B 2p and N 2p orbitals, which result in the strong covalent B-N bonding.

4. Conclusions

In summary, this BN phase has an orthorhombic structure and is an insulator with an indirect band gap of approximately 5.399 (5.207) eV. In this work, we have investigated the structure, elastic properties and elastic anisotropy of Pbca-BN by density functional

theory method with the ultrasoft pseudopotential scheme in the frame of LDA and GGA. We have investigated the pressure dependences of elastic constants, shear modulus, bulk modulus, elastic anisotropy and Debye temperature. It is found that the shear modulus, bulk modulus, and Debye temperature of Pbca-BN tend to increase with increasing pressure. For elastic anisotropy, we found that the compressibility along *b*-axis is the smallest, while along *c*-axis is the largest and Pbca-BN is slightly anisotropic in compressibility. Pbca-BN is mechanically stable and it has large bulk modulus 344 GPa, shear modulus 316 GPa, Young's modulus 718 GPa, small Poisson's ratio 0.14 and large Debye temperature 1734 K at $P = 0$ GPa. Moreover, the calculated total density of states of Pbca-BN indicates that it is an insulator and it has a broad gap similar to that of diamond. We also calculated the relationship between density of states and the pressure of Pbca-BN. And we found that the band gap energy decreases as the pressure increases. And with the pressure increasing, the electrons of the energy decrease. For Pbca-BN, there are no previous calculations and experimental values for comparison. More experimental and theoretical works are recommended.

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