

## First-principles calculations of thermodynamic properties of superhard orthorhombic $\beta$ -BC<sub>2</sub>N

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**Abstract.** We investigate the thermodynamic properties of the potential superhard orthorhombic structure boron-carbonitride  $\beta$ -BC<sub>2</sub>N by using *ab initio* plane-wave pseudopotential density functional theory method within both local density approximation (LDA) and generalized gradient approximation (GGA). The lattice parameters ( $a$ ,  $b$  and  $c$ ), equilibrium volume  $V$ , bulk modulus  $B_0$  and its pressure derivative  $B_0'$  have been calculated, and compared with those of diamond and cubic boron nitride (c-BN). The obtained results are in excellent agreement with the available experimental data and other theoretical results. Through the quasi-harmonic Debye model, we also investigate the thermodynamic properties of  $\beta$ -BC<sub>2</sub>N. The variation of the thermal expansion  $\alpha$ , the heat capacity  $C_V$  and the Grüneisen parameter  $\gamma$  with pressure  $P$  and temperature  $T$ , as well as the pressure-normalized volume ( $P$ - $V_n$ ) and the pressure-bulk modulus ( $P$ - $B$ ) relationship of  $\beta$ -BC<sub>2</sub>N are obtained systematically.

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**Key words:** density functional theory, thermodynamic properties, BC<sub>2</sub>N

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## 1 Introduction

Superhard materials are of important in modern high-pressure science and technology due to their outstanding properties, such as ultra-incompressible, high elastic modulus and hardness, scratch resistance, and so on. It is well-known that diamond and cubic boron nitride (c-BN) are considered to rank first and second among the known superhard materials, respectively. By mixing diamond with c-BN, one may create a new pseudo-diamond BC<sub>2</sub>N alloy compound, which is harder than c-BN. Such a kind of alloys are expected to be thermally and chemically more stable than diamond and harder than c-BN.

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The ternary boron-carbonitride systems, which are isoelectronic with diamond and c-BN, have been attracted more attention because the theoretical prediction that  $\beta$ - $C_3N_4$  compound should have a hardness comparable to diamond [1]. However, most of the synthesized B-C-N compounds have the turbostratic or amorphous structures so far. A majority of the previous experimental studies on this topic originated from the isoelectronic carbon and c-BN viewed should have the similar crystal structures to diamond and c-BN. The theoretically studied structures are all focus on high dense phases, such as cubic  $BC_2N$  [2–9], hexagonal  $BC_2N$  [10–14], and chalcopyrite  $BC_2N$  [15].

The ternary B-C-N compound,  $BC_2N$ , as a new ultra-hard material also known as diamond and c-BN, has an orthorhombic crystal structure belongs to space group  $Pmm2$ . Therefore, it likely supersede the expensive diamond in various potential applications. Recently, the lattice dynamics and thermodynamics of orthorhombic  $\beta$ - $BC_2N$  have been investigated by Cheng *et al.* [16]. To our knowledge, there are no report on the thermodynamic properties of orthorhombic  $\beta$ - $BC_2N$  under high pressure and temperature.

In this work, we investigate the structure and thermodynamic properties of  $\beta$ - $BC_2N$  through the Cambridge Serial Total Energy Package (CASTEP) program [17, 18] and the quasi-harmonic Debye model [19]. The results obtained are well consistent with the available experimental data and other theoretical results. The paper is organized as follows: In Section 2, we make a brief review of the theoretical method. The results and some discussion are presented in Section 3. Finally, the conclusions derived from our calculations are summarized in Section 4.

## 2 Theoretical method

### 2.1 Total energy electronic structure calculations

In our electronic structure calculations, we adopt the non-local ultrasoft pseudopotential (USPP) introduced by Vanderbilt [20] for the interactions of the electrons with the ion cores. The exchange and correlation terms are described by both the local density approximation (LDA-CAPZ) proposed by Vosko *et al.* [21] and the generalized gradient approximation (GGA-PBE) proposed by Perdew *et al.* [22]. The electronic wave functions are expanded in a plane wave basis set with energy cut-off of 550 eV. Pseudo-atom calculations are performed for B ( $2s^22p^1$ ), C ( $2s^22p^2$ ) and N ( $2s^22p^3$ ). For the Brillouin-zone  $k$ -point sampling, we use the Monkhorst-Pack mesh with  $10 \times 10 \times 7$   $k$ -points for both LDA and GGA calculations, where the self-consistent convergence of the total energy is  $5.0 \times 10^{-7}$  eV/atom. These parameters are sufficient in leading to well converged total energy and geometrical configurations. All total energy electronic structure calculations are implemented through the CASTEP code [17, 18].

## 2.2 Quasi-harmonic Debye model

To investigate the temperature and pressure dependences of thermodynamic properties of a crystal, the quasi-harmonic Debye model is applied, in which the phononic effect is considered. This model is described in detail in Ref. [19]. In the following, we make a brief description for this model.

In the quasi-harmonic Debye model, the non-equilibrium Gibbs function  $G^*(V;P,T)$  is taken in the form of

$$G^*(V;P,T) = E(V) + PV + A_{Vib}(\Theta(V);T), \quad (1)$$

where  $E(V)$  is the total energy,  $PV$  corresponds to the constant hydrostatic pressure condition, the vibrational contribution  $A_{Vib}$  can be written as [23, 24]

$$A_{Vib}(\Theta;T) = nk_B T \left[ \frac{9}{8} \frac{\Theta}{T} + 3 \ln(1 - e^{-\Theta/T}) - D(\Theta/T) \right], \quad (2)$$

where  $n$  is the number of atoms per formula unit, and  $D(\Theta/T)$  represents the Debye integral. For an isotropic solid, the Debye temperature  $\Theta$  is expressed by [23]

$$\Theta_D = \frac{\hbar}{k_B} [6\pi^2 V^{1/2} n]^{1/3} f(\sigma) \sqrt{\frac{B_S}{M}}, \quad (3)$$

where  $M$  is the molecular mass per unit cell,  $B_S$  is the adiabatic bulk modulus, and  $f(\sigma)$  is given by

$$f(v) = \left\{ 3 \left[ 2 \left( \frac{2(1+v)}{3(1-2v)} \right)^{3/2} + \left( \frac{1+v}{3(1-v)} \right)^{3/2} \right]^{-1} \right\}^{1/3}. \quad (4)$$

By solving the following equation with respect to  $V$

$$\left( \frac{\partial G^*(V;P,T)}{\partial V} \right)_{P,T} = 0, \quad (5)$$

one can obtain the isothermal bulk modulus  $B_T$ , the heat capacity  $C_V$ , and the thermal expansion coefficient  $\alpha$

$$B_T(P,T) = V \left( \frac{\partial^2 G^*(V;P,T)}{\partial V^2} \right)_{P,T}, \quad (6)$$

$$C_V = 3nk_B \left[ 4D(\Theta/T) - \frac{3\Theta/T}{e^{\Theta/T} - 1} \right], \quad (7)$$

$$\alpha = \frac{\gamma C_V}{B_T V}, \quad (8)$$

where  $\gamma$  is the Grüneisen parameter, which is defined as

$$\gamma = -\frac{d \ln \Theta(V)}{d \ln V}. \quad (9)$$

Through the quasi-harmonic Debye model, one could calculate the thermodynamic quantities of orthorhombic structure  $\beta$ -BC<sub>2</sub>N at any pressures and temperatures.

### 3 Results and discussion

#### 3.1 Structure and equation of state of $\beta$ -BC<sub>2</sub>N

For the  $\beta$ -BC<sub>2</sub>N compound with very low symmetry, we determine the static equilibrium lattice structure by seeking for the minimum total energy value of the crystal. The most stable ground state structure of  $\beta$ -BC<sub>2</sub>N is investigated by the total energy electronic structure calculations over a wide range of primitive cell volumes  $V$  from  $0.89V_0$  to  $1.12V_0$ , where  $V_0$  is the zero pressure equilibrium primitive cell volume. The detailed calculated procedures as follows: in the first step, for a given  $b$ , we fix the axial ratio  $c/a$ , and take a series of different lattice values  $a$  and  $c$  to calculate the total energies  $E$ . No constraints are imposed on the  $c/a$  ratio, that is, both lattice parameters  $a$  and  $c$  are optimized simultaneously. In the second step, this procedure is repeated over a wide range of ratio  $c/a$ . By obtaining the minimum total energy  $E$  for each fixed axial ratio  $c/a$ , the minimum total energy  $E$  is obtained for the given  $b$ . In the third step, we repeat the above two procedures for different  $b$ , and then find the minimum total energy  $E$  for each  $b$ . By fitting the  $E$ - $b$  data to a third-order polynomial, we obtained the minimum total energy of the  $\beta$ -BC<sub>2</sub>N. Meanwhile, the axial ratio  $c/a$  with minimum total energy is also obtained. The resulting equilibrium volumes  $V_0$  are 22.79 and 23.63 Å<sup>3</sup> with LDA and GGA, respectively, which is in agreement with the calculated volumes by Mattesini *et al.* [25] and Sun *et al.* [15,26]

The calculated equilibrium structure parameters  $a$ ,  $b$  and  $c$ , equilibrium volume  $V$ , bulk modulus  $B_0$  and its pressure derivative  $B_0'$  for  $\beta$ -BC<sub>2</sub>N with both LDA and GGA at  $P=0$  GPa and  $T=0$  K are listed in Table 1, in which the data of diamond and  $c$ -BN are also shown for comparison. It is not difficult found that our results are excellent agreement with the available experimental values and other theoretical results. Moreover, from the ground-state equilibrium structure parameters we can found that the calculated results with the LDA is much better than GGA, so in the following calculations, we all adopt the GGA exchange and correlation function.

From Table 1, we can see that the-zero pressure equilibrium volume, bulk modulus and its pressure derivative are also determined by fitting the calculated total energy-volume data to Birch-Murnaghan equation of state (EOS) [31]

$$P = 2B_0 \left( \frac{V_0}{V} \right) f_N \left[ 1 + \frac{3}{2}(B' - 2)f_N + \frac{3}{2} \left( 1 + B_0 B'' + (B' - 2) + (B' - 2)^2 \right) f_N^2 \right], \quad (10)$$

Table 1: Lattice parameters  $a$ ,  $b$ ,  $c$  (Å), equilibrium volume  $V$  (Å<sup>3</sup>), bulk modulus  $B_0$  (GPa) and its pressure derivative  $B'$  (GPa) for the  $\beta$ -BC<sub>2</sub>N as well as diamond and  $c$ -BN at 0 GPa and 0 K

	$a$	$b$	$c$	$V$	$B_0$	$B_0'$
$\beta$ -BC <sub>2</sub> N						
LDA(present)	2.5285	2.5024	3.5905	22.79	403.12	3.54
GGA(present)	2.5591	2.5338	3.6339	23.63	374.08	
Ref.[15]	2.536	2.510	3.605	22.95	383.2	
Ref.[25]	2.5280	2.5024	3.5871	22.69	408.95	3.54
Ref.[26]	2.556	2.528	3.631	23.46		
Diamond						
Ref.[27]	3.5707				442.8	3.43
Exp.[28]	3.567				443	3.67
$c$ -BN						
Ref.[29]	3.582					
Exp.[30]	3.616				369-382	4.0-4.5

where  $f_N = \ln(l/l_0)$  which may be written as  $f_N = \ln(V/V_0)/3$  for hydrostatic compression. The bulk modulus  $B_0$  is a factor to indicate the resistance to volume change due to the external pressure. The calculated bulk modulus  $B_0$  of  $\beta$ -BC<sub>2</sub>N is 403.12 GPa and 374.08 GPa within LDA and GGA levels, respectively, which is between diamond and  $c$ -BN, and in excellent agreement with those in Refs. [15,25]. It indicates that the lattice is more difficult to compress than  $c$ -BN near their respective equilibrium volumes.

The pressure  $P$  versus the normalized volume  $V_n (= V/V_0)$ , where  $V_0$  is the equilibrium volume at zero pressure) are also obtained through the following thermodynamic relationship

$$P = -\frac{dE}{dV} = \frac{B_0}{B_0'} [V_n^{-B_0'} - 1]. \quad (11)$$

The pressure  $P$  versus the normalized volume  $V/V_0$  are illustrated in Fig.1. Notice that, as the pressure  $P$  increases, the relative volume  $V/V_0$  are all decreases for  $\beta$ -BC<sub>2</sub>N, diamond and  $c$ -BN, and the normalized volume  $V/V_0$  of  $\beta$ -BC<sub>2</sub>N is less than diamond and more than  $c$ -BN at the same pressure. In Fig. 2, we illustrate the relations of the bulk modulus  $B$  as a function of pressure  $P$  up to 100 GPa at the temperatures  $T = 0$  K for  $\beta$ -BC<sub>2</sub>N, diamond and  $c$ -BN. It is shown from Fig. 2, the relationships between bulk modulus  $B$  and pressure  $P$  are nearly linear at  $T = 0$  K and increases with the elevated pressure  $P$ .

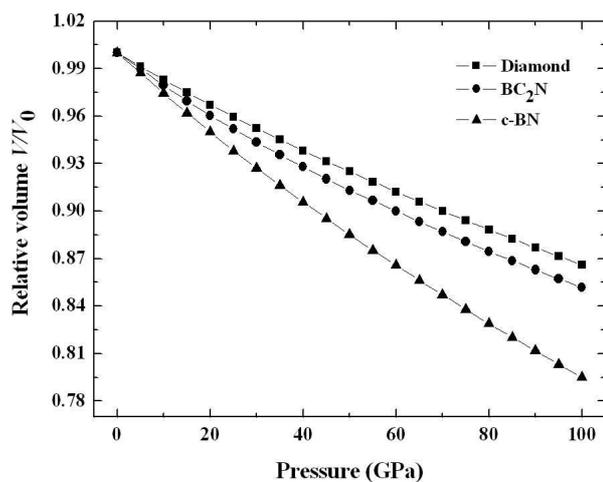


Figure 1: Calculated relative volume as a function of pressure for diamond, c-BN and  $\beta$ - $BC_2N$ .

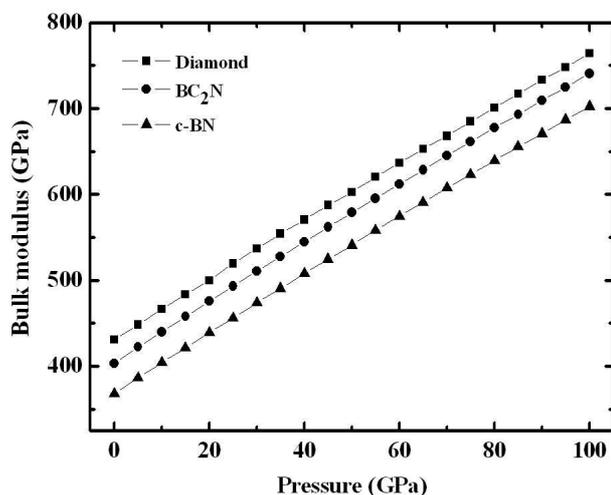


Figure 2: Calculated bulk modulus as a function of the pressure for diamond, c-BN and  $\beta$ - $BC_2N$ .

Therefore, Fig.1 and Fig.2 have similar relationships, that is, the bulk modulus value of  $\beta$ - $BC_2N$  is between the diamond and c-BN.

### 3.2 Thermodynamic properties of $\beta$ - $BC_2N$

Applying the quasi-harmonic Debye model to  $\beta$ - $BC_2N$ , we calculate the lattice heat capacity  $C_V$ , Debye temperature  $\Theta$  and the Grüneisen parameter  $\gamma$  of  $\beta$ - $BC_2N$  at different temperatures (0 K, 300 K, 600 K, 900 K, 1200 K) and different pressures (0 GPa, 20 GPa, 40 GPa, 60 GPa, 80 GPa, 100 GPa). All calculated results are listed in Table 2. The Debye temperature is an important fundamental parameter and closely related to many physi-

Table 2: Heat capacity  $C_V$  ( $\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$ ), Debye temperature  $\Theta$  (K), and Grüneisen constant  $\gamma$  of orthorhombic  $\beta$ - $\text{BC}_2\text{N}$  under temperatures  $T$  (K) and pressures  $P$  (GPa)

$T$	Parameters	$P$					
		0	20	40	60	80	100
0	$C_V$	0	0	0	0	0	0
	$\Theta$	1745.4	1865.7	1949.0	2010.7	2058.1	2095.0
	$\gamma$	2.028	1.488	1.154	0.920	0.743	0.602
300	$C_V$	28.23	24.68	22.49	21.01	19.94	19.15
	$\Theta$	1742.7	1864.4	1948.3	2010.4	2057.9	2094.8
	$\gamma$	2.041	1.493	1.157	0.921	0.744	0.603
600	$C_V$	68.21	64.57	62.16	60.42	59.11	58.10
	$\Theta$	1724.7	1856.2	1943.9	2007.9	2056.4	2093.8
	$\gamma$	2.130	1.527	1.174	0.931	0.749	0.607
900	$C_V$	84.17	81.65	80.02	78.84	77.95	77.27
	$\Theta$	1690.9	1841.8	1936.3	2003.5	2053.7	2092.0
	$\gamma$	2.304	1.588	1.204	0.947	0.759	0.614
1200	$C_V$	91.08	89.15	88.01	87.21	86.60	86.14
	$\Theta$	1636.0	1822.9	1926.5	1998.0	2050.3	2089.8
	$\gamma$	2.606	1.670	1.242	0.968	0.772	0.622

cal properties of solids, such as specific heat and melting temperature. As is well known to all, when below Debye temperature, quantum mechanical effects are very important in understanding the thermodynamic properties, while above Debye temperature quantum effects can be neglected. In this work, we obtained the Debye temperature  $\Theta_D = 1745$  K at  $P = 0$  GPa and  $T = 0$  K, consistent with the theoretical values 1700 K, as reported by Cheng *et al.* [16].

It is seen from Table 2 that, when the applied pressure is from 0 GPa to 100 GPa, the heat capacity decreases by 0.0%, 32.16%, 14.82%, 8.20%, 5.42% and the Debye temperature increases by 20.03%, 20.20%, 21.40%, 23.72%, 27.74% at 0 K, 300 K, 600 K, 900 K and 1200 K, respectively. As the pressure increases, the heat capacity decreases more quickly at low temperature than at high temperature except at 0 K. However, the Debye temperatures  $\Theta$  increase more quickly at high temperature than at low temperature.

Grüneisen constant  $\gamma$  describes the anharmonic effects in the vibrating lattice, and it has been widely used to characterize and extrapolate the thermodynamic behavior of a material at high pressures and temperatures, such as the thermal expansion coefficient and the temperature dependence of phonon frequencies and line-widths. Moruzzi *et*

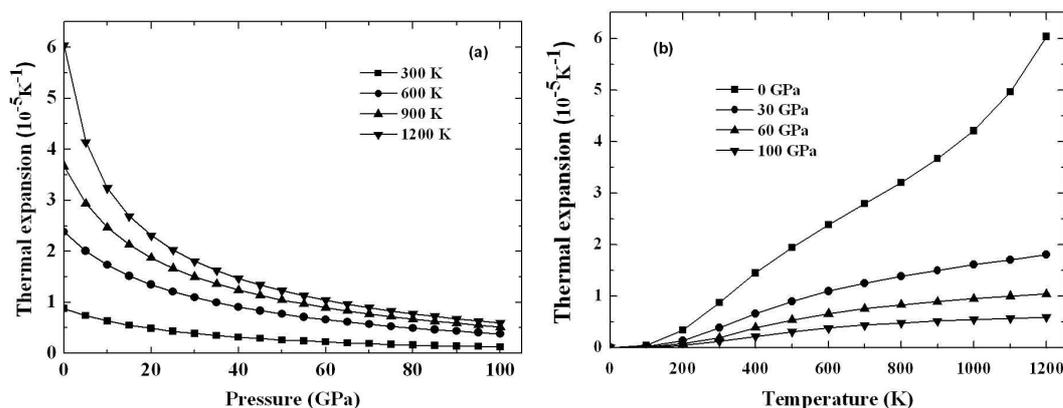


Figure 3: Calculated thermal expansion of  $\beta$ -BC<sub>2</sub>N as a function of pressure (a) and temperature (b).

*al.* [32] reviewed that the Grüneisen parameter is dominated by lower-frequency transverse modes at low temperature. The Slater's expression for  $\gamma$  assumes that equal excitation of all modes is effectively at high-temperature. In Table 2, we also list the obtained Grüneisen constant  $\gamma$ . It is noted that the Grüneisen constant  $\gamma$  decrease with increasing pressure at a given temperature, and increase with increasing temperature at a given pressure.

In Fig.3, we present the pressure and temperature dependences thermal expansion coefficient  $\alpha$  of the orthorhombic  $\beta$ -BC<sub>2</sub>N. In Fig.3 (a), we can see that, for a given temperature, the thermal expansion coefficient  $\alpha$  decreases drastically with the pressure increasing. Moreover, the higher the temperature is, the faster the thermal expansion coefficient  $\alpha$  reduces. When the pressure is above 50 GPa, the thermal expansion  $\alpha$  of 1200 K is just a little larger than that of 900 K. However, in Fig. 3 (b), the effect of the pressure  $P$  on the thermal expansion coefficient  $\alpha$  are very small at low temperature, the effect are increasingly obvious as the temperature increases. The thermal expansion coefficient  $\alpha$  increase rapidly with temperature especially at low temperature at zero pressure, and gradually approaches a linear increase at high temperatures. Finally, the increasing trend becomes gentler. This shows that the temperature dependence of expansion coefficient  $\alpha$  is very small at high pressure and high temperature. And the impact of temperature is much greater than the impact of pressure on the thermal expansion coefficient  $\alpha$  of this material. These results are in accordance with the results of the Debye theory which applies to many kinds of material.

The variation of the heat capacity at constant pressure  $C_p$  and the constant volume heat capacity  $C_v$  with temperature  $T$  and pressure  $P$  is shown in Fig. 4. From which we can see that the variation of  $C_p$  with  $T$  is similar to the thermal expansion coefficient  $\alpha$ , especially at  $P=0$  GPa. Nevertheless, the effect of the pressure is not as significant as that of the pressure on the thermal expansion coefficient  $\alpha$ . At  $T=0$  K, the difference between the constant pressure heat capacity  $C_p$  and the constant volume heat capacity  $C_v$  is almost zero, but the difference increases almost linearly with the temperature  $T$ . This cannot be

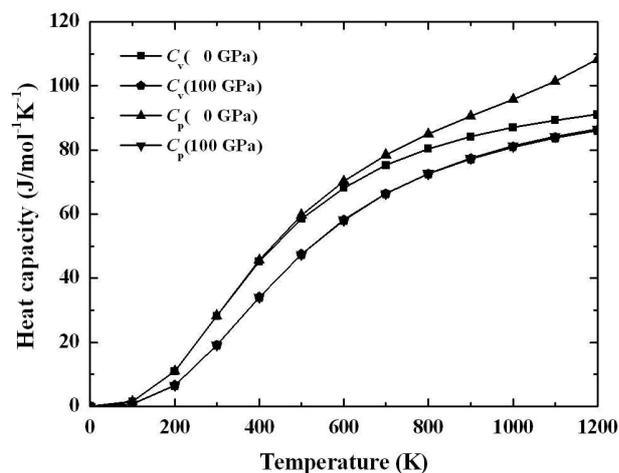


Figure 4: Variation of the heat capacity  $C_P$  and  $C_V$  with temperature under different pressures for  $\beta$ -BC<sub>2</sub>N.

ignored, especially at higher temperatures, as the temperature increase, the heat capacity at constant pressure  $C_P$  increases almost linearly with  $T$ , whereas the constant volume heat capacity  $C_V$  approaches a constant value. As the pressure increases, the difference between the constant pressure heat capacity  $C_P$  and the constant volume heat capacity  $C_V$  decreases. In addition, due to the anharmonic approximations of the Debye model used here, for higher temperatures, the anharmonic effect on  $C_V$  is suppressed, and  $C_V$  is very close to the Dulong-Petit limit, where  $N$  represents the Avogadro's constant.

## 4 Conclusions

In summary, based on the *ab initio* plane-wave pseudopotential density functional theory (DFT) and quasi-harmonic Debye model, we have investigated the structure and thermodynamic properties of the potential superhard boron-carbonitride  $\beta$ -BC<sub>2</sub>N. Some structural parameters are presented in this work. All of these results are in excellent agreement with the available experimental and other theoretical results. Finally, we have investigated the thermodynamic properties of  $\beta$ -BC<sub>2</sub>N. The vibration relations of the thermal expansion  $\alpha$ , the heat capacity  $C_V$  and the Grüneisen parameter  $\gamma$  with pressure  $P$  and temperature  $T$  are also obtained systematically.

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