

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/243738550>

Tersoff Potential Parameters for Simulating Cubic Boron Carbonitrides

Article in *Japanese Journal of Applied Physics* · January 2000

DOI: 10.1143/JJAP.39.L48

CITATIONS

181

READS

1,611

3 authors, including:



Katsuyuki Matsunaga
Nagoya University

216 PUBLICATIONS 6,378 CITATIONS

[SEE PROFILE](#)



Craig A. J. Fisher
Japan Fine Ceramics Center

129 PUBLICATIONS 8,902 CITATIONS

[SEE PROFILE](#)

Tersoff Potential Parameters for Simulating Cubic Boron Carbonitrides

Katsuyuki MATSUNAGA, Craig FISHER and Hideaki MATSUBARA

Japan Fine Ceramics Center, 2-4-1 Mutsuno, Atsuta-ku, Nagoya 456-8587, Japan

(Received September 30, 1999; accepted for publication November 19, 1999)

We have developed Tersoff potential parameters for boron in order to simulate cubic boron carbonitride systems by molecular dynamics. Combined with parameters for C and N available from the literature, our parameters are shown to reproduce the lattice parameters and bulk moduli of boron nitride and boron carbonitride ($C_{0.33}(BN)_{0.67}$) with good accuracy. By simulating several systems of formula $(C_x(BN)_{1-x})$ over a wide range of carbon contents ($x = 0$ to 1), we observed the same trends in the deviation from ideal mixing as found experimentally. We attribute this deviation to the relatively longer C–N bonds distributed randomly throughout the intermediate C content systems.

KEYWORDS: molecular dynamics, Tersoff potentials, boron carbonitride, solid solution, bulk modulus

Boron nitride, BN, is of considerable interest due to its outstanding physical properties such as extreme hardness, high melting point, low dielectric constant and wide band gap.¹⁾ These properties are advantageous in practical applications such as protective coating materials, abrasives and microelectronic devices.

Although boron nitride normally has a hexagonal structure (*h*-BN), cubic BN (*c*-BN) with the zinc blende structure can be produced at high pressures and high temperatures.²⁾ The cubic phase has a hardness comparable to that of diamond.^{3,4)} *c*-BN and diamond also share a number of other features including similar phase diagrams and atomic sizes, so that it is reasonable to expect these materials to form solid solutions. Indeed, cubic-structured ternary B–C–N compounds have recently been prepared.^{5–8)} Since B–C–N compounds may display properties superior to or distinct from those of the parent materials (diamond and *c*-BN), their development is of both technological and scientific importance.

Synthesis of cubic B–C–N has been reported by a number of groups. Badzian prepared mixed B–C–N crystals with a diamond-like structure by a high-pressure and high-temperature treatment starting from a hexagonal B–C–N phase.⁵⁾ Knittle *et al.* produced $C_x(BN)_{1-x}$ ($x = 0.3$ – 0.6) solid solutions with the zinc blende structure by laser heating at high pressure.⁶⁾ The lattice parameters of $C_x(BN)_{1-x}$ were found to be slightly larger than those predicted by Vegard's Law. These authors also determined that cubic $C_{0.33}(BN)_{0.67}$ has a bulk modulus of 355 GPa, which is smaller than that estimated by assuming an ideal solid solution. Kakudate *et al.* prepared a cubic BC_2N compound by shock compression of hexagonal $BC_{2.5}N$.⁷⁾ Their cubic BC_2N material had a high bulk modulus of 401 GPa, which is substantially larger than that of $C_{0.33}(BN)_{0.67}$ reported by Knittle *et al.*⁶⁾ The physical properties of cubic B–C–N compounds therefore appear to depend strongly on their chemical composition.

In practice, a systematic study of the relationship between composition and properties in B–C–N materials is difficult because of the very high temperatures and pressures involved in their synthesis. Computer simulation techniques, on the other hand, are not limited by the same physical constraints and are therefore a powerful means of investigating materials where extreme conditions are concerned.

In this letter, we report a study of the structural and elastic properties of cubic-structured B–C–N solid solutions by the molecular dynamics (MD) technique as incorporated in the program MASPHYC (Fujitsu). Systems of 216 atoms, con-

sisting of 27 unit cells with the zinc blende structure, were simulated under conditions of constant pressure and temperature (isothermal-isobaric ensemble) and 3D periodic boundaries. The temperature was set at 300 K for all runs. The equations of motion were integrated using a time interval of 0.25×10^{-15} s (0.25 fs). Structural properties of simulated systems were obtained from time averages taken over more than 20000 steps (5.0 ps) after equilibration, where changes in internal energy with time were less than 10^{-4} eV/atom.

The arrangement of atoms in cubic-structured ternary B–C–N compounds has been discussed in a number of papers. According to experiments by Knittle *et al.*⁶⁾ and Komatsu *et al.*,⁸⁾ the material is a single phase solid solution having a diamond-like structure without regular ordering of the constituent atoms. Each atom in the material is tetrahedrally coordinated to give C–C, C–B, C–N and B–N nearest neighbor pairs. B–B and N–N pairs were not found. It is conjectured, therefore, that B and N atoms occupy individual *fcc* sublattices just as in *c*-BN, with a certain number of B and N atoms replaced by C atoms. Based on this assumption, we constructed systems of 216 particles with half the C atoms randomly distributed on B sites, and the other half on N sites.

The accuracy and validity of MD studies depend crucially on the interatomic potentials used to describe the energy surface between particles. Among several potential models developed in recent years, the Tersoff potential has been particularly successful in modeling covalent materials. Details of the Tersoff functional form are described in ref. 9. Originally, Tersoff potential parameters were independently determined for elements C, Si and Ge.^{10–12)} Parameters for nitrogen have also recently been developed.^{13,14)} In order to extend the use of these potentials to multi-component systems such as SiC, Tersoff introduced a single additional parameter, χ_{i-j} for a pair of unlike atoms, so that the potential is generalized to treat mixtures of elements.¹²⁾

To date, two sets of potential parameters for boron have been reported. Sekkal *et al.* developed Tersoff parameters for B by fitting to bulk properties of *c*-BN.¹⁵⁾ In their procedure, however, *c*-BN was treated as a one-component system, where B atoms were equivalent to N atoms, so that identical potential parameters were given to both B and N. These parameters are not transferable to B–C–N systems since the difference between B–C and B–N interactions is ignored. In a separate paper, Albe¹⁶⁾ developed interatomic potentials for *c*-BN based on a functional form proposed by Brenner¹⁷⁾ which is similar to the Tersoff form. Although Albe's pa-

rameters give a good description of the physical properties of *c*-BN, they are not easily transferred to B–C–N systems because of the slight differences between the Brenner and Tersoff functional forms. We therefore sought to derive our own set of Tersoff parameters for boron compatible with the parameters for C and N already in the literature.

Table I shows the potential parameters for B determined in this study. Parameters for C and N as proposed by Tersoff¹²⁾ and Kroll,¹³⁾ respectively, are also listed. These parameter sets include χ_{C-N} and ω_{C-N} terms and were found to reproduce the crystal structure and bulk modulus of β -C₃N₄.¹³⁾ In our fitting procedure, we first determined the parameters for boron empirically by an iterative method to reproduce the experimentally measured lattice constant, bulk modulus and binding energy of *c*-BN *via* MD simulation. The parameters *c*, *d* and *h*, which determine the bond-angle dependence of bonding interactions between B and neighboring atoms, were taken to be identical with those of Albe.¹⁶⁾ Next, for the B–C interaction, the parameter χ_{B-C} was adjusted to reproduce the lattice constant and bulk modulus of cubic C_{0.33}(BN)_{0.67} experimentally reported by Knittle *et al.*⁶⁾

To determine the isothermal bulk modulus B_0 at zero pressure for *c*-BN and C_{*x*}(BN)_{1-*x*}, we have analyzed simulated data at different pressures from 0.1 MPa to 5.0 GPa using the Birch equation,^{18,19)} which is an expansion of the Eulerian strain parameter, *f*:

$$p = 3B_0 f (1 + 2f)^{5/2} (1 + af) \quad (1)$$

$$f = \frac{1}{2} \left\{ \left(\frac{V}{V_0} \right)^{-2/3} - 1 \right\} \quad (2)$$

where *a* is a constant and V_0 is the volume at zero pressure.

Table I. Tersoff interatomic potential parameters used in this study. Parameters for C and N were taken from Tersoff¹²⁾ and Kroll,¹³⁾ respectively.

Elements	B	N ¹³⁾	C ¹²⁾
A (eV)	2.7702×10^2	1.1000×10^4	1.3936×10^3
B (eV)	1.8349×10^2	2.1945×10^2	3.467×10^2
λ (Å ⁻¹)	1.9922	5.7708	3.4879
μ (Å ⁻¹)	1.5856	2.5115	2.2119
β	1.6000×10^{-6}	1.0562×10^{-1}	1.5724×10^{-7}
<i>n</i>	3.9929	12.4498	0.72751
<i>c</i>	5.2629×10^{-1}	7.9934×10^4	3.8049×10^4
<i>d</i>	1.5870×10^{-3}	1.3432×10^2	4.384×10^0
<i>h</i>	0.5000	-0.9973	-0.57058
<i>R</i> (Å)	1.8	2.0	1.8
<i>S</i> (Å)	2.1	2.3	2.1
Interactions (<i>i</i> – <i>j</i>)	B–N	B–C	C–N ¹³⁾
χ_{i-j}	1.1593	1.0025	0.9685
ω_{i-j}	1.0000	1.0000	0.6381

Table II. Calculated and experimental properties of *c*-BN and *c*-C_{0.33}(BN)_{0.67}.

	<i>c</i> -BN		<i>c</i> -C _{0.33} (BN) _{0.67}	
	This work	Experiment ^{3,4)}	This work	Experiment ⁶⁾
Lattice constant (Å)	3.658	3.615	3.641	3.613
B_0 (GPa)	385	369–400	342	355
B'_0	3.7	4.0	4.7	4.0
Binding energy (eV/atom)	-6.63	-6.6	-6.58	—

The pressure derivative B'_0 is related to the constant *a* by $B'_0 = 2a/3 + 4$. This equation provides an excellent description of compression of solids.¹⁹⁾

Figure 1 shows the pressure dependence of volume V/V_0 for *c*-BN and *c*-C_{0.33}(BN)_{0.67} from our MD results. It can be seen that *V* decreases smoothly with increasing pressure. The resulting structural and elastic properties for *c*-BN and *c*-C_{0.33}(BN)_{0.67} at zero pressure are summarized in Table II along with experimental values. The simulated lattice constants compare favorably with the observed values, with errors of only 1.2% for *c*-BN and 0.8% for *c*-C_{0.33}(BN)_{0.67}. The calculated B_0 and B'_0 values also match well with experiment. Although these values were obtained from 216-atom systems, we made extra MD simulations of 1000 atoms for *c*-C_{0.33}(BN)_{0.67} in order to examine a system-size dependence. The obtained lattice constant and B_0 were found to be 3.639 Å and 345 GPa, respectively. Thus, we found no significant system-size dependence for simulated structural properties.

In order to test the transferability of our potential parameters, we have calculated the structural properties of cubic C_{*x*}(BN)_{1-*x*} systems with different C contents by MD. In the same manner as for C_{0.33}(BN)_{0.67}, systems of 216 atoms with randomly distributed C atoms were simulated for carbon contents of 20%, 50%, 67%, 80% and 100% (diamond) at 300 K. Figure 2 shows the calculated molar volumes of cubic C_{*x*}(BN)_{1-*x*} against the fraction of C. Experimental values from ref. 6 are also plotted in the same figure. Both experimental and simulation results show that the molar volume of *c*-C_{*x*}(BN)_{1-*x*} decreases with increasing C content. Furthermore, the molar volumes are larger than those expected by assuming an ideal mixture of diamond and *c*-BN (i.e. Vegard's law) as indicated by dashed lines in Fig. 2.

The simulated molar volumes of *c*-C_{*x*}(BN)_{1-*x*} with lower

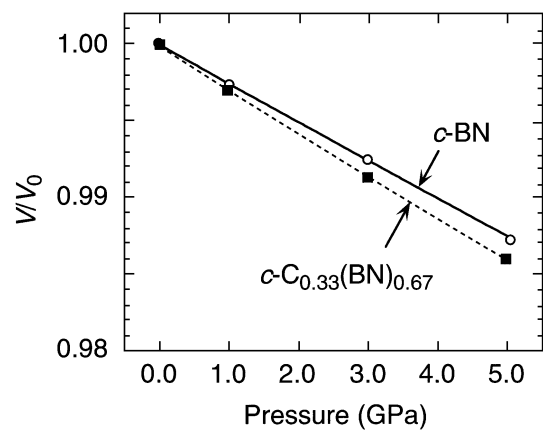


Fig. 1. Normalized volume vs pressure for compositions BN and C_{0.33}(BN)_{0.67}.

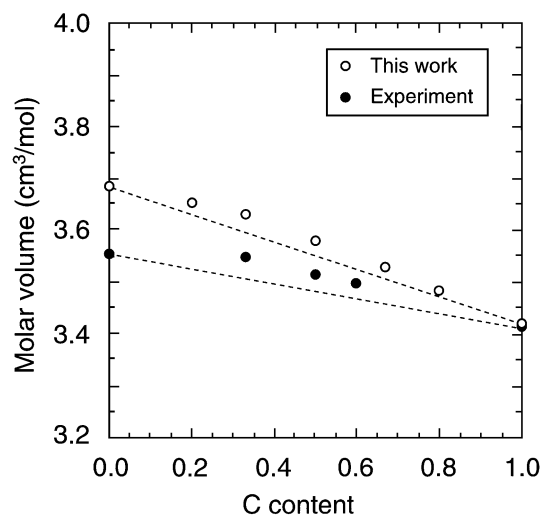


Fig. 2. Molar volumes of $c\text{-C}_x(\text{BN})_{1-x}$ vs BN content calculated using our Tersoff potential parameters. Open circles indicate the simulation results, while solid circles the ones obtained by Knittle *et al.*⁶⁾

C contents are larger by about 3% than those from experiment. When BN contents in $c\text{-C}_x(\text{BN})_{1-x}$ systems decrease with increasing C contents, we can see from Fig. 2 that the difference in molar volume between MD and experiment also tends to decrease proportionally to BN contents. Thus, such overestimation by MD may be due to that our proposed parameters give a larger molar volume for $c\text{-BN}$ than that by experiment. However, the important points to notice here are that the difference in lattice constant between MD and experiment is less than 1.2% even in $c\text{-BN}$, and that our parameters can describe the deviation of molar volumes from ideality as observed experimentally.

The reason for the molar volume expansion can be understood in terms of the local atomic structure in $c\text{-C}_x(\text{BN})_{1-x}$. Table III lists average bond lengths and bond populations of atomic pairs in $c\text{-C}_{0.5}(\text{BN})_{0.5}$. There are no atomic pairs of B–B and N–N in our simulated systems. The bond lengths of C–C, B–N and B–C are in good agreement with nearest neighbor distances in diamond, $c\text{-BN}$ and BC_3 which were obtained experimentally⁶⁾ and theoretically.²⁰⁾ In contrast, C–N pairs exhibit longer bond lengths by about 5% than those of C–C, B–N and B–C pairs. Thus, the presence of C–N pairs, which are randomly distributed throughout the system, will give rise to a slight expansion of the $c\text{-BN}$ lattice relative to a simple proportional combination of the end member (i.e. diamond and $c\text{-BN}$) molar volumes.

Figure 3 shows the isothermal bulk moduli B_0 of $c\text{-C}_x(\text{BN})_{1-x}$ systems as a function of C content. The open squares represent the bulk moduli calculated from our MD results. The bulk moduli of $c\text{-C}_x(\text{BN})_{1-x}$ are smaller than expected for an ideal mixing of diamond and $c\text{-BN}$ (indicated by the solid line). A more sophisticated relationship between density ρ and bulk modulus B_0 was derived by Knittle *et al.*⁶⁾ using experimental data for diamond, $c\text{-BN}$ and $c\text{-C}_x(\text{BN})_{1-x}$:

$$\left(\frac{B_0}{\rho}\right)^{1/2} = 19.5\rho - 57.5. \quad (3)$$

The bulk moduli predicted by this equation are indicated by the dashed line in Fig. 3. Although the calculated B_0

Table III. Average bond lengths and bond populations for atomic pairs in $c\text{-C}_{0.5}(\text{BN})_{0.5}$.

Atomic pair	$c\text{-C}_{0.5}(\text{BN})_{0.5}$	
	Bond length (Å)	Population (%)
B–N	1.54	26
B–C	1.56	26
C–C	1.54	24
C–N	1.64	24

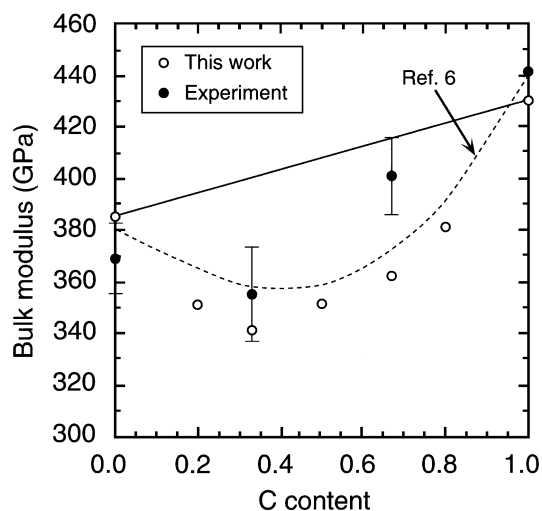


Fig. 3. Bulk moduli vs C content in solid solutions of $c\text{-C}_x(\text{BN})_{1-x}$. Solid circles indicate experimental data.^{3,6,7)} Solid line represents values expected by ideal mixing (Vegard's Law).

of $c\text{-C}_{0.67}(\text{BN})_{0.33}$ is smaller by 10% than that of Kakudate *et al.*,⁷⁾ the relationship between B_0 and C content can be seen to be in close agreement with that given by eq. (3).

In summary, we have derived potential parameters for boron based on the Tersoff functional form which, when combined with parameters for nitrogen and carbon available in the literature, successfully reproduce structural and elastic properties of cubic B–C–N compounds. These potentials will be used to study in greater detail the structure and physical properties of various compositions in this important class of materials.

- 1) *Synthesis and Properties of Boron Nitride*, eds. J. J. Pouch and S. A. Alterovitz (Trans-Tech, Ackermannsdorf, Switzerland, 1990).
- 2) F. P. Bundy and R. H. Wentorf, Jr.: *J. Chem. Phys.* **38** (1963) 1144.
- 3) E. Knittle, R. M. Wentzcovitch, R. Jeanloz and M. L. Cohen: *Nature* **337** (1989) 349.
- 4) M. Grimsditch, E. S. Zouboulis and A. Polian: *J. Appl. Phys.* **76** (1994) 832.
- 5) A. R. Badzian: *Mater. Res. Bull.* **16** (1981) 1385.
- 6) E. Knittle, R. B. Kaner, R. Jeanloz and M. L. Cohen: *Phys. Rev. B* **51** (1995) 12149.
- 7) Y. Kakudate, M. Yoshida, S. Usuda, H. Yokoi, S. Fujiwara, M. Kawaguchi and T. Sawai: *Advanced Materials '93*, eds. M. Wakatsuki, J. C. Angus, A. T. Collins, N. Fujimori, H. Kawarada and H. Komiyama (Elsevier, Amsterdam, 1994) Vol. 14B, p. 1447.
- 8) T. Komatsu, M. Nomura, Y. Kakudate and S. Fujiwara: *J. Mater. Chem.* **6** (1996) 1799.
- 9) J. Tersoff: *Phys. Rev. B* **37** (1988) 6991.
- 10) J. Tersoff: *Phys. Rev. Lett.* **61** (1988) 2879.
- 11) J. Tersoff: *Phys. Rev. B* **38** (1988) 9902.
- 12) J. Tersoff: *Phys. Rev. B* **39** (1989) 5566.
- 13) P. M. Kroll: Ph. D. Thesis, Technische Hochschule Darmstadt, 1996.

- 14) F. de Brito Mota, J. F. Justo and A. Fazzio: Phys. Rev. B **58** (1998) 8323.
- 15) W. Sekkal, B. Bouhafs, H. Aourag and M. Certier: J. Phys.: Condens. Matter **10** (1998) 4975.
- 16) K. Albe and W. Moeller: Comput. Mater. Sci. **10** (1998) 111.
- 17) D. Brenner: Phys. Rev. B **42** (1990) 9458.
- 18) F. Birch: J. Geophys. Res. **57** (1952) 227.
- 19) F. Birch: J. Geophys. Res. **83** (1978) 1257.
- 20) D. Tomanek, R. M. Wentzcovitch, S. G. Louie and M. L. Cohen: Phys. Rev. B **37** (1988) 3134.