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Vladimir Solozhenko. On crystal structure of superhard cubic BC₂N. Journal of Superhard Materials, 2023, 45 (5), pp.399-401. 10.3103/S106345762305009X . hal-04127483v2

HAL Id: hal-04127483

<https://hal.science/hal-04127483v2>

Submitted on 23 Jun 2023

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On crystal structure of superhard cubic BC₂N

Vladimir L. Solozhenko* 

LSPM–CNRS, Université Sorbonne Paris Nord, 93430 Villetaneuse, France

Crystal chemistry analysis and accurate calculations of the mechanical properties of the recently proposed cubic diamondlike BC₂N indicate that this hypothetical phase is not related to the experimentally synthesized cubic BC₂N.

Keywords: superhard B-C-N phases, structure, hardness, elastic moduli.

At the turn of the millennium, cubic BC₂N (*c*-BC₂N), a ternary compound that is halfway between diamond and BN in composition has been synthesized at pressures above 18 GPa and temperatures higher than 2200 K by direct solid-state phase transition of graphite-like (BN)_{0.5}C_{0.5} [1]. The load-independent Vickers hardness of *c*-BC₂N is 76(4) GPa [2] which made it the second after diamond hardest phase and a member of the ultrahard materials family. At ambient pressure in an argon atmosphere, *c*-BC₂N remains stable up to 1800 K [3], and is therefore characterized by a significantly higher thermal stability than polycrystalline diamond of the same grain size.

An eight-atom zinc-blende-structured cubic unit cell with lattice parameter $a = 3.642(2)$ Å, where B, C, and N atoms are uniformly distributed over the lattice, has been proposed as the crystal structure of the synthesized *c*-BC₂N [1]. Later, several theoretical structures based on first-principles calculations were suggested [4-6], the analysis of which allows us to give preference to the "low-density" structure proposed by Kim *et al.* [6] (Fig. 1a), which is characterized by the absence of C-C, B-B and N-N bonds, and is in excellent agreement with available experimental data, particularly with respect to the mechanical properties (hardness and elastic moduli).

Very recently Wang *et al.* [7] claimed to have uncovered the hitherto unknown cubic structure of diamondlike BC₂N (*dia*-BC₂N). The 64-atom unit cell of the hypothetical *dia*-BC₂N with lattice parameter $a = 7.216$ Å (space group *P*-43*m*) is characterized by the presence of C-C bonds and contains an embedded carbon superstructure (Fig. 1b), which is in contradiction with the experimental data [1]. Vickers hardness of 77 GPa for hypothetical *dia*-BC₂N was predicted by the authors using empirical "microscopic" model of hardness [8], which, as shown by us [9], is not reliable in the case of superhard compounds of light elements. For such compounds, the use of the thermodynamic model based on thermodynamic properties and crystal structure [10] is preferred since it shows surprising agreement with available experimental data [11]. Our assessment of

* vladimir.solozhenko@univ-paris13.fr

dia-BC₂N in the framework of the thermodynamic model shows that this hypothetical phase should have a Vickers hardness of the order of 66 GPa (Table 1). An even lower hardness value of 50 GPa was obtained for *dia*-BC₂N using the Lyakhov-Oganov model [12], which takes into account the topology of the crystal structure, the strength of covalent bonding and the degree of ionicity. Table 1 presents the hardness as well as bulk, shear and Young's moduli, and Poisson's ratio of *dia*-BC₂N compared to the corresponding experimental values for cubic BC₂N. It is easy to see that mechanical properties of these two phases are drastically different, which clearly indicates that the hypothetical *dia*-BC₂N has nothing in common with the experimentally synthesized cubic BC₂N.

The author thanks Prof. H. Liu for providing the CIF-file of hypothetical diamondlike BC₂N and Prof. A.R. Oganov for fruitful discussion and valuable comments.

References

1. Solozhenko, V.L., Andraut, D., Fiquet, G., Mezouar, M., Rubie, D.C. Synthesis of superhard cubic BC₂N. *Appl. Phys. Lett.*, 2001, vol. 78, No. 10, pp. 1385-1387.
2. Solozhenko, V.L., Dub, S.N., Novikov N.V. Mechanical properties of cubic BC₂N, a new superhard phase. *Diam. Relat. Mater.*, 2001, vol. 10, No. 12, pp. 2228-2231.
3. Solozhenko, V.L., High-pressure synthesis of novel superhard phases. in: "Comprehensive Hard Materials" (eds. V.K. Sarin and C.E. Nebel), Elsevier, 2014, pp. 641-652.
4. Tateyama, Y., Ogitsu, T., Kusakabe, K., Tsuneyuki, S., Itoh S. Proposed synthesis path for heterodiamond BC₂N. *Phys. Rev. B*, 1997, vol. 55, No. 16, pp. R10161-R10164.
5. Sun, H., Jhi, S.-H., Roundy, D., Cohen, M.L., Louie, S.G. Structural forms of cubic BC₂N. *Phys. Rev. B*, 2001, vol. 64, 094108.
6. Kim, E., Pang, T., Utsumi, W., Solozhenko, V.L., Zhao Y. Cubic phases of BC₂N: A first-principles study. *Phys. Rev. B*, 2007, vol. 75, No. 18, 184115.
7. Wang, X., Wang, Y., Zhang, M., Liu, H. Superhard BC₂N in cubic diamondlike structure. *Phys. Rev. B*, 2023, vol. 107, No. 13, 134101.
8. Y. Tian, B. Xu, Z. Zhao, Microscopic theory of hardness and design of novel superhard crystals. *Int. J. Refract. Met. Hard Mater.* **33** (2012) 93-106.
9. Solozhenko, V.L., Matar, S.F. Prediction of novel ultrahard phases in the B-C-N system from first principles: Progress and problems. *Materials*, 2023, vol. 16, 886.
10. Mukhanov, V.A., Kurakevych, O.O., Solozhenko V.L. The interrelation between hardness and compressibility of substances and their structure and thermodynamic properties. *J. Superhard Mater.*, 2008, vol. 30, No. 6, pp. 368-378.
11. Matar, S.F., Solozhenko, V.L. Crystal chemistry and ab initio prediction of ultrahard rhombohedral B₂N₂ and BC₂N. *Solid State Sci.*, 2021, vol. 118, 106667.
12. Lyakhov, A.O., Oganov, A.R. Evolutionary search for superhard materials: Methodology and applications to forms of carbon and TiO₂. *Phys. Rev. B*, 2011, vol. 84, No. 9, 092103.
13. Tkachev, S.N., Solozhenko, V.L., Zinin, P.V., Manghnani, M.H., Ming, L.C. Elastic moduli of the superhard cubic BC₂N phase by Brillouin scattering. *Phys. Rev. B*, 2003, vol. 68, No. 5, 052104.

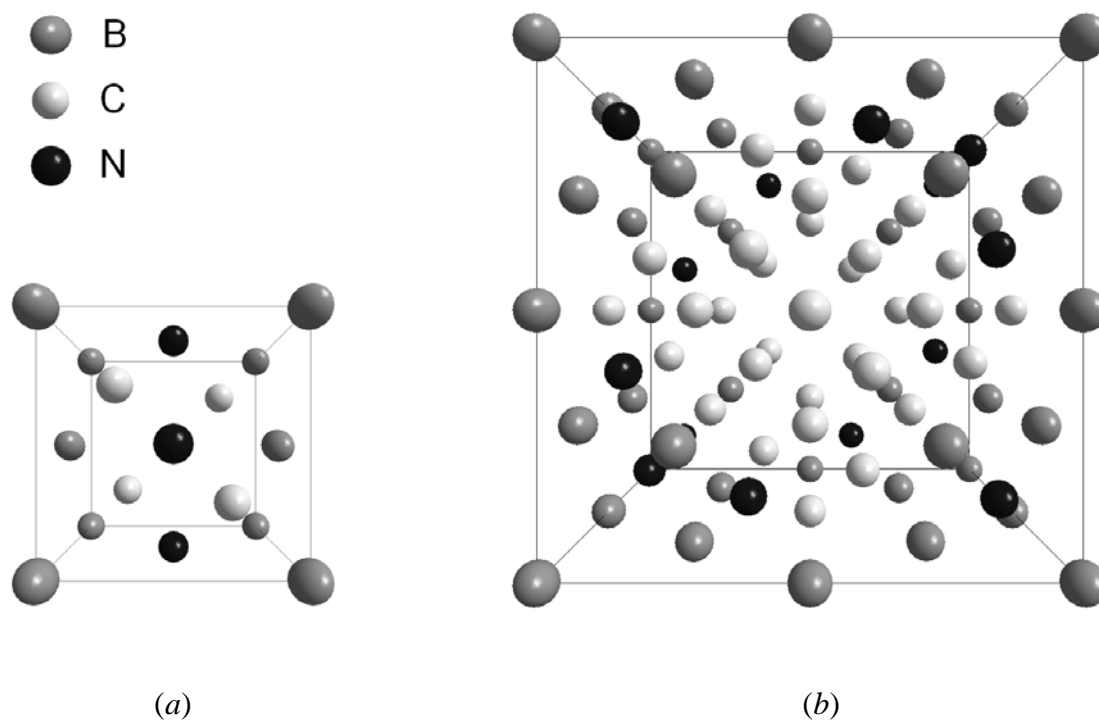


Figure 1 Crystal structures of cubic BC_2N [6] (a) and hypothetical *dia*- BC_2N [7] (b).

Table 1 Mechanical properties of cubic BC₂N [1] and hypothetical *dia*-BC₂N [7]: Vickers hardness (H_V), bulk modulus (B), shear modulus (G), Young's modulus (E) and Poisson's ratio (ν)

	H_V		B		G_V	E^\ddagger	ν^\ddagger
	T^*	LO^\dagger	B_0^*	B_V			
	GPa						
cubic BC ₂ N	76(4) ^[1,2]		282(15) ^[1] 259(22) ^[13]		238(8) ^[13]	557 ^{pw}	0.171 ^{pw}
<i>dia</i> -BC ₂ N	66 ^{pw}	50 ^{pw}	397 ^{pw}	392 ^[7]	439 ^[7]	959 ^{pw}	0.092 ^{pw}

* Thermodynamic model [10]

† Lyakhov-Oganov model [12]

‡ E and ν values calculated using isotropic approximation

^{pw} present work