

## STRUCTURAL, ELECTRONIC AND MECHANICAL PROPERTIES OF SUPERHARD B<sub>4</sub>C FROM FIRST PRINCIPLES

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**Abstract:** *Boron carbide (B<sub>4</sub>C) has attracted great attention as a semiconducting material with excellent properties and has found various technological applications. High hardness value makes it a potentially superhard material as well as a low density, high degree of chemical inertness, high melting temperature, thermal stability, abrasion resistance, and excellent neutron absorption, contributed to the use of boron carbide as an abrasive material for extreme conditions, wear resistance components, body armors and as a nuclear absorber or solid-state neutron detector. However, B<sub>4</sub>C is known for its unusual structure, bonding, and substitutional disordering whose nature is not yet fully understood, and exhibits brittle impact behavior. In this study we investigated the chain-model structure with an arrangement of 12-boron atom icosahedra and linear 3-carbon atom chains, using available experimental data. We employed the DFT method with LDA and GGA-PBE functional, as implemented in the CRYSTAL17 software package. Electronic properties of boron carbide have been investigated by calculating the density of states (DOS) and band structure. Calculated mechanical properties have been investigated: bulk modulus, shear modulus, Young modulus, Poisson's ratio, hardness, and elastic tensor constants, and compared with available experimental data.*

**Keywords:** *boron carbide; B<sub>4</sub>C, superhard, ab initio; DFT; electronic structure; mechanical properties*

### 1. Introduction

Boron carbide (B<sub>4</sub>C) has attracted great attention as a material with excellent properties and has found various technological applications. This material possesses an extreme hardness of about 30 GPa and has been found as the third hardest material known and less expensive and easier to prepare than diamond and cubic BN, which hardness may be higher than in a diamond at temperatures above 1200 °C [1]. In comparison with Al<sub>2</sub>O<sub>3</sub> and SiC, B<sub>4</sub>C has a higher hardness and lower density [2]. In addition to low density, this semiconductor can sustain a high temperature, has a high degree of chemical inertness, high melting temperature, high thermal stability, high abrasion resistance, and excellent neutron absorption [1, 3]. These properties are used in abrasive materials at extreme conditions, wear resistance components, body armors, and as a nuclear absorber or solid-state neutron detector. The boron carbide also shows high efficiency direct thermoelectric conversion, the possibility of making superconducting materials and doped semiconductors, and can be used as a non-oxide matrix for composite materials with application in environmental monitoring, etc. [1–4]. However, there are some failures, such as substitution disordering whose nature is not yet fully understood, and exhibits brittle impact behavior.

Many authors have investigated various properties of boron carbide, both experimentally and theoretically, particularly structure, electronic, and mechanical properties [5–23]. The first-principles calculations of the crystalline polar (B<sub>11</sub>C-C-B-C) and chain (B<sub>12</sub>C-C-C) B<sub>4</sub>C structures showed that only the chain structures have hexagonal symmetry, while the rest of the theoretical samples in that

study was found to be composed of disordered icosahedra that are connected by an amorphous B-C matrix, and do not contain linear chains [11]. Furthermore, Ivashchenko *et al.* [11] reported that no chain atoms are found in amorphous samples, due to their lower bulk moduli than those in crystalline samples, while the substitution of boron atoms by carbon atoms in the linear chains could cause *p*-type semiconducting properties of chain B<sub>4</sub>C. The results of Nelmes *et al.* research [23] showed that the boron-rich structures have bulk moduli smaller than those of comparably hard materials. Lazzari *et al.* [16] investigated the atomic structure of B<sub>4</sub>C and  $\alpha$ -boron and suggested considering them as members of a new class of covalently bonded materials. Some authors investigated boron carbide stability under stress in line with the available experimental and theoretical work and it has been estimated the amorphization pressure for the (B<sub>12</sub>)CCC polymorph and found compelling evidence that the (B<sub>12</sub>)CCC configuration does not exist in nature [13, 14] while some authors found that the configurational disorder of B and C atoms is of large importance for the elastic properties of boron carbide [18]. Therefore, there are still many open questions regarding B<sub>4</sub>C structure and structure-property relationship, which leaves yet an unexplored field to investigate, although a great amount of theoretical and experimental work has been performed.

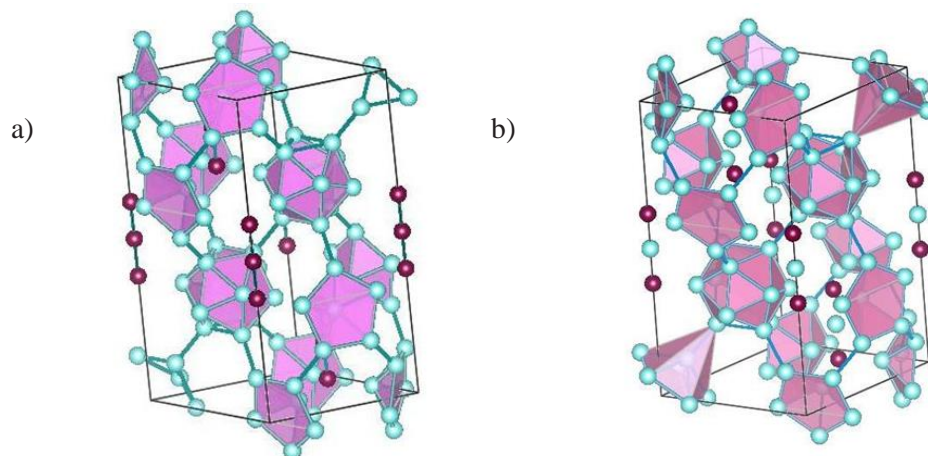
## 2. Computational details

The calculations from first principles have been performed using the CRYSTAL17 software package [24], which is based on a linear combination of atomic orbitals (LCAO) as the basis set. For boron atom a [3s2p1d] all-electron basis set has been used [25, 26], and for carbon atom a [3s2p1d] C<sub>6-21G\*\_catti\_1993</sub> AEBS basis set [27] has been used adopted from Crystal basis sets library [28]. *Ab initio* calculations were performed using density functional theory (DFT) method and two exchange-correlation functionals, Local-density approximation (LDA) with Perdew–Zunger (PZ) correlation functional [29], and generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional [30]. Experimental data of initial structure for rhombohedral boron carbide (B<sub>4</sub>C), have been adopted from the Inorganic crystal structure database (ICSD) [31, 32]. Full structure optimization of B<sub>4</sub>C structure has been obtained using correction keyword TOLINTEG, tolerance for Coulomb and HF exchange sums: ITOL1= $-\log_{10} \times 7$  for overlap threshold for Coulomb integrals, ITOL2= $-\log_{10} \times 7$  for penetration threshold for Coulomb integrals, ITOL3= $-\log_{10} \times 7$  for overlap threshold for HF exchange integrals, and ITOL4= $-\log_{10} \times 7$ , and ITOL5= $-\log_{10} \times 14$  for pseudo-overlap (HF exchange series), for calculation with LDA functional, while calculation with GGA-PBE functional has not required any correction. Calculations of second-order elastic constants (SOEC) as implemented in the CRYSTAL17 code are fully automated [33, 34]. Structure analysis and visualization were performed using the KPLOT [35] and VESTA [36] programs, while electronic properties were visualized using XMGrace.

## 3. Results and discussion

### 3.1. Structural properties of boron carbide

Boron carbide as a B<sub>4</sub>C compound has been found in rhombohedral space group *R-3m* (no. 166). However, structural features were greatly discussed in the literature. The x-ray and neutron diffraction techniques have so far failed to locate the C atoms in the B<sub>4</sub>C structure [37, 38]. By comparing experimental vibrational spectra with those obtained by *ab initio* calculations, the most likely C locations have been identified but did not solve the intrinsic defects nor the type of disorder. The structure of solid boron carbide has an arrangement of 12-atom icosahedra and linear 3-atom chains, with six atoms that sit at the polar sites and are covalently linked to the atoms in neighboring icosahedra, and six atoms with equatorial sites (Fig. 1) [5, 6, 36, 37]. The most theoretically obtained structures of the 15-atom periodic unit cell are the chain-, polar-, and equatorial-model and the one similar to the polar model. In the literature, the boron carbide was mostly described as B<sub>13</sub>C<sub>2</sub> and used B<sub>12</sub>C<sub>3</sub> structure type within the same rhombohedral space group [5, 6, 10, 13, 39]. At higher pressures, boron carbide is described as B<sub>4</sub>C structure type but with the use of partial occupancy within the same space group *R-3m* (no. 166) [40] or with lowering the space group to *P3<sub>2</sub>21* (no. 154), but keeping the rhombohedral symmetry [41].



**Figure 1.** Boron carbide showing: **a)** the  $B_{12}C_3$  (or  $B_4C$ ) modification, space group  $R-3m$  (no. 166), chain-model (experimental data [10] and calculated using GGA and LDA); **b)** the  $B_{13}C_2$  structure type, space group  $R-3m$  (no. 166), [5, 6], adopted from ICSD database [31, 32] and visualized by VESTA program [38].

In this study, we have used the  $B_4C$  structure type by Clark *et al.* [10] as the initial structure from the ICSD, in order to have correct stoichiometry. Optimized unit cell parameters, atomic positions in the crystallographic unit cell, and calculated total energy values are given in Table 1, compared with experimental data of initial structure parameters (adopted from ICSD database) [10]. Our results are in good agreement with experimental data and both calculated structures were successfully compared to the experimental data using the CMPZ algorithm in the KPLOT [42]. In particular, we note that in the common  $B_{13}C_2$  structure type boron is situated at 3b Wyckoff position (Fig. 1b) [5, 6, 13, 38], while in the  $B_{12}C_3$  (or  $B_4C$ ) structure, a carbon atom is located at Wyckoff 3b position (Fig. 1a) [10]. This might help in the future investigation of boron carbide related compounds as well as structure-property relationship studies.

**Table 1.** Optimized unit cell parameters, atomic positions in the crystallographic unit cell, and calculated total energy of boron carbide ( $B_4C$ ) obtained by DFT method with LDA and GGA functional as implemented in CRYSTAL17 software package [24].

Structural parameters of $B_4C$			
Method	LDA-PZ	GGA-PBE	EXP - ICSD [10]
Unit cell parameters	$a = 5.59 \text{ \AA}$ $c = 12.03 \text{ \AA}$ $V = 325.25 \text{ \AA}^3$ $R-3m$ (s. g. 166)	$a = 5.67 \text{ \AA}$ $c = 12.20 \text{ \AA}$ $V = 339.20 \text{ \AA}^3$ $R-3m$ (s. g. 166)	$a = 5.61 \text{ \AA}$ $c = 12.14 \text{ \AA}$ $\gamma = 120^\circ$ $V = 330.88 \text{ \AA}^3$ $R-3m$ (s. g. 166)
Wyckoff and atomic positions	(18h) $B_1$ -0.1661 0.3322 0.3590 (18h) $B_2$ -0.1078 -0.2156 0.1137 (6c) $C_1$ 0 0 0.3887 (3b) $C_2$ 0 0 $\frac{1}{2}$	$B_1$ -0.1661 -0.3321 0.3591 $B_2$ -0.1081 -0.2161 0.1139 $C_1$ 0 0 0.3893 $C_2$ 0 0 $\frac{1}{2}$	$B_1$ -0.1667 0.1667 0.36 $B_2$ -0.106 0.106 0.113 $C_1$ 0 0 0.385 $C_2$ 0 0 $\frac{1}{2}$
Total energy	-408.4474 Ha -11.114 keV	-412.0337 Ha -11.212 keV	-

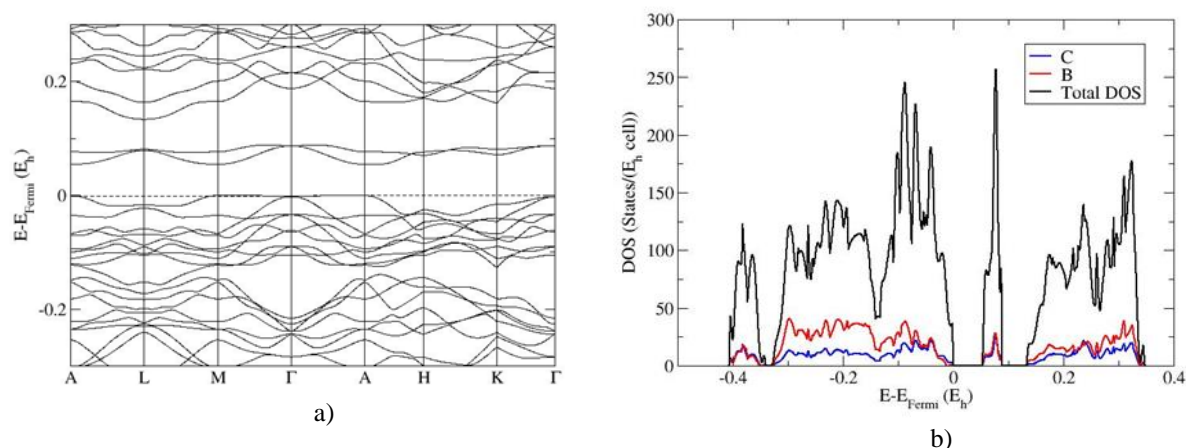
Furthermore, a detailed crystallographic analysis of the calculated structures using LDA and GGA and comparison to the experimental data from the ICSD database has been performed. The results of the calculated and experimental interatomic distances are given in Table 2, suggesting very good agreement with experimental data.

**Table 2.** Interatomic distances of boron carbide optimized by DFT method with LDA-PZ and GGA-PBE functional using CRYSTAL17 code, compared with initial experimental data [10].

B <sub>4</sub> C structure - interatomic distances (Å)		
LDA-PZ	GGA-PBE	EXP – ICSD [10]
B <sub>1</sub> – B <sub>1</sub> = 1.7326	B <sub>1</sub> – B <sub>1</sub> = 1.7578	B <sub>1</sub> – B <sub>1</sub> = 1.7441
B <sub>1</sub> – B <sub>2</sub> = 1.7725	B <sub>1</sub> – B <sub>2</sub> = 1.7989	B <sub>1</sub> – B <sub>2</sub> = 1.7647
B <sub>1</sub> – C <sub>1</sub> = 1.6467	B <sub>1</sub> – C <sub>1</sub> = 1.6710	B <sub>1</sub> – C <sub>1</sub> = 1.6477
B <sub>1</sub> – C <sub>2</sub> = 2.3366	B <sub>1</sub> – C <sub>2</sub> = 2.3688	B <sub>1</sub> – C <sub>2</sub> = 2.3476
B <sub>2</sub> – B <sub>2</sub> = 1.7090	B <sub>2</sub> – B <sub>2</sub> = 1.7260	B <sub>2</sub> – B <sub>2</sub> = 1.7572
B <sub>2</sub> – B <sub>2</sub> = 1.8074	B <sub>2</sub> – B <sub>2</sub> = 1.8371	B <sub>2</sub> – B <sub>2</sub> = 1.7840
B <sub>2</sub> – C <sub>1</sub> = 2.9363	B <sub>2</sub> – C <sub>1</sub> = 2.9766	B <sub>2</sub> – C <sub>1</sub> = 2.9614
B <sub>2</sub> – C <sub>2</sub> = 2.9216	B <sub>2</sub> – C <sub>2</sub> = 2.9620	B <sub>2</sub> – C <sub>2</sub> = 2.9394
C <sub>1</sub> – C <sub>2</sub> = 1.3383	C <sub>1</sub> – C <sub>2</sub> = 1.3506	C <sub>1</sub> – C <sub>2</sub> = 1.3961

### 3.2. Electronic properties of boron carbide

Band structure and density of states (DOS) calculations were performed after structural optimizations. Previous band structure and DOS investigations in boron carbide related compounds have produced a large span of the results [1, 11, 13, 18, 43, 44]. It is well known that semiconductor materials investigated using DFT methods underestimate the size of the band gap [45] which was also observed within this investigation. The value of the indirect band gap obtained by band structure optimization calculation was 1.417 eV (0.05206 hartrees E<sub>h</sub>) determined by LDA-PZ functional, and 1.492 eV (0.05484 hartrees E<sub>h</sub>) obtained with GGA-PBE functional. The calculated results of the size of the band gap were in reasonably good agreement with experimental data (2.09 eV [13]) and previous theoretical data (~1.5–3.5 eV) [11, 13, 43]. We observed the direct band gap at A or M point of the Brillouin zone (Fig. 2), although it can easily convert to indirect band gap, as observed in many other studies. We would like to highlight that this is the first band structure of B<sub>4</sub>C modification in space group *R-3m* (no. 166) using a hexagonal setting (Fig. 2a). The density of states for calculated boron carbide structures using GGA-PBE functional is presented in Fig. 2b (confirmed by similar results obtained using LDA functional).



**Figure 2.** Band structure a) and DOS b) of boron carbide optimized by DFT method with GGA-PBE functional, using CRYSTAL17 code.



### 3.3. Mechanical properties of boron carbide

Mechanical properties of boron carbide have been investigated using the ELASTCON keyword for CRYSTAL calculations. We have analyzed elastic constants according to hexagonal structure symmetry, while bulk modulus  $K$ , shear modulus  $G$ , Young modulus  $E$ , and Poisson's ratio  $\nu$  were all obtained according to Voight-Reuss-Hill. Mechanical stability that are given in Ref. [46] have been determined for elastic tensor constants  $C_{11-13}$ ,  $C_{33}$ , and  $C_{44}$ . Hardness  $H_v$  has been calculated according to Eq. (1) given in Ref. [47, 48]:

$$H_v = 0.92 (G/B)^{1.137} G^{0.708} \quad (1)$$

Obtained results compared with available experimental and theoretical data are given in Tables 3 and 4. Calculated mechanical properties show very good agreement with previously calculated or experimentally observed data of  $B_4C$  (Table 3). The hardness value of 36.54 GPa calculated using LDA functional showed an excellent agreement with available experimental data proving this material as superhard, while GGA-PBE calculations of bulk modulus and Poisson's ratio showed values closest to the experimentally measured. Calculated elastic tensor constants showed good agreement with previously calculated constants of  $B_4C$  (Table 4).

**Table 3.** Calculated values of mechanical properties: bulk modulus  $K$ , shear modulus  $G$ , Young modulus  $E$ , Poisson's ratio  $\nu$ , according to Voight-Reuss-Hill, calculated by DFT method with LDA-PZ and GGA-PBE functional; hardness calculated according to Ref. [47, 48]; available experimental and theoretical data.

Mechanical properties of $B_4C$					
Method	$K$ (GPa)	$G$ (GPa)	$E$ (GPa)	$\nu$	$H_v$ (GPa)
LDA-PZ	169.43	173.89	388.70	0.118	36.54
GGA-PBE	220.66	172.32	410.18	0.190	26.55
Available experimental data	XRD 245 [16]	200 [13, 49]	472 [13, 49]	0.18 [13, 49]	36.82 [17]
	Neutron scattering 220 [16, 22]	197 [13, 50]	462 [13, 50]	0.17 [13, 50]	-
	Ultrasound 247[16, 22]	188 [13, 51]	448 [13, 52]	0.21 [13, 52]	-
	247 [13, 49]	-	441 [13, 51]	-	-
	235 [13, 50]	-	-	-	-
	199 [13]	-	-	-	-
Available theoretical data	248 [16]	156 [18, $B_{13}C_2$ ]	379 [18, $B_{13}C_2$ ]	0.22 [18, $B_{13}C_2$ ]	-
	246 [13, 50]	200 [18, $B_4C$ ]	469 [18, $B_4C$ ]	0.17 [18, $B_4C$ ]	-
	234 [13, 20, 53]	-	-	-	-
	248 [13, 16]	-	-	-	-
	239 [13, 54]	-	-	-	-
	220 [13]	-	-	-	-
	222 [18, $B_{13}C_2$ ]	-	-	-	-
239 [18, $B_4C$ ]	-	-	-	-	

**Table 4.** Elastic tensor constants of B<sub>4</sub>C obtained by DFT method with LDA-PZ and GGA-PBE functional compared with available theoretically obtained data.

Elastic tensor constants (GPa)	LDA-PZ	GGA-PBE	Available theoretical data				
			Theory [13]	GGA [19]	GGA [20]	LDA B <sub>13</sub> C <sub>2</sub> [21]	Theory B <sub>13</sub> C <sub>2</sub> [18]
C <sub>11</sub>	448.15	484.83	561.8	517	531	500	516
C <sub>12</sub>	65.36	108.76	123.6	118	105	125	118
C <sub>13</sub>	34.29	71.13	69.6	73	54	74	74
C <sub>33</sub>	468.03	514.31	517.7	453	528	430	451
C <sub>44</sub>	138.03	139.86	-	114	167	-	106

#### 4. Conclusion

In this study, we have performed *ab initio* calculations using DFT approximation with two independent exchange-correlation functionals (LDA-PZ and GGA-PBE) within the CRYSTAL17 software package. Detailed structural, electronic, and mechanical properties of boron carbide (B<sub>4</sub>C) have been investigated. We investigated the chain-model structure using available experimental data, and our results are in very good agreement with literature data. Furthermore, we manage to clarify structural features related to the B<sub>13</sub>C<sub>2</sub> and B<sub>12</sub>C<sub>3</sub> structure types. Electronic properties of boron carbide have been investigated by calculating the density of states (DOS) and band structure. Our calculations are in good agreement with previous studies and we show the first band structure of B<sub>4</sub>C using the hexagonal setting. Calculated mechanical properties have been investigated: bulk modulus, shear modulus, Young modulus, Poisson's ratio, hardness, and elastic tensor constants, and compared with available experimental data. Again our results are in good agreement with previous theoretical and experimental work, while the hardness value of 36.54 GPa calculated by LDA functional showed an excellent agreement. Thus, the results show new structural features of B<sub>4</sub>C, promising semiconducting properties, and great potential of B<sub>4</sub>C as a superhard material.

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