

# Structural, Mechanical and Dynamic Properties of Super-Hard Carbon-Boron Binary Materials

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**Abstract.** A number of potentially super-hard materials were examined using ab-initio methods. Compound phases of varying lattice stoichiometry in the carbon-boron (B-C) binary system, in the forms,  $C_{8-x}B_x$  were proposed as possible super-hard materials with useful applications. The materials with  $x = 0$  to 3, i.e.: diamond (C), cubic  $C_7B$  ( $c$ - $C_7B$ ), rhombohedral  $C_3B$  ( $r$ - $C_3B$ ) and orthorhombic  $C_5B_3$  ( $o$ - $C_5B_3$ ) were found to be dynamically and mechanically stable, diamond was used as a standard for comparison. On the basis of bulk modulus results these materials were found to potentially have super-hard characteristics. Systematic trends were established, the hardness was observed to reduce with increasing boron content. The materials under study were all determined as being brittle with diamond being the most brittle,  $C_3B$  and  $C_5B_3$  were the least brittle. Of the materials studied, diamond was determined to have the lowest degree of anisotropy while  $C_5B_3$  had the highest.

## 1. Introduction

Super-hard materials have a Vickers hardness ( $H_V$ ) which is greater than 40 GPa [1, 2]. Diamond and cubic boron nitride ( $c$ -BN) are the super-hard materials that are known best. Diamond has the drawback of its oxidation reactions [3] or redox reactions with metallic elements [4] at temperatures exceeding 80 K. Despite the high oxidation resistance temperature and high chemical inertness of  $c$ -BN, its hardness is only about half that of diamond [5]. A lot of theoretical and experimental work has therefore been devoted to the search for new ultra-hard materials with a view to replace diamond and  $c$ -BN [2, 6-8]. Materials with a value of the bulk modulus exceeding 250 GPa are expected to have super-hard characteristics [9]. Hardness is known to scale well with the bulk and shear modulus in diamond-like materials [10]. The elastic response of a single crystal is seldom isotropic, essentially all the known crystals are elastically anisotropic meaning that the elastic moduli are generally dependent on the different crystal orientations. The degree of anisotropy in the properties of materials is very important in their application. The generation of microcracks and lattice distortions in materials is often related to the elastic anisotropy. Ledbetter and Migliori [11] point out the effects of elastic anisotropy in dislocation dynamics, phase transformations and other crystal phenomena. There have been studies reported on the carbon-boron (C-B) system [12-15]. We make an extension of this research work by studying the structural, mechanical, dynamic properties and anisotropy of compound phases with varying lattice stoichiometry in the form,  $C_{8-x}B_x$ .

## 2. Computational methods

The method of calculation applied in this work is based on the density functional theory (DFT) [16]. We have adopted the Quantum Espresso [17] software package implementation of DFT. The exchange-correlation interaction between the electrons was modeled using the generalized gradient approximation (GGA-PBE) [18]. The ultra-soft pseudo-potential method was used to calculate the interaction between the electrons and the ion cores. The cut-off energy used for the plane-wave function was 50 Ry and the  $k$ -point mesh Brillouin zone sampling was taken as  $6 \times 6 \times 6$  Monkhorst Pack [19]. The convergence threshold of the self-consistent field (SCF) was within  $10^{-3}$  eV/atom.

Unit cells of eight atoms in the diamond lattice structure were considered with C or B atoms representing a particular stoichiometry at the lattice points. The lattice positions and atomic types at each position were stored in matrix arrays. A C++ template library for linear algebra called Eigen [20] was used to randomise the atomic

placement. Variable-cell dynamics calculations were performed on the starting cell to optimize the atomic position geometry and cell parameters using the Quantum Espresso [17] package. This was achieved by performing some relaxation operations which allowed the atomic positions to self-adjust in accordance with the inter-atomic forces while allowing the unit cell to vary; equilibrium atomic structures were thereby achieved. The space-group and symmetry operations of these equilibrium configurations were identified using the utility program, SGROUP [21].

The procedure of randomising the atomic placement (using Eigen) in the starting cell, variable-cell relaxation (using Quantum Espresso) and identification of the final converged configurations (using SGROUP), was carried out several times for each value of  $x$  in  $C_{8-x}B_x$  where  $x = 0$  to 7. The most ‘favoured’ outcome, i. e., the final configuration that was observed the most times after several runs (in some cases it was the only configuration repeatedly observed) was chosen for further investigation. These configurations were visualized using the crystalline structure visualization and analyser software package, Xcrysden [22] after which they were tested for dynamic stability as explained in the next section. The dynamically stable structures were then analysed using the Elastic software package [23], which was used to calculate the second-order elastic constants (SOECs) using the numerical differentiation of the total lattice energy with respect to the associated strain. Three types of averaging calculations were carried out in order to obtain the bulk and shear moduli of the various compounds: the Voigt [24] calculation which assumes a uniform strain, the Reuss [25] calculation which is valid for uniform stress and the Hill [26] averaging calculation which considers the Voigt and Reuss values as the uppermost and lowest predictions respectively. The bulk and shear moduli in the Voigt calculation are given by:

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

and

$$G_V = \frac{1}{15} [(C_{11} + C_{22} + C_{33}) - (C_{12} + C_{13} + C_{23}) + 3(C_{44} + C_{55} + C_{66})] \quad (2)$$

respectively, where  $C_{ij}$  are the stiffness constants.

In the Reuss calculation the bulk and shear moduli are given by:

$$B_R = [(S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{13} + S_{23})]^{-1} \quad (3)$$

and

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

respectively, where  $S_{ij}$  are the compliances.

The Hill-averaged bulk and shear moduli are given by:

$$G_H = \frac{1}{2}(G_V + G_R) \quad (5)$$

and

$$B_H = \frac{1}{2}(B_V + B_R). \quad (6)$$

The Hill-averaged Young moduli,  $E_H$  and Poisson ratios,  $\nu_H$  are given by the expressions:

$$E_H = \frac{9B_H G_H}{3B_H + G_H} \quad (7)$$

and

$$\nu_H = \frac{3B_H - 2G_H}{2(3B_H + G_H)}. \quad (8)$$

The elastic constant results presented for all materials in this work are Hill-averaged, unless indicated otherwise.

In cubic crystals, the linear bulk modulus is the same for all directions and hence the shear anisotropy alone determines the elastic anisotropy. For other types of crystals, the elastic anisotropy arises from the anisotropy of the linear bulk modulus in addition to the shear anisotropy. An appropriate way to quantify the degree of anisotropy for both the shear and the bulk contributions is by using the universal elastic anisotropy index,  $A_U$  [27] which is given by,

$$A_U = 5 \frac{G_V}{G_R} + \frac{B_V}{B_R} - 6. \quad (9)$$

The shear modulus is  $G$  and the bulk modulus is  $B$ , the subscripts  $V$  and  $R$  represent the Voigt and Reuss estimates, respectively. If a single crystal is isotropic then,  $G_V = G_R$  and  $B_V = B_R$ , making  $A_U$  equal to zero. In cubic crystals  $B_V = B_R$  but  $G_V \neq G_R$ . The departure of  $A_U$  from zero defines the extent of single crystal anisotropy.

### 3. Results

The value,  $x = 0$  represents diamond which was used as a standard for comparison. Crystal structure diagrams were visualized using Xcrysden [22]. The unrelaxed unit cell of CB is shown in Fig. 1.

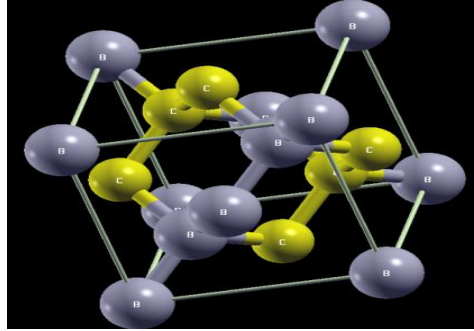


Fig. 1. Unrelaxed unit cell crystal structure of CB.

Dynamic stability considers the complete vibrational spectrum of a material: a material is dynamically stable when theoretical calculations show no imaginary or negative phonon frequencies. The Quantum Espresso [17] implementation of Density-Functional Perturbation Theory can be used to calculate phonon frequencies of compounds at a chosen reciprocal lattice vector of the respective Brillouin zone. The results of our phonon calculations at the center of the Brillouin zones (gamma point) are presented in Table 1 for  $C_{8-x}B_x$  materials where  $x = 0$  to 7. This table shows that the materials where  $x = 0$  to 3, i.e., diamond (C),  $C_7B$ ,  $C_3B$  (or  $C_6B_2$ ) and  $C_5B_3$  have no negative phonon frequencies, these four materials are therefore dynamically stable. The calculation covered 24 frequencies for each material but Table 1 only shows the first 6, all other frequencies were positive. The few relatively low frequencies in the table are indicative of acoustic modes while the higher frequencies belong to the optical modes of vibration. The Elastic software package [23] was used to obtain the elastic constants for the four materials that were identified as being dynamically stable; the results are shown in Table 2.

The materials in Table 2 were determined to be mechanically stable, as will be discussed in the next section. This qualified these materials for the determination of their bulk,  $B$ , shear,  $G$  and Young,  $E$  moduli. The Hill averaged values of  $B$ ,  $G$  and  $E$  were obtained from the stiffness constants,  $C_{ij}$  and compliances,  $S_{ij}$ ; the results are shown in Table 3. The table also shows the  $B/G$  ratio and the Poisson ratio.

Table 1. Results of phonon calculations for the compounds, at the  $\Gamma$  point of the Brillouin zones. Only 6 out of 24 frequencies covered for each material are shown in the table, all other frequencies were positive.

MATERIAL AND CRYSTAL STRUCTURE	C Cubic F (fcc)	$C_7B$ Cubic I (bcc)	$C_3B$ Rhombohedral I	$C_5B_3$ Orthorhombic	CB Orthorhombic	$C_3B_5$ Orthorhombic	$CB_3$ Rhombohedral I	$CB_7$ Cubic I (bcc)
FREQUENCY NUMBER	$cm^{-1}$	$cm^{-1}$	$cm^{-1}$	$cm^{-1}$	$cm^{-1}$	$cm^{-1}$	$cm^{-1}$	$cm^{-1}$
1	186	148	26	46	-1675	-181	-297	-182
2	186	148	48	52	-171	-80	-297	-182
3	806	148	48	87	-138	-48	-113	-182
4	806	671	505	361	-63	98	-61	87
5	806	671	590	429	73	310	-61	87
6	806	671	590	450	80	380	195	87

Table 2. Independent stiffness constants,  $C_{ij}$  and compliances,  $S_{ij}$  for  $C_{8-x}B_x$  materials where  $x = 0$  to 3.

Material	Crystal Structure	Stiffness matrix elements, $C_{ij}$ (GPa) and compliances, $S_{ij}$ ( $\times 10^{-5}$ GPa $^{-1}$ )									
		$C_{11}$	$C_{12}$	$C_{13}$	$C_{14}$	$C_{22}$	$C_{23}$	$C_{33}$	$C_{44}$	$C_{55}$	$C_{66}$
		$S_{11}$	$S_{12}$	$S_{13}$	$S_{14}$	$S_{22}$	$S_{23}$	$S_{33}$	$S_{44}$	$S_{55}$	$S_{66}$
Diamond C	Cubic F (fcc)	1064 97	133 -11						561 178		
C <sub>7</sub> B	Cubic I (bcc)	689 176	237 -45						476 210		
C <sub>3</sub> B	Rhombohedral I	612 201	193 -55	194 -46	-72 51			612 193	358 300		
C <sub>5</sub> B <sub>3</sub>	Orthorhombic	455 296	264 -139	98 19		604 284	285 -123	547 243	334 300	303 330	334 300

Table 3. Hill bulk moduli,  $B$ , shear moduli,  $G$  and Young moduli,  $E$  for the four dynamically stable materials. The  $B/G$  ratio and Poisson ratio are also presented.

Material	Crystal Structure	Bulk Modulus (GPa)	Shear Modulus (GPa)	Young Modulus (GPa)	$B/G$	Poisson Ratio, $\nu$
Diamond C	Cubic F (fcc)	443	521	1122	0.850	0.08
C <sub>7</sub> B	Cubic I (bcc)	388	353	812	1.099	0.15
C <sub>3</sub> B	Rhombohedral I	333	253	606	1.316	0.20
C <sub>5</sub> B <sub>3</sub>	Orthorhombic	309	235	563	1.315	0.20

Table 4 presents the Voigt and Reuss bulk and shear moduli together with the universal elastic anisotropy index, calculated using Equation (9).

Table 4. The Voigt and Reuss bulk and shear moduli together with the universal elastic anisotropy index for the materials.

Material	Crystal Structure	$B_V$ (GPa)	$B_R$ (GPa)	$G_V$ (GPa)	$G_R$ (GPa)	Universal Elastic Anisotropy Index, $A_U$	Percentage Anisotropy
Diamond C	Cubic F (fcc)	443	443	523	518	0.041	0.4%
C <sub>7</sub> B	Cubic I (bcc)	388	388	376	330	0.699	7.0%
C <sub>3</sub> B	Rhombohedral I	333	333	269	238	0.650	6.5%
C <sub>5</sub> B <sub>3</sub>	Orthorhombic	322	295	258	213	1.160	11.6%

#### 4. Discussion

Materials with a value of the bulk modulus exceeding 250 GPa are expected to have super-hard characteristics [9]. The bulk modulus results shown in Table 2 indicate that all the compounds with  $x = 0$  to 3 could potentially have super-hard characteristics.

The original conditions for mechanical stability were proposed by Born-Huang [28]. We adopt the modified conditions of Mouhat and Coudert [29] in this work. A general necessary but not sufficient Born stability

condition noted by Fedorov [30] is that all diagonal elements should be positive ( $C_{ii} > 0, \forall i$ ). An examination of all the diagonal elements in Table 2 shows that all the compounds studied satisfy this condition.

Another necessary general Born stability condition is,

$$(C_{ij})^2 < C_{ii}C_{jj} \quad \forall i, j. \quad (10)$$

An examination of the elastic constants in Tables 2 also shows that all the compounds studied satisfy the condition in Equation (10). The compounds were further tested to see if their elastic constants satisfy the Mouhat and Coudert [29] sufficient conditions for mechanical stability.

The sufficient mechanical stability conditions for the cubic system, which only has three independent elastic constants, are:

$$C_{11} - C_{12} > 0; \quad C_{11} + 2C_{12} > 0. \quad (11)$$

Using the results shown in Table 2 we see that the elastic constants for diamond and  $C_7B$ , which both have the cubic bravais lattice, satisfy the sufficient Born stability conditions given in Equation (11). These compounds are therefore mechanically stable. According to Mouhat and Coudert [29] the sufficient criteria for the rhombohedral I class, which has 6 independent elastic constants, are:

$$\left. \begin{aligned} C_{11} &> |C_{12}|; \\ C_{13}^2 &< \frac{1}{2}C_{33}(C_{11} + C_{12}); \\ C_{14}^2 &< \frac{1}{2}C_{44}(C_{11} - C_{12}). \end{aligned} \right\} \quad (12)$$

The elastic constants for  $C_3B$  (or  $C_6B_2$ ), as presented in Table 2, show that the sufficient criteria for this rhombohedral I compound, as given in Equation (12), are satisfied. This compound is therefore mechanically stable. The sufficient Born criterion for an orthorhombic system [28], with 9 independent elastic constants is:

$$C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 > 0. \quad (13)$$

Using the results shown in Tables 2, we find that the elastic constants for  $C_5B_3$ , which has an orthorhombic bravais lattices, satisfy the sufficient Born stability condition given by Equation (13). It follows that this materials is mechanically stable. The variation of the bulk, shear and Young moduli as a function of the values of  $x$  in  $C_{8-x}B_x$  materials is represented graphically in Fig. 2.

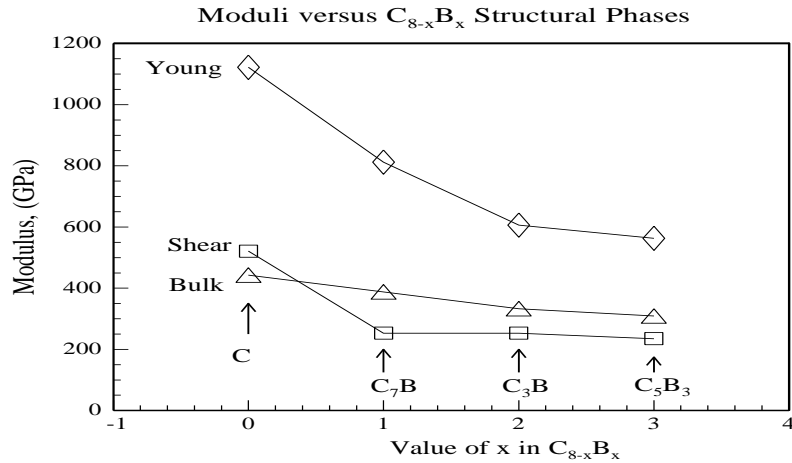


Fig. 2. Graph for the trend in bulk, shear and Young moduli in  $C_{8-x}B_x$  materials.

It is seen in Fig. 2 that the values of the three moduli reduce with increasing boron content. The ratio of  $B/G$  can be used to determine the brittleness of a material. Push [31] reports that  $B/G=1.75$  is a critical value for distinguishing between ductility and brittleness, for ductile materials,  $B/G>1.75$ . Brittle materials have values of this ratio which are less than 1.75. As seen in Table 3, the four materials under study are all brittle with diamond being the most brittle.  $C_3B$  and  $C_5B_3$  are the least brittle with a  $B/G$  value of 1.32. While the Young modulus relates the stress to the resulting strain in the same direction, the Poisson ratio relates the lateral strain to the axial strain. The ratio not only reflects the volume change of the material in the case of uniaxial deformation, but also reflects the stability of a crystal to resistant shear. The higher the Poisson ratio, the greater the plasticity of a material. The results in Table 3 indicate that the plasticity of the materials increases with increased boron content. We see in Table 4 that diamond has the lowest degree of anisotropy with a Universal Elastic Anisotropy Index of only 0.041.  $C_5B_3$  has the highest anisotropy ( $A_U = 1.160$ ), this material is therefore likely to be the most

susceptible to microcracks. The table shows that  $B_V = B_R$  for the two cubic structures, C and C<sub>7</sub>B as expected. Interestingly, the same condition is observed for C<sub>3</sub>B which is not cubic, indicating that this material is also isotropic in terms of the linear bulk modulus alone.

## 5. Conclusion

The first paragraph after a heading is not indented It has been determined that the the four materials: diamond (C), cubic C<sub>7</sub>B (*c*-C<sub>7</sub>B), rhombohedral C<sub>3</sub>B (*r*-C<sub>3</sub>B) and orthorhombic C<sub>5</sub>B<sub>3</sub> (*o*-C<sub>5</sub>B<sub>3</sub>) are all dynamically and mechanically stable. On the basis of the bulk modulus results shown in Table 3, these compounds could potentially have super-hard characteristics; their respective values of the bulk modulus exceeding 250 GPa as is expected in super-hard materials [9]. Fig. 2 suggests that the hardness reduces with increasing boron content. As seen in Table 3, the materials under study are all brittle with diamond being the most brittle. C<sub>3</sub>B and C<sub>5</sub>B<sub>3</sub> are the least brittle with B/G values of 1.32. Table 3 shows that diamond has the lowest degree of anisotropy with a Universal Elastic Anisotropy Index of only 0.041 while C<sub>5</sub>B<sub>3</sub> has the highest anisotropy ( $A_U = 1.160$ ), which makes the latter material more susceptible to microcracks.

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