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Elastic and thermodynamic properties of potentially superhard carbon boride materials

Boron icosahedral structures are the basic building structures of many important hard borides and especially B_4C . The structural and thermodynamic properties of B_4C have been examined applying molecular dynamics simulation with the use of both ab initio and bond order Tersoff potentials. Various physical quantities of B_4C including the elastic constants, thermal expansion coefficients, and specific heat have been examined.

Keywords: diamond, boron, electronic structure, elastic constants, molecular dynamics.

INTRODUCTION

Lightweight atoms such as carbon, boron, nitrogen, and oxygen [1] are very important for hard materials. Carbides, borides, nitrides, and oxides have high melting points, good thermal conductivity, and high chemical resistance [2–5]. Cubic boron nitride is an important hard material, which behaves as an electrical insulator and has several properties similar to diamond. Recent work has focused on alloying diamond with BN to identify superhard materials with a B–C–N structure [6–8]. The hope is that a high pressure solid solution of diamond and BN would exhibit novel properties and be a superhard material. B–C–N phases are expected to be harder than cBN, but still retain good thermal and chemical stability. This therefore would be an excellent material for high-speed cutting and polishing of ferrous alloys where diamond fails.

Another interesting class of lightweight materials are boron-rich solids. Boron has several crystallographic allotropes, many of which are classified as semiconductors and capable of forming stable covalent-bonded molecular networks with high strength [9, 10]. The crystal structures mainly contain B_{12} icosahedra as essential common structural building blocks [11–13] and these solids have similar physical properties such as high electrical conductivity, high melting points, low density, high chemical resistance. They also have low corrosivity and high hardness. The boron icosahedra primarily determine the electronic structure and chemical bonding in these solids and this is the reason, why such materials display similar characteristics. They also have advantages of being easily synthesized and stable up to very high temperatures [14]. Recent theoretical works [12, 15] have concluded that the incorporation of other atoms between the icosahedra indirectly influences the bonding between the boron atoms and is responsible for the enhanced hardness.

There are several allotropes of boron, although three of them, α , β , and tetragonal, are important. The allotrope β -boron is synthesized at a high temperature, while α -boron is metastable at ambient conditions, unstable thermodynamically, and synthesized only at low temperatures. Tetragonal phases are intermediate

between α and β -boron. The boundary temperature depends on the preparation method and has been estimated to be about 1500 K [16, 17]. In the case of the B_{50} allotropes, a B_{192} structure may be more appropriate [18]. Boron carbides are among the best studied [18, 19] for potential as a hard material. B_4C has often been considered to have a structure similar to α -boron [18]. Technical applications of such boron–carbon structures are limited with variable homogeneity range over a specific stoichiometry around B_4C . However, detailed investigation of fundamental properties of such boron compounds has been impeded because it is difficult to grow large crystals. There have been several speculations concerning the structure of B_4C . However, recently it has been shown that the polar structure (where C enters the icosahedra) is more likely associated with a $B_{13}C_2$ stoichiometry [20] than the conventional chain structure (where C does not enter the icosahedra) with B_4C [21–23].

Computer modeling techniques have also been used to study boron and boron-rich compounds. Li and Ching [24] studied the structure and properties of four B_{12} -based crystals using the self-consistent orthogonalized linear combination with the local density approximation (LDA) of the density functional theory (DFT) to calculate the band structures and ground state properties. Their results were in good agreement with other existing first-principle calculations using the pseudopotential plane-wave method. Various attempts have been made to study the ground state and finite temperature properties of α - and β -boron using *ab initio* pseudopotentials method with LDA [15, 16]. These have clarified the features of β -boron by comparing them to those of the α -boron phase. Electronic structures of various other borides that hold potential for superhard material properties have also been investigated [12]. Recently [23] the mechanical properties and structure of amorphous and crystalline B_4C prepared using various plasma-based techniques have been investigated and it has been suggested that carbon could eventually segregate into clusters when the material attains an amorphous structure at elevated temperatures.

In the present work we investigated structural and thermodynamic properties of selected boron icosahedra materials and B_4C using both the *ab initio* and molecular dynamic simulations. The molecular dynamic simulations are employed as being a way to investigate the behavior of large numbers of atoms and thus the material behavior at high temperatures. The results are presented for the lattice expansion and specific heat of B_4C . Finally it is shown that the behavior of carbon appears to play an important role at high temperatures.

CALCULATIONS

The computer simulation gives information at a microscopic atomic level [24, 25], from which experimental properties are derived or predicted. *Ab initio* approaches can accurately predict many physical properties but have computational limitations as to practical realization to deal with a relatively low number of atoms. In the present work, first-principles calculations have used the VASP code [26], which performs plane-wave pseudopotential total energy calculations. The electronic structure of the materials have been investigated using several methods [27, 28] and here they are calculated using the density functional theory (DFT) in the local density approximation (LDA) with the Ceperley and Alder [29] correlation used to treat the exchange and correlation functional. In all calculations, plane waves are employed with an energy cut-off to 500 eV, and the Brillouin zone sampling is fixed at $8 \times 8 \times 8$ Monkhorst-Pack [30] scheme with PAW pseudopotentials

[31]. All the calculations carried out are fully relaxed and optimized with respect to volume with an energy convergence criteria of 10^{-5} eV/atom.

For large numbers of atom simulations we have used the Tersoff bond-order potential as implemented either through the codes DLPOLY [32] or GULP [33]. This potential has now been applied to a large variety of different systems [34–36] and is one of the commonly used functional forms for modeling covalent systems. The functional form of the Tersoff potential is:

$$V = \sum_i v_i = \frac{1}{2} \sum_{i \neq j} v_{ij}; \quad (1)$$

$$v_{ij} = f_C(r_{ij})[f_R(r_{ij})b_{ij}f_A(r_{ij})], \quad (2)$$

where V is the total potential energy of the system, f_R and f_A are the repulsive and attractive pair potentials, respectively, and f_C is a cutoff function. These are given by

$$f_R(r_{ij}) = A_{ij}(r_{ij})e^{-\lambda_{ij}r_{ij}}; \quad (3)$$

$$f_A(r_{ij}) = -B_{ij}(r_{ij})e^{-\lambda_{ij}r_{ij}}; \quad (4)$$

$$f_C(r_{ij}) = \begin{cases} 1 & \text{at } r_{ij} < R - D; \\ \frac{1}{2} - \frac{1}{2} \sin\left[\frac{\pi}{2} \frac{(r_{ij} - R)}{D}\right] & \text{at } R - D < r_{ij} < R + D; \\ 0 & \text{at } r > R + D; \end{cases} \quad (5)$$

where r_{ij} is the bond distance between atoms i and j with D and R cutoff radii for the interaction potential. The A , B and λ_{ij} potential parameters and the strength of each bond depend upon the local environment as measured by another empirical parameter χ_{ij} . In the case of the boron only system the cut off parameter D was adjusted to simulate icosahedral boron potentials, whereas for B_4C the parameter χ_{B-C} was adjusted. The parameters we have used in this work are listed in Table 1.

Table 1. Tersoff potential parameters used in this study. Parameters for B and C are taken from Matsunaga [37] and Munetoh [38]. Some parameters were adjusted as discussed in the text

	B	C
A , eV	$2.7702 \cdot 10^2$	$1.3936 \cdot 10^3$
B , eV	$1.8349 \cdot 10^2$	$3.467 \cdot 10^2$
λ , \AA^{-1}	1.992	3.4879
μ , \AA^{-1}	1.5856	2.2119
B	$1.6000 \cdot 10^{-6}$	$1.5724 \cdot 10^{-7}$
N	3.9929	0.72751
C	$5.2629 \cdot 10^{-1}$	$3.8049 \cdot 10^4$
D	$1.5870 \cdot 10^{-3}$	4.384
H	0.500	-0.57058
R , \AA	1.8	1.8
D , \AA	1.7–2.1	2.1
Interactions ($i-j$)	B–C	
χ_{ij}	1.0025	
ω_{ij}	0.9810	

Structural properties

Initially we examined the structural properties of some boride phases as well as B_4C . The boron structures studied are α -boron, tetragonal boron and crystal structures of these together with the B_4C phase we have considered are shown in Fig. 1. The reason for choosing these borides is to attempt some indication of the reliability of the Tersoff potential, although we stress that our prime motivation here is to explore properties of B_4C . Details of the final geometries are given in Table 2.

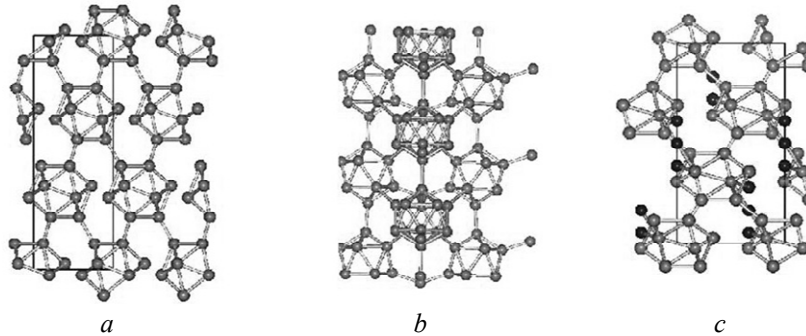


Fig. 1. Various boride phases (a) α -boron, (b) tetragonal boron, (c) B_4C .

Table 2. Lattice parameter (\AA) and bulk moduli of some boron-related compounds. Bulk moduli are obtained from the Birch-Murnaghan equation of state

Material	Tersoff	<i>Ab initio</i>	Experiment	$B, (B')$ (Tersoff)	$B, (B')$ (<i>ab initio</i>)	Experiment
α - B_{12} ($R3m$)	$a = 4.404$ $c = 12.286$	$a = 4.844$ $c = 12.286$	$a = 5.507$ [39]	212, (2.26)	226, (3.80)	213–224 [36] (4.0)
T- B_{50} ($P4_2/nm$)	$a = 7.940$ $c = 4.718$	$a = 8.734$ $c = 5.010$	$a = 8.75$ [40, 41] $c = 5.06$ [42]	208, (1.84)	206, (3.80)	
B_4C ($R3m$)	$a = 5.174$ $c = 11.695$	$a = 5.577$ $c = 11.286$	$a = 5.61$ $c = 12.14$	246, (5.380)	229, (3.50)	199–241 [37] (1.0, 4.0)

We have then applied a uniform pressure to each of the phases and fitted the energy results to the Birch-Murnaghan equation of state using the molecular dynamics code DLPOLY. The pressure–volume relation is shown in Fig. 2 for borides and the B_4C structure.

It is clear that the compressibility of B_4C is better than of the boron structures and this is reflected in the value of the bulk moduli obtained from a least squares fit to the Birch-Murnaghan equation of state that is given in Table 2. However the bulk modulus derived in this way does not reflect the full elastic properties of the system. To this end we specifically investigated the full elastic constants of the B_4C material and such values are given in Table 3 as obtained from the GULP program molecular dynamics code. We have also included results of the elastic constants obtained using *ab initio* calculations through the VASP code. As seen from Table 3 overall there is quite good agreement between the Tersoff and *ab initio* results, and with previous calculations, and experiment where available. This

gives some confidence in applying the Tersoff potential to finite temperature simulations, where large numbers of atoms are really needed and the system may become disordered.

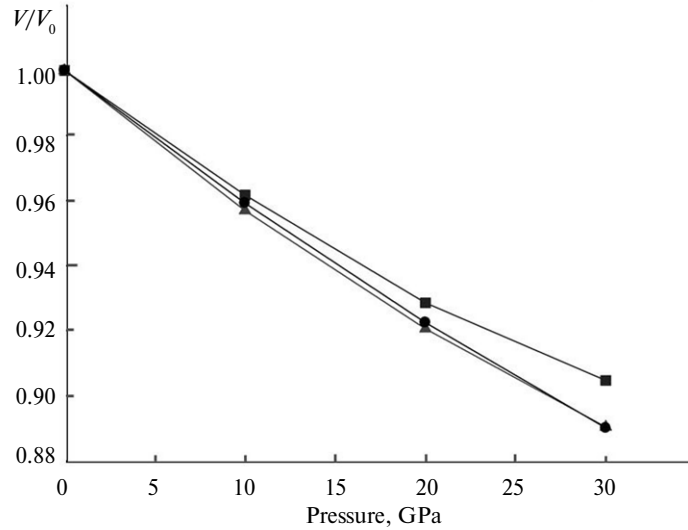


Fig. 2. Pressure–volume relations of α -boron (B_{12}) (\bullet), tetragonal–boron (B_{50}) (\blacktriangle) and B_4C (polar) (\blacksquare).

Table 3. Calculated elastic properties of B_4C (GPa). Other calculation and experimental values are listed. Voigt bulk (B), shear (G) and Young (E) moduli obtained from the elastic moduli tensors

	c_{11}	c_{12}	c_{13}	c_{23}	c_{33}	c_{55}	B	G	E
Present (Tersoff)	540	180	91	32	520	305	234	200	467
Present (<i>ab initio</i>)	539	181	79	82	480	139	236	178	427
Other calc. [44]	562	123	69	17	517	–	234	–	–
Expt. [45]	543	132	63		534	164	241	193	457
Expt. [46]							235	197	462

Thermal properties of B_4C

An increase in the temperature increases the kinetic energy of atoms and the increased interaction between the atoms gives an effective expansion of the unit lattice cell. The possibility of disorder in the structures at very high temperatures cannot be ruled out. To investigate, this needs quite a large number of atoms. For this we have used supercells consisting of up to 2880 atoms. All simulations have been performed using a NVT ensemble with the DLPOLY code, and employing a Verlet algorithm, with a time step of 1 ps.

First in Fig. 3 are the plots of the lattice expansion of B_4C at zero pressure. We note small changes in the lattice occurring around $T = 1500$ K. For this reason we have fitted the calculated results to a polynomial and this is shown in the figures. Thermal expansion coefficients α_a and α_c along a and c axes in MD simulation can be computed directly from the temperature derivative of the lattice parameter along those axes

$$\alpha_{(a,c)} = \frac{1}{(a,c)} \frac{\partial(a,c)}{\partial T}, \quad (6)$$

where a and c are the lattice parameters along the a or c axes. The thermal expansion coefficient increases linearly with temperature and we obtained a slightly larger thermal expansion along the c axis than along the a axis at 300 K.

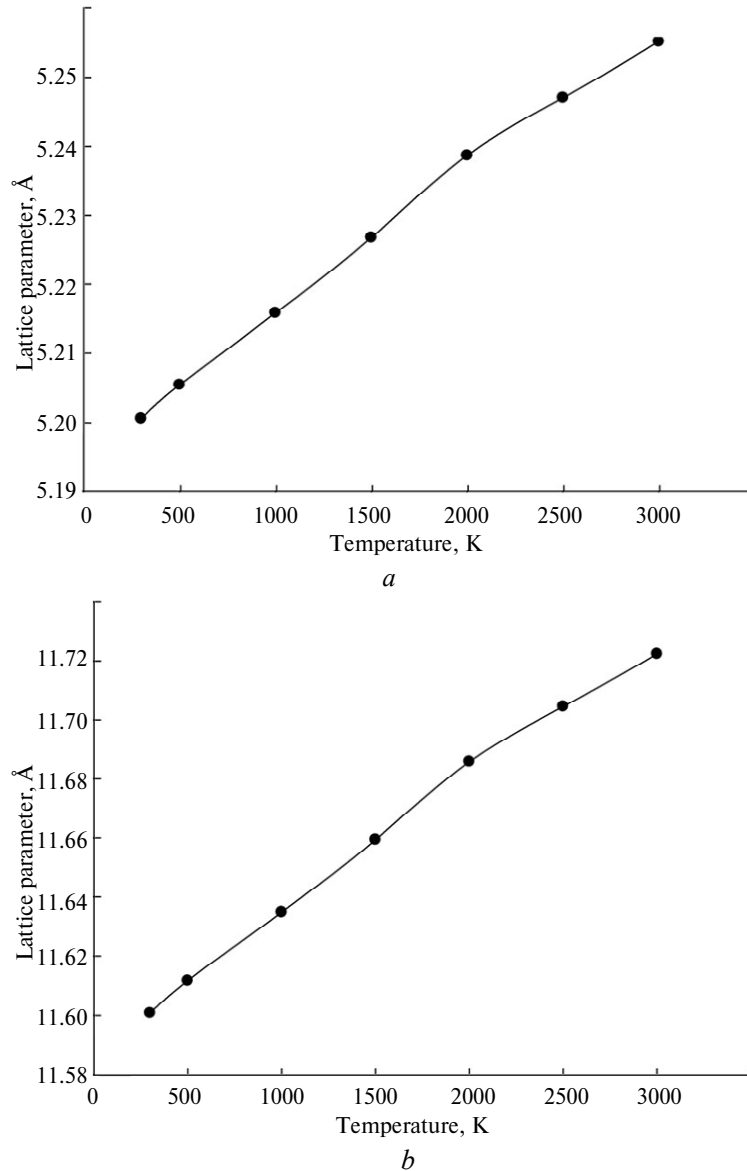


Fig. 3. Temperature dependence of the a - and c -axes of B_4C : (a) $a_{300\text{K}}(T) = -1.437 \cdot 10^{-9}T^2 + 2.517 \cdot 10^{-5}T + 5.193$, $a_{1500\text{K}}(T) = -3.800 \cdot 10^{-9}T^2 + 3.574 \cdot 10^{-5}T + 5.182$; (b) $c_{300\text{K}}(T) = -3.374 \cdot 10^{-9}T^2 + 5.636 \cdot 10^{-5}T + 11.58$, $c_{1500\text{K}}(T) = -8.600 \cdot 10^{-9}T^2 + 8.022 \cdot 10^{-5}T + 11.56$.

An average linear thermal expansion coefficient, α_l , was calculated using the formula

$$\alpha_l = \frac{1}{3}(2\alpha_a + \alpha_c). \quad (7)$$

The results for the average expansion coefficient of these borides starting at 300 and 1500 K computed using the above equation are listed in Table 4. These results are compared with two strongest known hard materials diamond and boron nitride.

Although the melting of solids is one the most common observations of a phase transition, the mechanism of melting is still an outstanding problem in condensed matter physics [42]. On the basis of the thermodynamics theory a phase transition is characterized by an abrupt change in the slope of the total energy against the temperature curve. Figure 4 shows the variation of energy against the temperature for borides.

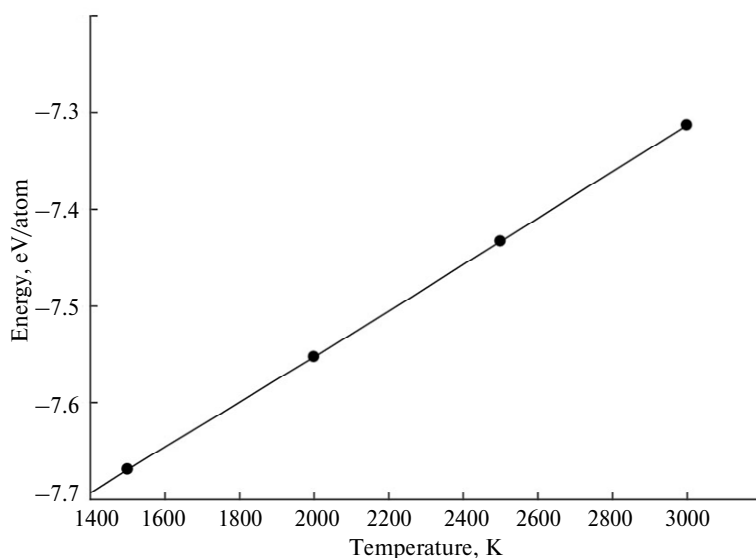


Fig. 4. Temperature variation of the total energy of B_4C : $E(T) = 2.375 \cdot 10^{-4}T - 8.027$.

There is a very slight change in the slope around 1500 K. This suggests a possible change of a phase. But the energy/temperature behavior also allows some deduction of the specific heat of the materials. The values so deduced are given in Table 4 for B_4C . These values are also compared with two other hard materials, namely diamond and cBN. As expected, the values compare quite well.

Table 4. Thermodynamic properties of B_4C compared to other hard materials

	Diamond	BN	B_4C (calculated)
$\alpha_{1500K}, 10^{-6} K^{-1}$	1.017 ^b	1.8 ^d	3.116
$\alpha_{300K}, 10^{-6} K^{-1}$	5.181 ^b	5.47 ^c	4.598
		6-8 ^f	4.5
$C_v(k_B)$	2.97 ^a	3.02 ^c	2.76
		5.16 ^e	

Note. The data taken from the following Refs. are indicated as: [43]^a, [44]^b, [45]^c, [46]^d, [47]^e, [48]^f.

We have to explore further the apparent change taking place around 1500 K. To understand this we have examined the radial distribution function (RDF) of the C

and B atoms as obtained from the MD calculations. Figure 5 shows the RDF for B_4C at 300, 1500 and 3000 K. The results are quite striking in the case of C. Overall some peaks decreased, while others broadened at high temperatures, the broadening of the larger distance peaks is characteristic of some amorphization. The retention of the lower peaks related to B shows that the B icosahedra are still quite stable even at elevated temperature, but the pronounced change in the C peak suggest some mobility of C and even the formation of carbon related defects as suggested in [23].

CONCLUSIONS

In summary we have calculated the properties of boron icosahedral structures using molecular dynamics simulations. The Tersoff parameters used are found to be reasonably reliable to investigate structural and thermodynamic properties of the boron icosahedral structures studied here when compared with *ab initio* results and

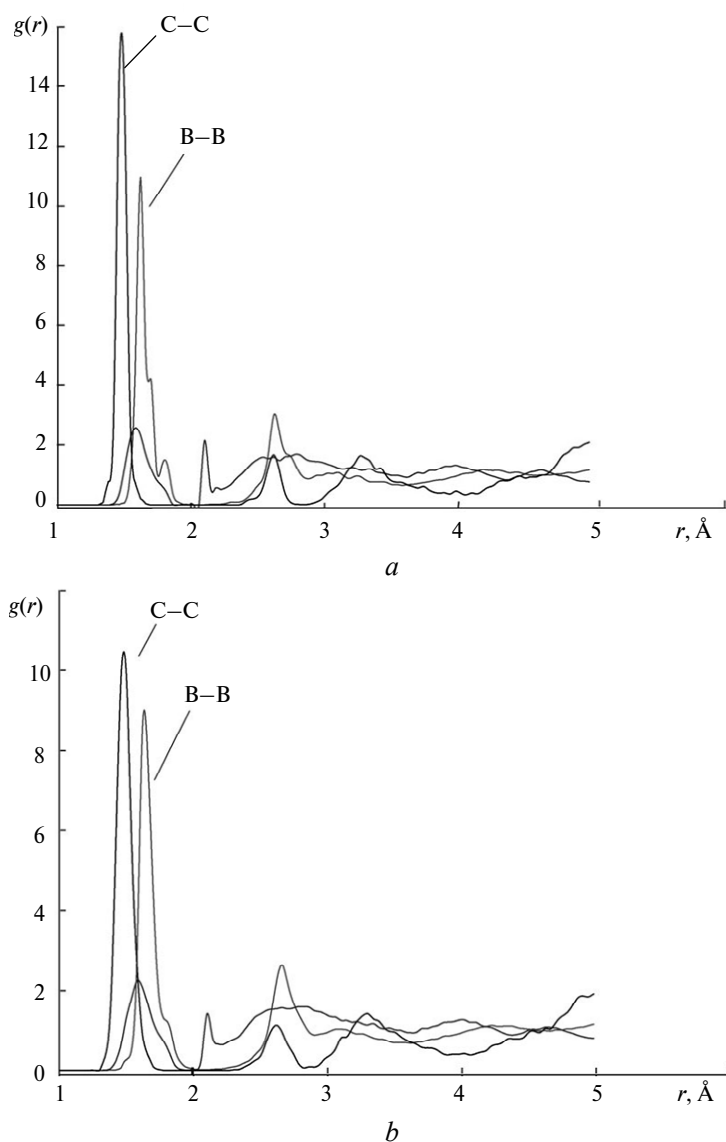


Fig. 5. Radial distribution of various atomic interactions in B_4C : 300 (a), 1500 (b), 3000 (c) K.

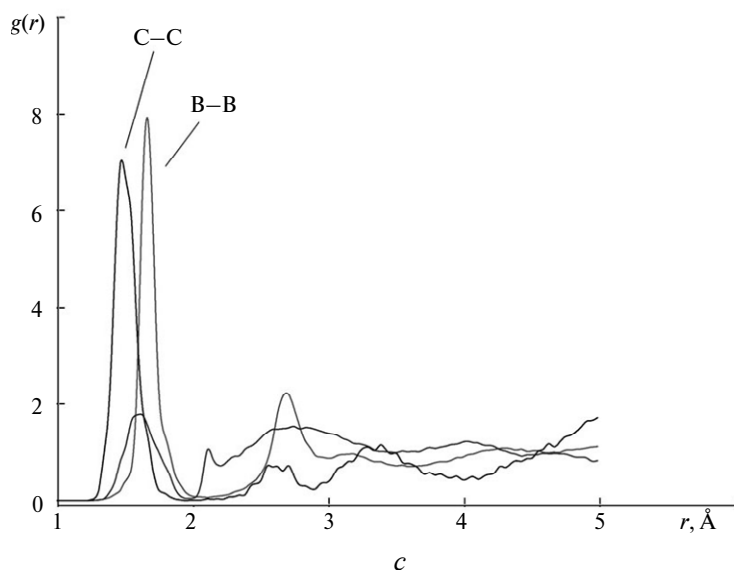


Fig. 5. (Contd.)

we suggest that with proper adjustment of the parameters they can be used to give insight into the complex structures. In the case of several thousands of atoms (as needed for very high temperature examination) possibly the Tersoff potential method is tentatively a way forward. Using the potential we also predicted thermodynamic properties such as linear thermal expansion coefficient and specific heat of the B_4C structure and compared this with experiment. It has been suggested on the basis of the Tersoff results that the structure of B icosahedra seems to be quite stable even at high temperature, whereas C atoms are more mobile and this could lead to some clustering of the C atoms.

Ікосаедрічні структури бору є основними будівельними конструкціями багатьох важливих твердих боридів і особливо це стосується B_4C . Досліджено структурні та термодинамічні властивості B_4C при застосуванні моделювання динаміки молекул з використанням як ab initio розрахунків, так і потенціалів Терсоффа. Розглянуті різні фізичні характеристики B_4C , включаючи пружні константи, коефіцієнти теплового розширення і теплоємність.

Ключові слова: алмаз, бор, електронна структура, пружні константи, молекулярна динаміка.

Ікосаэдрические структуры бора являются основными строительными конструкциями многих важных твердых боридов и особенно это касается B_4C . Исследованы структурные и термодинамические свойства B_4C с применением моделирования динамики молекул, используя как ab initio расчеты, так и потенциалы Терсоффа. Рассмотрены различные физические характеристики B_4C , включая постоянные упругости, коэффициенты теплового расширения и теплоемкость.

Ключевые слова: алмаз, бор, электронная структура, постоянные упругости, динамика молекул.

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