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Diamond-like BC$_3$ as a superhard conductor identified by ideal strength calculations

Jun Yang[1]**, Hong Sun**[1,4]**, Julong He**[2]**, Yongjun Tian**[2] **and Changfeng Chen**[3,4]

[1] Department of Physics, Shanghai Jiao Tong University, Shanghai 200030, People's Republic of China
[2] State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, People's Republic of China
[3] Department of Physics and High Pressure Science and Engineering Center, University of Nevada, Las Vegas, NV 89154, USA

E-mail: hsun@sjtu.edu.cn and chen@physics.unlv.edu

Abstract

We present first-principles calculations on the ideal strength of a diamond-like (d-) BC$_3$ phase under tensile and shear deformation. The results show that d-BC$_3$ is comparable in strength to cubic BN, the second (only to diamond) hardest material known. Moreover, the calculated electronic density of states reveal that d-BC$_3$ is metallic not only at equilibrium but also under large tensile and shear deformation, making it the hardest conductor studied to date. We identify a metastable graphitic BC$_3$ precursor that has a low energy barrier to transform into d-BC$_3$.

(Some figures in this article are in colour only in the electronic version)

Diamond has a wide electronic band gap, but boron doping can introduce electrical conductivity [1] or even superconductivity [2] in this hardest material known. Meanwhile, superhard materials with high boron concentrations, such as cubic (c-) BN and c-BC$_2$N, show superior resistance to oxidation at high temperature compared to diamond [3–5]. It is expected that B–C compounds may exhibit superior mechanical strength, oxidation resistance and electrical conductivity, a desirable combination in many applications. Very recently, a diamond-like (d-) BC$_3$ structure was proposed [6, 7] as a conducting and potentially superhard material with a calculated bulk modulus around 360 GPa, close to that of c-BN (368 GPa), the second hardest material. Experimentally, several attempts were made to synthesize c-BC$_x$ using graphitic (g-) BC$_x$ as precursors [8, 9]. Very high pressure and temperature (45 GPa at 2230 K) are required for the graphitic-to-cubic transformation [9]. At lower pressure and

[4] Authors to whom any correspondence should be addressed.
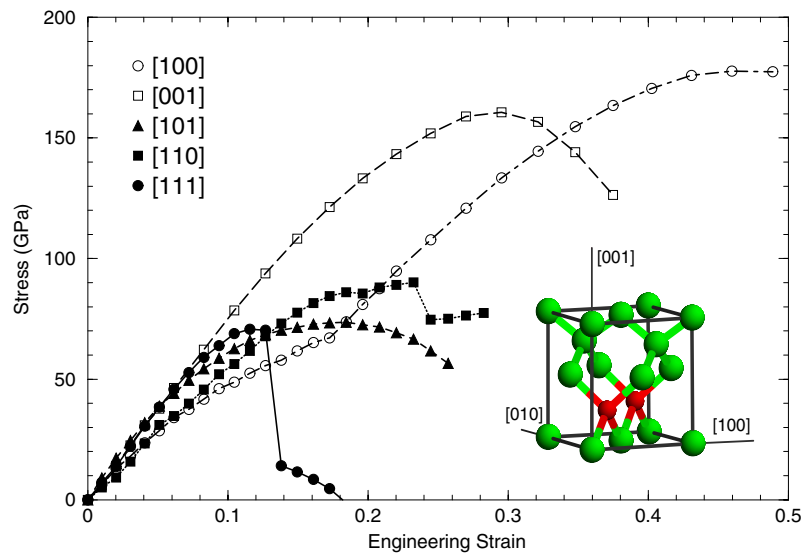
Figure 1. The calculated stress–strain curves under tensile strains along various high symmetrical directions for the d-BC$_3$ structure shown in the inset.

temperature, phase separation into BC$_4$ and a lightly boron-doped diamond structure was observed [8]. On the theoretical side, first-principles calculations of ideal strength [10–14] have been developed in recent years to determine the critical stress at which a perfect lattice becomes unstable. It provides an assessment of the upper limit of the material strength that can be directly compared to nanoindentation measurements [15], and is more accurate in predicting material strengths than the conventional criteria of elastic constants like bulk and shear moduli obtained at the equilibrium structure. This is because ideal strength calculations examine the stress–strain relation at large structural deformation and, therefore, can reveal any potential structural softening due to bond-charge redistribution under strain [13, 14].

In the present work, we perform first-principles calculations on the ideal strength of the d-BC$_3$ structure (see figure 1) that has the lowest total energy among many different BC$_3$ structures [7]. Our results show that d-BC$_3$ has ideal tensile (70.6 GPa) and shear (50.3 GPa) strength comparable to those of c-BN (65.6 GPa and 70.5 GPa, respectively). The larger ideal tensile strength indicates that d-BC$_3$ is more difficult to cleave, and the lower ideal shear strength shows that it is slightly less hard compared to c-BN. The calculated electronic density of states indicate that d-BC$_3$ is metallic at equilibrium and under large deformation. These results place d-BC$_3$ as the hardest conductor studied to date.

For the total-energy calculations we use the *PARATEC* code [16], adopting the *ab initio* pseudopotential and local-density approximation (LDA) with a plane-wave basis set [17–19]. The norm-conserving Troullier–Martins pseudopotentials [20] were used with cutoff radii of 1.3 and 1.5 au for C and B, respectively. The exchange–correlation functional of Ceperley and Alder [18] as parameterized by Perdew and Zunger [21] was used. The total energy of the structures was minimized by relaxing the structural parameters using a quasi-Newton method [22]. The total-energy and stress calculations used an eight-atom zinc-blende-structured unit cell (see figure 1), a $10 \times 10 \times 10$ Monkhorst–Pack [23] k-point grid for its metallic band structure, and a 100 Ryd energy cutoff. The error in the calculated stresses due to the energy cutoff and k-point grid was less than 0.1 GPa, based on convergence tests. The

quasistatic ideal strength and relaxed loading path were determined using a method described previously [10, 11].

In figure 1, we plot the calculated stress–strain curves under tensile strains along various high symmetrical directions for the d-BC$_3$ structure (see the inset in figure 1). Obviously, the [111] direction has the lowest tensile stress peak (70.6 GPa) at the engineering tensile strain $\epsilon_E = 0.1157$, although the peak tensile stress (73.6 GPa at $\epsilon_E = 0.1843$) in the [101] direction is only slightly higher than the former. However, the d-BC$_3$ structure can endure much larger tensile strain in the [101] direction (at $\epsilon_E = 0.1843$) than in the [111] direction (at $\epsilon_E = 0.1157$) before the structure becomes unstable. This is because in the [101] direction the tensile strain causes both bond-angle widening and bond-length stretching, while in the [111] direction it stretches the bond length directly, causing the bond to break early. The d-BC$_3$ structure is close to but not exactly cubic, with the calculated lattice parameters $a = b = 3.511$ Å and $c = 3.886$ Å, in good agreement with the previous calculations [6, 7]. So we examined more carefully its energy, stress, and bond-length dependence on the tensile strain along two possible weak directions: (i) the diagonal [111] direction $\mathbf{n}_1 = a\mathbf{i} + a\mathbf{j} + c\mathbf{k}$ and (ii) the direction normal to the (111) plane $\mathbf{n}_2 = \mathbf{i}/a + \mathbf{j}/a + \mathbf{k}/c$. We found that the peak tensile stress in the $\mathbf{n}_2$ direction is 4 GPa larger than that in the $\mathbf{n}_1$ direction. The latter is therefore determined to be the weakest tensile direction, and the corresponding calculated results are shown in figure 2. A fit to the energy–strain curve is carried out and used to obtain the tensile stress $\sigma = [(1 + \epsilon_E)/V(\epsilon_E)]\partial E/\partial \epsilon_E$, where V is the volume of the unit cell and ϵ_E is the engineering strain [11]. The results obtained are in excellent agreement with those from direct stress calculations up to the peak stress. The peak tensile stress in the weakest $\mathbf{n}_1$ direction (i.e., the ideal tensile strength) is 70.6 GPa. This is about 8% higher than that of c-BN (65.5 GPa). The bond length–strain curve and snapshot (at S$_2$) both show that under the $\mathbf{n}_1$ (and $\mathbf{n}_2$, but not shown here) tensile stress, the B–C bond breaks before the C–C bond. This is opposite to the case of c-BC$_2$N, where the breaking order of B–C and C–C bonds is reversed under the (111) tensile stress [24]. This demonstrates that the relative strength of the B–C and C–C bonds is sensitive to the structural and compositional variation in the otherwise quite similar environment. The shear stresses of d-BC$_3$ are calculated in the planes normal to $\mathbf{n}_1$ and $\mathbf{n}_2$ in the directions $\mathbf{t} = [11\overline{m}]$, where m is determined by requiring $\mathbf{n}_1 \cdot \mathbf{t}_1 = 0$ and $\mathbf{n}_2 \cdot \mathbf{t}_2 = 0$, respectively. Both directions reduce to the $(111)[11\overline{2}]$ shear direction when the structure becomes cubic ($c \to a$). The calculated peak shear stresses in these two directions turn out to be essentially the same, which gives the ideal shear strength. The calculated results for d-BC$_3$ under shear strains in the ($\mathbf{n}_1$) plane along the [$\mathbf{t}_1$] direction are shown in figure 3. Again, the shear stresses obtained from fitting the energy curve and using $\sigma = [1/V(\epsilon_T)]\partial E/\partial \epsilon_T$, where ϵ_T is the true strain [11], are in excellent agreement with those from direct stress calculations. The peak shear stress in the weakest ($\mathbf{n}_1$)[$\mathbf{t}_1$] shear direction (i.e., the ideal shear strength) is 50.3 GPa, about 30% lower than that of c-BN (70.5 GPa). Consequently, d-BC$_3$ is expected to be somewhat less hard than c-BN but, nevertheless, still a superhard material.

In figure 4, we show the calculated density of states for d-BC$_3$ at equilibrium, under $\mathbf{n}_1$ tensile and ($\mathbf{n}_1$)[$\mathbf{t}_1$] shear strains at the peak stresses. It clearly shows the metallic nature of d-BC$_3$ at equilibrium and under strains, with the largest ideal tensile and shear strength among all known electric conducting materials reported to date.

Finally we comment on the synthesis of d-BC$_3$. Recent experiments indicated that very high pressure and temperature are required for the direct transformation from g-BC$_x$ to c-BC$_x$ [9]. This is understood as the strong covalent bonds needing to be broken and rearranged in the transformation process when the most stable graphitic BC$_3$ (shown in figure 5(b)) [25, 26] is used as precursor, as was probably the case in the reported experiment. Meanwhile, the calculated energy–strain relation in figure 2 shows that the potential barrier along the structural
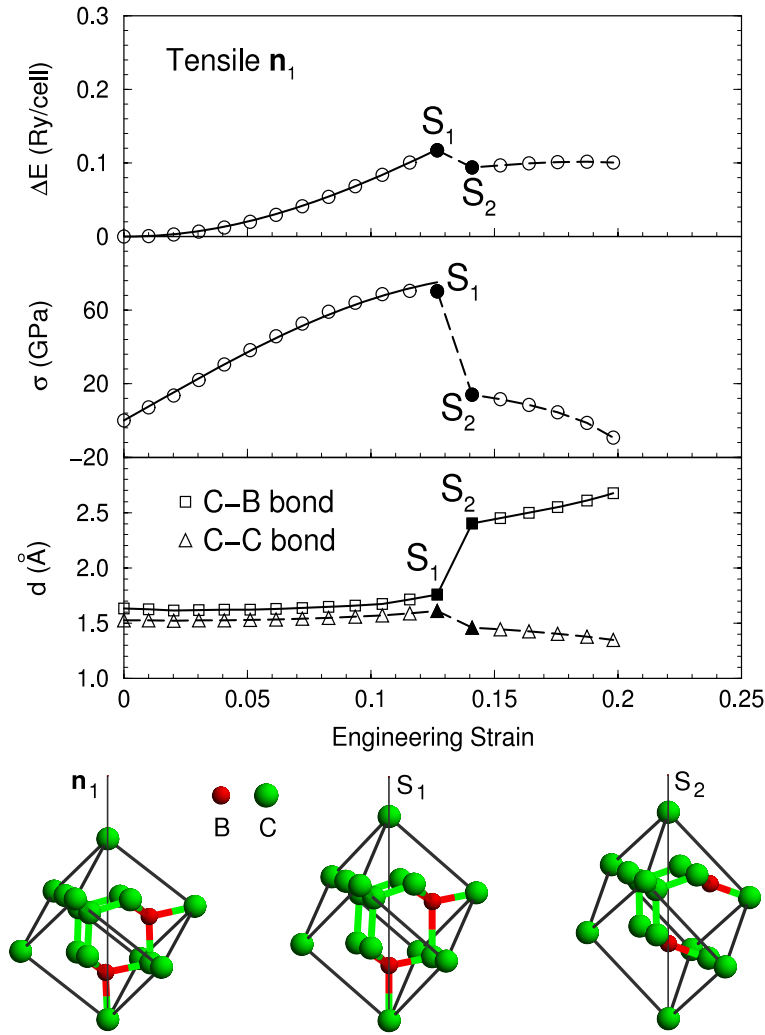
Figure 2. The calculated (symbols) energy (ΔE), stress (σ) and bond length (d) as functions of the tensile strain for diamond-like BC_3 in the weakest $\mathbf{n}_1$ tensile direction. The solid line in the top panel is a fitting curve that gives the stress–strain (solid) curve by $\sigma = [(1 + \epsilon_E)/V]\partial E/\partial \epsilon_E$ where ϵ_E is the engineering strain. The equilibrium structure and snapshots of the unit cell at two key points (S_1 and S_2) just before and after the tensile breaking are shown at the bottom.

transformation path from the layered structure obtained by breaking the C–C and C–B bonds in the $\mathbf{n}_1$ direction to the d-BC_3 structure is very low. We obtained the metastable layered BC_3 structure by breaking the C–C and C–B bonds with large tensile strains in the $\mathbf{n}_1$ direction followed by a full structural relaxation that shifts the structure from the ABCABC$\cdots$ stacking to AAA$\cdots$ stacking. Figure 5(a) shows the intralayer atomic arrangement of the metastable g-BC_3 structure. The calculated lattice parameters are $a = 2.509$ Å, $b = 4.488$ Å and the interlayer distance $c/3 = 3.033$ Å. This structure has a total energy of about 0.2 eV/atom higher than that of the most stable g-BC_3 structure (figure 5(b)) [25, 26]. The energy barrier for the transformation from this metastable g-BC_3 to d-BC_3 is low because no bonds need to
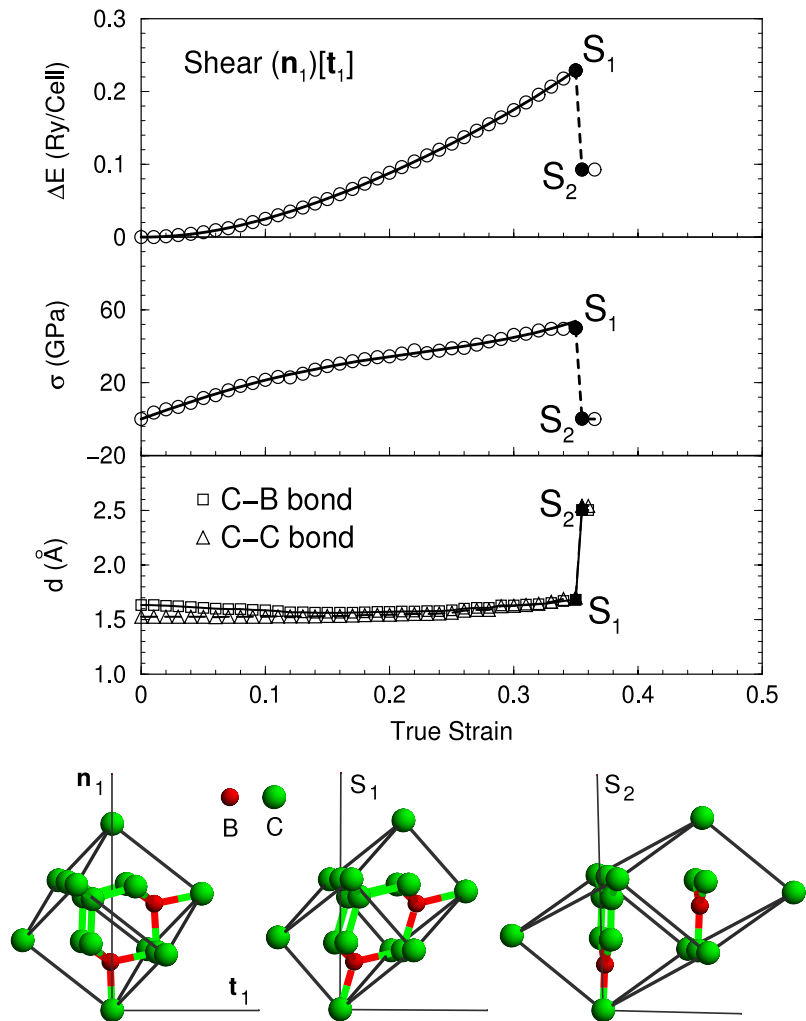
Figure 3. The calculated (symbols) energy (ΔE), stress (σ) and bond length (d) as functions of the shear strain for diamond-like BC$_3$ in the weakest ($\mathbf{n}_1$)[$\mathbf{t}_1$] shear direction. The solid line in the top panel is a fitting curve that gives the stress–strain (solid) curve by $\sigma = (1/V)\partial E/\partial \epsilon_T$, where ϵ_T is the true strain. The equilibrium structure and snapshots of the unit cell at two key points (S$_1$ and S$_2$) just before and after the shear breaking are shown at the bottom.

be broken in the process. The preparation of this precursor, if possible for instance by chemical methods, can lead to the synthesis of d-BC$_3$ at much reduced pressure and temperature.

In summary, our first-principles calculations show that d-BC$_3$ is a superhard material with its ideal tensile and shear strength comparable to those of c-BN. Its ideal tensile strength is 40% larger than its ideal shear strength, making it much less brittle than diamond and c-BN. Moreover, d-BC$_3$ is metallic at equilibrium and remains so under large strains, which places it as the hardest conductor studied to date. We identify a metastable g-BC$_3$ that can easily transform into d-BC$_3$ through a proposed synthesis route at much reduced pressure and temperature.
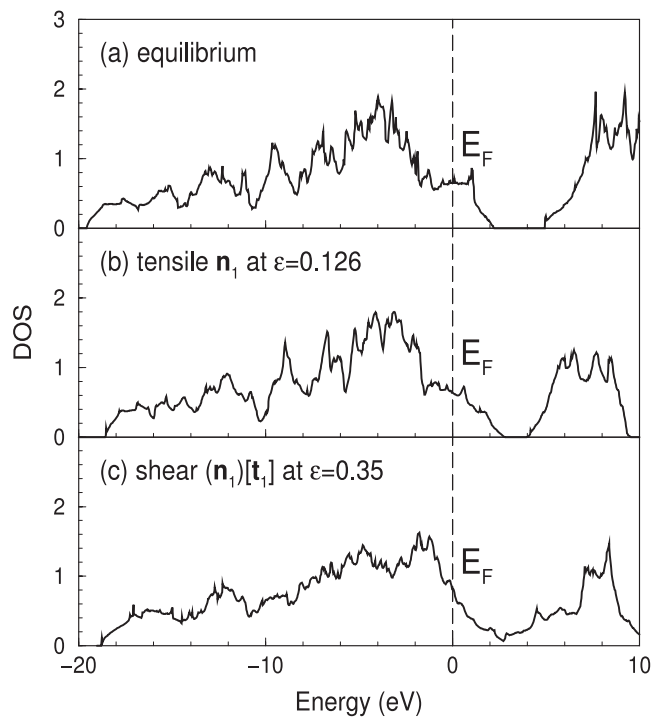
Figure 4. The calculated density of states for diamond-like BC$_3$ at equilibrium, under $\mathbf{n}_1$ tensile and $(\mathbf{n}_1)[\mathbf{t}_1]$ shear strains at the peak stresses. The Fermi energy (E_F) is shifted to zero energy, indicated by the vertical dashed line in the figure.
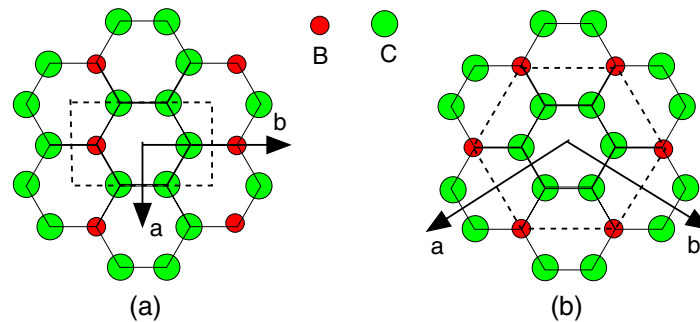
Figure 5. (a) The layered BC$_3$ structure obtained by breaking the C–C and C–B bonds along the $\mathbf{n}_1$ direction in the diamond-like BC$_3$ structure. (b) The most stable layered BC$_3$ structure. The dashed lines indicate the unit cells.

References

[1] Mamin R F and Inushima T 2001 *Phys. Rev.* B **63** 033201
[2] Ekimov E A, Sldorov V A, Bauer E D, Mel'nik N N, Curro N J, Thompson J D and Stishov S M 2004 *Nature* **428** 542
[3] Knittle E, Kaner R B, Jeanloz R and Cohen M L 1995 *Phys. Rev.* B **51** 12149
[4] Solozhenko V L, Andrault D, Fiquet G, Mezouar M and Rubie D C 2001 *Appl. Phys. Lett.* **78** 1385
[5] Zhao Y, He D W, Daemen L L, Shen T D, Schwarz R B, Zhu Y, Bish D L, Huang J, Zhang J, Shen G, Qian J and Zerda T W 2002 *J. Mater. Res.* **17** 3139
[6] Lowther J E 2005 *J. Phys.: Condens. Matter* **17** 3221
[7] Liu Z Y, He J, Yang J, Guo X, Sun H, Wang H T, Wu E and Tian Y 2006 *Phys. Rev.* B **73** 172101
[8] Solozhenko V L, Dubrovinskaia N A and Dubrovinsky L S 2004 *Appl. Phys. Lett.* **85** 1508
[9] Zinin P V, Ming L C, Kudryashov I, Konishi N, Manghanni M H and Sharma S K 2006 *J. Appl. Phys.* **100** 013516
[10] Roundy D, Krenn C R, Cohen M L and Morris J W Jr 1999 *Phys. Rev. Lett.* **82** 2713
[11] Luo W D, Roundy D, Cohen M L and Morris J W Jr 2002 *Phys. Rev.* B **66** 094110
[12] Roundy D, Krenn C R, Cohen M L and Morris J W Jr 2001 *Phil. Mag.* A **81** 1725
[13] Zhang Y, Sun H and Chen C F 2004 *Phys. Rev. Lett.* **93** 195504
     Zhang Y, Sun H and Chen C F 2005 *Phys. Rev. Lett.* **94** 145505
[14] Pan Z C, Sun H and Chen C F 2004 *Phys. Rev.* B **70** 174115
     Zhang Y, Sun H and Chen C F 2006 *Phys. Rev.* B **73** 064109
     Zhang Y, Sun H and Chen C F 2006 *Phys. Rev.* B **73** 144115
[15] Gouldstone A, Koh H J, Zeng K Y, Giannakopoulos A E and Suresh S 2000 *Acta Mater.* **48** 2277
[16] See the web site http://www.nersc.gov/projects/paratec/
[17] Ihm J, Zunger A and Cohen M L 1979 *J. Phys. C: Solid State Phys.* **12** 4409
[18] Ceperley D M and Alder B J 1980 *Phys. Rev. Lett.* **45** 566
[19] Cohen M L 1982 *Phys. Scr.* T **1** 5
[20] Troullier N and Martins J L 1991 *Phys. Rev.* B **43** 1993
[21] Perdew J P and Zunger A 1981 *Phys. Rev.* B **23** 5048
[22] Pfrommer B G, Cote M, Louie S G and Cohen M L 1997 *J. Comput. Phys.* **131** 233
[23] Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5188
[24] Pan Z C, Sun H and Chen C F 2006 *Phys. Rev.* B **73** 214111
[25] Tomanek D, Wentzcovitch R M, Louie S G and Cohen M L 1988 *Phys. Rev.* B **37** 3134
[26] Sun H, Ribeiro F J, Li J L, Roundy D, Cohen M L and Louie S G 2004 *Phys. Rev.* B **69** 024110