First-Principles study of Elastic properties, Hardness and Debye temperature of O-BN under pressures

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Abstract. An orthorhombic structure boron nitride (O-BN, space group: Pbam) was studied by first-principles calculations. The structural, elastic properties, Possion's ratio, elastic anisotropy, hardness, wave velocity and Debye temperature of O-BN were investigated by density functional theory method with the ultrasoft pseudopotential scheme in the frame of the generalized gradient approximation (GGA). The results for the equilibrium structural parameters of O-BN, c-BN and w-BN are consistent with experimental values and other theoretical results. It is found that O-BN has a bulk modulus of 365 GPa, a shear modulus of 362 GPa, a Young's modulus of 816 GPa, the hardness of 59.2 GPa, a large Debye temperature 1842 K and a small Possion's ratio 0.13 under zero temperature and zero pressure; O-BN has elastic anisotropy, and shear anisotropy of shear plane {100}, {010} and {001} increases with the increase of pressures. When the pressure increases, the compression along the b-axis is much larger than those along the a-axis and b-axis in the basal plane, and the compression along the c-axis is the smallest; O-BN can satisfy the criteria for mechanical stability of orthorhombic phase, so it is mechanically stable.

1. Introduction

Nowadays extensive attention has been aroused by BN due to its extensive application in industry [1]. The structure of BN crystal is quite similar with carbon's, which can present as many crystalline forms, such as cubic zinc-blende BN (c-BN)[2], wurtzite BN(w-BN)[3], hexagonal BN(h-BN)[4], BN fullerene [5], BN nanotubes(BNNTs)[6], 5H-BN[7], Amorphous BN[8] , Primitive-centered tetragonal BN(Pct-BN)[9-11], Orthorhombic BN (O-BN)[12] and the new types of BN compound[9,13-17]. Their particular electronic and mechanical properties have been studied in systematized methods, which shows that O-BN(66.4 GPa[18], 65.10 GPa[12])has a performance of super-hardness no inferior than c-BN（62.82 GPa[13]). However, it is still an important project in material research to explore the material with fine performances including high hardness, good thermal conductivity, high insulation and anti-corrosion class.

It has been put forward that O-BN is the potential material with super hardness; however, there is still a lack for the research on its performance especially under diverse pressures. As is well-known, when the temperature falls down to a certain degree, the Energy Equipartition Theorem will be invalid, Debye temperature is just the stagnation temperature [19], so it has a significant meaning to study on Debye temperature. The paper adopted the First-Principles to study on the O-BN crystal structure, elastic properties, elastic anisotropy, Debye temperature and hardness and forecasted the elastic properties，elastic anisotropy and Debye temperature under different pressures, which aimed at discussing the performance under pressure, thus to extend application range of O-BN.

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2. Computing method

First Principle software package CASTEP was adopted in the structure optimization and properties computing of BN which is based on density functional theory (DFT) [20-21]. Perdew-Burke-Ernzerh (PBE) method of GGA was used to complete the calculating, while broyden fletcher goldfarb shanno algorithm (BFGS) was utilized in the structure optimization and relaxation[23]. The interaction between valence electron and ion core was described by ultra-soft pseudo potential, and valence electron was chosen as B: 2s2 2p1, N: 2s2 2p3, plane wave truncation thermo was chosen as 520 eV. The K point of Brillouin was divided by Monkhorst-Pack grid as 3×6×8 (O-BN), 8×8×8 (c-BN), 9×9×6 (w-BN). Thermo convergence precision was 1×10^{-6} eV/atom and the average pressure on the atom was smaller than 0.02 eV/nm.

3. Results and discussion

3.1Crystal structure and model

O-BN belongs to orthorhombic system, whose space group is Pbam. Atom coordinate of crystal cell is B 4h (0.834, 0.172, 0.5), B 4g (0.912, 0.672, 0), N 4h (0.334, 0.699, 0.5), N 4g (0.411, 0.200, 0). Crystal structure of O-BN is showed in picture 1. Crystal structure was optimized above all, and the optimized O-BN、c-BN and w-BN lattice constant is showed in Table 1. After comparison with others' experiment results or theory data of lattice constant, it was found that error was less than 3.5%, which proved the above our calculating parameters reliable.

Lattice constant Ratio a/a_0, b/b_0, c/c_0 of O-BN and bulk pressure ratio V/V_0 of O-BN, c-BN, w-BN was changing as the intensity of pressure changed, which was showed in picture 2. a_0, b_0, c_0 and V_0 were the lattice constants and primitive cell volume in balanced condition under zero temperture and zero pressure. It can be seen that O-BN compressed by the least degree along axis c, while the most along axis b. The bulk compression ratios ranged as c-BN > O-BN > w-BN.

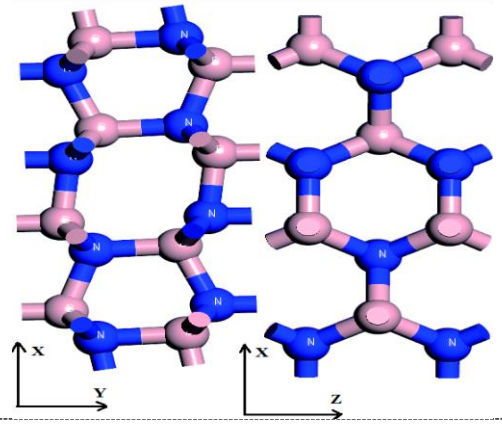

Figure 1. The crystal structure of O-BN viewed along the two direction.

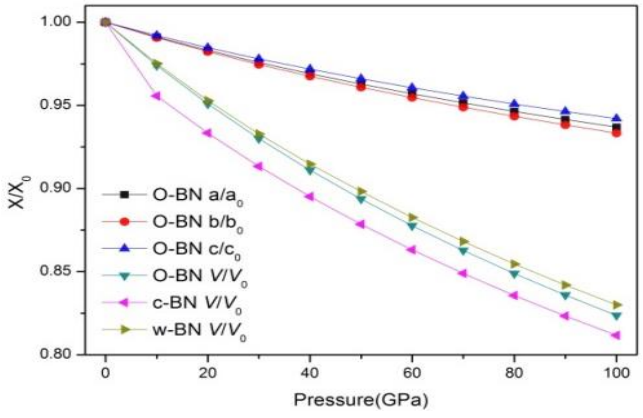

Figure 2. *The lattice constants a/a_0 , b/b_0 , c/c_0 compression as functions of for O-BN, and primitive cell volume V/V_0 for O-BN, c-BN and w-BN.*

3.2Elastic properties and anisotropy

Elastic property is one of the important properties of solid, it is not only closely associated with all kinds of basic solid phenomenon, such as the bonding between atoms, state equation, phonon spectrum, etc., and also bound up with thermodynamic properties for example specific heat, thermal expansion coefficient and Debye temperature, besides many macroscopic properties can be obtained by the elastic constants. O-BN bulk elastic modulus (B), shear modulus (G), Young's modulus (E) and Poisson's ratio (v) can be calculated through the elastic constants [24], and Vickers hardness can be calculated by the following empirical formula[25]. Table 2 shows the calculated elastic constants Cij, bulk modulus B, shear modulus G, Young's modulus E and Poisson's ratio v, Vickers hardness, etc. It

can be seen from the table that calculated data is very close to other theoretical data and experimental result. Bulk modulus indicates the ability to resist deformation of material under the action of hydrostatic pressure. Bulk modulus of O-BN, c-BN and w-BN are respectively 365 GPa, 362 GPa and 379 GPa, it can be seen that the bulk modulus of O-BN is a little larger than that of c-BN, and the theory hardness of O-BN is 59.2 GPa, which was very close to that of c-BN, just to prove O-BN is a kind of potential material with super-hardness.

Table 1. Equilibrium and experimental lattice constants of c-BN and h-BN nm

Phase	Space group	Method	a	b	c
O-BN	Pbam	This word(GGA)	8.818	4.255	2.528
		GGA[18]	8.787	4.243	2.525
c-BN	F-43m	This word(GGA)	3.625	3.625	3.625
		Exp.[4]	3.62	3.62	3.62
		GGA[17]	3.6224	3.6224	3.6224
w-BN	P63mc	This word(GGA)	2.538	2.538	4.197
		Exp.[4]	2.55	2.55	4.20
		GGA[13]	2.555	2.555	4.225

$$H_v = 2\left(\frac{G^3}{B^2}\right)^{0.585} - 3 \qquad (1)$$

According to the Born mechanical stability criterion[26] of orthogonal crystal system as follows:

$$\begin{cases} C_{11} > 0; C_{11}C_{12} > C_{12}^2 \\ C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} \\ \quad - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 > 0 \\ C_{44} > 0; C_{55} > 0; C_{66} > 0 \end{cases} \qquad (2)$$

The calculated elastic constants of O-BN under the pressure was shown in table 3, obviously elastic constant of O-BN in table 3 met the mechanical stability criterion, which proved that the O-BN being calculated under the selected pressure had a stable mechanics structure. Based on the Voigt-Reuss-Hill approximation, bulk elastic modulus GH and shear modulus BH can be calculated via the elastic constants. As for orthogonal crystal system, bulk modulus BV and BR and shear modulus GV and GR can be gained by the following formula [24, 27].

$$B_V = \frac{1}{9}\left[C_{11} + C_{22} + C_{33} + 2\left(C_{12} + C_{13} + C_{23}\right)\right] \qquad (3)$$

$$G_V = \frac{1}{15}\left[C_{11} + C_{22} + C_{33} + 3\left(C_{44} + C_{55} + C_{66}\right) - \left(C_{12} + C_{13} + C_{23}\right)\right] \qquad (4)$$

$$B_R = \Delta\left[C_{11}\left(C_{22} + C_{33} - 2C_{23}\right) + C_{22}\left(C_{33} - 2C_{13}\right) - 2C_{12}C_{33} + C_{12}\left(2C_{23} - C_{12}\right) + C_{13}\left(2C_{12} - C_{13}\right) + C_{23}\left(2C_{13} - C_{23}\right)\right]^{-1} \qquad (5)$$

$$G_R = 15\left\{4\left[C_{11}\left(C_{22} + C_{33} + C_{23}\right) + C_{22}\left(C_{33} + C_{13}\right) + C_{12}C_{33} - C_{12}\left(C_{23} + C_{12}\right) - C_{13}\left(C_{12} + C_{13}\right) - C_{23}\left(C_{13} + C_{23}\right)\right]/\Delta + 3\left(1/C_{44} + 1/C_{55} + 1/C_{66}\right)\right\}^{-1} \qquad (6)$$

$$\Delta = C_{13}\left(C_{12}C_{23} - C_{13}C_{22}\right) + C_{23}\left(C_{12}C_{13} - C_{11}C_{23}\right) + C_{33}\left(C_{11}C_{22} - C_{12}^2\right) \qquad (7)$$

Table 2. Calculated elastic constant C_{ij}(GPa), bulk modulus B (GPa), shear modulus G (GPa), Young's modulus E (GPa), Poisson's ratio v and hardness of O-BN, c-BN and w-BN.

	C_{11}	C_{12}	C_{13}	C_{22}	C_{23}	C_{33}	C_{44}	C_{55}	C_{66}	B	G	E	*v*	H_v
O-BN	871	82	123	902	71	961	342	385	283	365	362	816	0.13	59.2
	890[18]	82[18]	129[18]	910[18]	70[18]	986[18]	344[18]	393[18]	279[18]	372[18]	370[18]	834[18]	0.13[18]	66.4[18]
c-BN	769	159					444			362	382	848	0.11	66.0
	779[17]	165[17]					446[17]			370[17]	384[17]	856[17]	0.12[17]	63.1[17]
w-BN	948	122	53			1059	342			379	397	883	0.11	67.0
										388[18]	409[18]	908[18]	0.11[18]	67.7[18]

Table 3. Elastic constant C_{ij}, bulk modulus B_H (GPa) and shear modulus G_H (GPa) of O-BN under presure (GPa)

Presure	C_{11}	C_{12}	C_{13}	C_{22}	C_{23}	C_{33}	C_{44}	C_{55}	C_{66}	B_H	G_H
0	871	82	123	902	71	961	342	385	283	365	362
10	937	100	151	972	88	1027	353	401	290	401	377
20	1001	118	180	1042	106	1090	364	417	296	438	392
30	1061	137	209	1108	125	1147	373	431	299	472	404
40	1120	157	239	1168	144	1203	382	444	303	507	415
50	1174	175	269	1231	165	1258	388	457	308	542	426
60	1231	194	298	1289	184	1312	397	469	312	576	437
70	1284	215	326	1347	204	1365	403	481	316	609	447
80	1332	238	354	1402	223	1416	410	493	321	642	457
90	1386	254	384	1457	243	1466	414	503	327	674	466
100	1425	280	414	1511	263	1515	417	513	332	707	474

There is constant relationship among Bulk elastic modulus B_H, shear modulus G_H, bulk modulus B_V, B_R and shear modulus G_V, G_R.

$$G_H = \frac{1}{2}\left(G_R + G_V\right) \qquad (8)$$

$$B_H = \frac{1}{2}\left(B_R + B_V\right) \qquad (9)$$

As is known to all, the elastic anisotropy has important applications in engineering science and crystal physics, elastic anisotropy under the high pressure has important significance in understanding the evolution process of the atomic bonds in the solid. In order to predict overall elastic properties of O-BN, elastic anisotropy under different pressure was discussed. As for orthogonal crystal system, elastic anisotropic factor can be gained through the following formula[28]:

$$A_1 = \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}} \qquad (10)$$

$$A_2 = \frac{4C_{55}}{C_{22} + C_{33} - 2C_{23}} \qquad (11)$$

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

In the formula, A1 is shear anisotropy factor of shear plane {100} between <011> and <010>, A2 is shear anisotropy factor of shear plane {010} between <101> and <001>, A3 is shear anisotropy factor of shear plane {001} between <110> and <010>. As for isotropic crystals, A1, A2 and A3 must be all equal to 1. If A1, A2 or A3 of a crystal is not equal to 1, it means that the crystal is anisotropic. Figure 3 showed elastic anisotropic factor of O-BN under different pressures. It can be seen from the graph that three anisotropy factor is less than 1, which proved O-BN is anisotropic. A1, A2 and A3 reduced

to be far from 1 with the increase of pressure, which indicated shear anisotropy of three shear planes {100}, {010} and {001} increased with the increase of pressure.

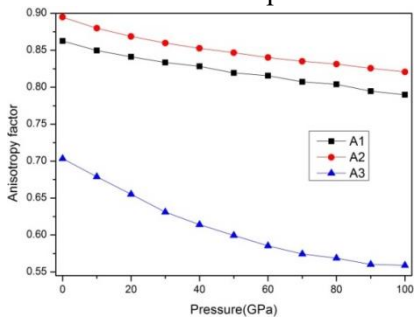

Figure 3. *Anisotropy factors A1, A2 and A3 of O-BN at 0 K as a function of pressure*

3.3Debye temperature

Bulk modulus B and shear modulus G obtained by calculation can help to calculate Debye temperature. Debye temperature(Θ_D) is an important basic physical quantity of material, and it is closely related to the elastic constants, specific heat and fusion point, which is usually used to distinguish high and low temperature area of solid. When $T > \Theta_D$, all patterns have the energy of k_BT[29]; when $T < \Theta_D$, all of the high frequency modes are invalid. Θ_D can be obtained by following formula[30] :

$$\Theta_D = \frac{h}{k_B}\left[\frac{3}{4\pi}V_a\right]^{1/3} v_m \qquad (13)$$

$$v_m = \left[\frac{1}{3}\left(\frac{2}{v_s^3}+\frac{1}{v_l^3}\right)\right]^{1/3} \qquad (14)$$

$$v_l = \left[\left(B+\frac{4}{3}G\right)\frac{1}{\rho}\right]^{1/2},\ v_s = \left[\frac{G}{\rho}\right]^{1/2} \qquad (15)$$

In the formula, h is Planck's constant, k_B is Boltzmann constant, V_a is atomic volume, v_m is average velocity of sound, v_l is vertical velocity, v_s is transverse velocity, B is bulk modulus, G is shear modulus. Longitudinal velocity, lateral velocity, average velocity and Θ_D of O-BN under different pressures were shown in table 4.

Because O-BN has a higher bulk modulus B and shear modulus G, the average elastic wave velocity having been calculated is relatively higher, more than 11000 m/s. Θ_D of O-BN was 1842K under zero temperature and zero pressure, while it increased with the increase of pressure. Under normal circumstances, the higher Θ_D is, the greater hardness material has. Θ_D can also be used to describe the covalent strength of solid. It can be seen from the table 4 that Θ_D increased and covalent strength magnified with the increase of pressure. There is no other theoretical and experimental data for comparison; however, it is ensured that forecasting Θ_D of O-BN is reasonable, which can be a reference to experiment.

Table 4. Theoretically calculated thermal properties of O-BN, including v_l, v_s, v_m and Θ_D

Pressure	ρ/g·cm^{-3}	v_l/m·s^{-1}	v_s/m·s^{-1}	v_m/m·s^{-1}	Θ_D/K
0	3.4459	15684	10250	11233	1842
10	3.5376	15983	10323	11330	1875
20	3.6235	16282	10401	11430	1907
30	3.7050	16516	10442	11489	1931
40	3.7821	16744	10475	11538	1952
50	3.8555	16968	10511	11590	1974

60	3.9260	17179	10550	11644	1995
70	3.9937	17370	10580	11686	2013
80	4.0590	17558	10611	11730	2032
90	4.1220	17727	10633	11763	2048
100	4.1832	17891	10645	11785	2062

4. Conclusion

The paper adopted the First-principles to study on the O-BN elastic properties, hardness and Θ_D etc. and forecasted the elastic properties，bulk elastic modulus, shear modulus, Young's modulus, sonic speed, Θ_D, Poisson's ratio and elastic anisotropy under different pressures. The research showed that:

1) O-BN is a stable orthogonal crystal system structure and keeps mechanical stability under normal temperature. It has a larger bulk elastic modulus of 365 GPa, shear modulus of 362 GPa, Young's modulus of 816 GPa, hardness of 59.2 GPa, Θ_D of 1842 K and a smaller Poisson's ratio of 0.13 without pressure;

2) Because A1, A2 and A3 are not equal to 1, O-BN is a kind of anisotropic crystal, and the shear anisotropy of three shear planes {100}, {010} and {001} increases with the increase of pressure;

3) As for elasticity anisotropic, it was found that compressibility increased by the least degree along axis c, the most along axis b;

4) O-BN is a potentially super-hardness coated material, which is worthy for further theoretical and experimental research.

Acknowledgments

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