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Thermodynamic and dynamical properties of cubic boron nitride from the quasi-harmonic approach

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Abstract

The thermodynamic properties of cubic zinc-blende (B3) boron nitride (BN) under high pressure of 100 GPa have been investigated using the quasi-harmonic approach. The investigated properties were : the unit cell volume, bulk modulus, Debye temperature, constant-volume heat capacity, and entropy. All these properties are detailed for temperatures ranging from 0 to 1000 K, offering a comprehensive insight into the behavior of this remarkable material under extreme conditions. Both the isothermal bulk modulus and the Debye temperature of BN semiconducting compound are conditioned by temperature: they consistently decrease with increasing temperature and rise with increasing pressure. The results obtained at standard ambient temperature are compared to other data in the literature. Upon the whole, a good agreement was obtained. Furthermore, the vibrational properties are also treated in this paper, the results confirme the stability of c-BN and the strong covalent bonding between boron and nitrogen.

The reported results in this paper will help facilitate an adequate understanding of the investigated properties of this compound. Meanwhile, it may be useful for future applications in semiconductor-based devices.

Keywords: *Thermodynamic Properties, vibrational properties, High-Pressure, Boron Nitride, Quasi-Harmonic Approach.*

1. Introduction

Boron-based semiconducting materials can be defined as compounds which belong to III-V group [1-4]. These materials have attracted a great deal of researchers' attention over the past few years. This can be rightly owing to their significant technological interest in electronic, manufacturing of optical devices, and high temperature applications [4]. Boron phosphide (BP) semiconducting material possesses specific physical properties, such as extremely high thermal conductivity, wide band-gap energy, low density and large resistivity [4]. Boron nitride (BN), renowned for its super-hard properties, is typically found in the hexagonal structure [2]. As far as we are awre, the zinc-blende phase of boron nitride(*c*-BN)binary semiconductor was synthesized in 1957 by Wentorf. [5]. Goncharov *et al.* [6] reported on thermal equation of state of cubic boron nitride, while Datchi *et al.* [7] reported x-ray diffraction on equation of state of cubic boron nitride at high-pressures and high-temperatures (up to 160 GPa at 295 K and 80 GPa in the range 500-900 K). In a parallel development, the materials BP and Bas were experimentally realized in 1958 [1]. Perri et al. [1] maintained that both boron phosphide (BP) BP and boron arsenide (BAs) crystallize in cubic zinc-blende structure. Their research also revealed that when the BP compound is heated in a phosphorus atmosphere, it remains stable at least up to 1250 °C, whereas BAs compound is stable up only to approximately 920 °C. We believe that the zinc-blende phase of boron antimonite (BSb), was synthesized in 1967 by Clougherty and Kaufman [8]. The existing literature indicates that there has been relatively inadequate focus on investigating the physical properties of boron antimonite (BSb) semiconducting compound in comparison to previous studies conducted on other materials [9-12]. Similarly, Bioud *et al.* [13] have investigated the structural stability and the thermodynamic properties of cubic BSb compound under high-pressure up to 60 GPa and high-temperature up to 1200 K using the quasi-harmonic Debye model approach.

Recently, Benmakhlouf and R. Mezouar [14] have studied the non-static contributions to the internal energy, pressure derivative of the isothermal bulk modulus, Grüneisen parameter and volumetric thermal expansion coefficient of cubic zinc-blende boron nitride (c-BN) as a function of temperature, ranging from 0 to1000 K and pressure ranging from 0 to 100 GPa using the quasi-harmonic Debye model.
In the current study, we have studied the vibrational properties of cubic zinc-blende boron nitride (*c*-BN). Furthermore, we have predicted the unit cell volume, the isothermal bulk modulus, the Debye temperature, the isochoric heat capacity as well as the entropy of boron nitride at different temperatures and pressures ranging from 0 to 100 GPa. Our findings on the thermodynamic properties of boron nitride are meticulously examined, thoroughly analyzed, and compared with existing theoretical data in the literature.

2. Computational method

In order to investigate the thermodynamic properties of cubic zincblende boron nitride compound, we drew upon the quasi-harmonic approach [15]. Our computations are conducted using the Gibbs code [16], which predicts the thermodynamic properties through the minimization of Energy-Volume (E, V) data [17]. The E-V data can be acquired from various codes [2]. For a profound explanation of the procedure adhered to for determining thermodynamic properties of materials using the quasi-harmonic approach, please consult Refs [15, 16].

To explore the vibrational properties of cubic BN, our calculations were carried out within the theory of density functional perturbation theory DFPT [18] as implemented in Quantum Espresso code [19]. The SG15 optimized norm-conserving Vanderbilt pseudopotentials (ONCV) were used, and the exchange correlation potential was treated using the generalized gradient approximation GGA [20]. The wave functions were expanded with an energy cutoff of 100 Rydberg, which is sufficient to achieve convergence with an energy threshold of 1×10-4 Ry. Integration over the Brillouin zone was performed using a 21×21×21 Monkhorst-Pack [21] mesh. First, our material was fully relaxed, and the dynamical matrices were computed with a 4×4×4 q-point mesh. Then, Fourier interpolation was used to obtain the phonon dispersion curve.

3. Results and discussions

3.1. Thermodynamical properties

The thermodynamic properties of boron nitride semiconductor in the B3 phase at temperatures ranging from 0 to 1200 K and at high pressures in the 0 to 100 GPa pressure range have been meticulously studied and analyzed. The initial phase involved the examination of the temperature and pressure dependence of the primitive unit cell V (the volume of the conventional unit cell divided by the number of sites) and the isothermal bulk modulus BT, which is expressed as follows [16] :

$$\text{ვ}_T = -V\left(\frac{\partial P}{\partial V}\right)_T \quad (1)$$

Fig.**1** displays the variations of *V* and B_T as a function of pressure at zero-temperature, 300 K, 600 K and at 1000 K. The obtained results indicate that the unit cell volume decreases progressively with increasing pressure, and the fall in unit cell volume becomes relatively more important at 1000 K than at other lowest temperatures. On the other hand, the isothermal bulk modulus B_T gradually increases with increasing pressure up to 100 GPa. These behaviors were also observed in both cubic zinc-blende BSb compound [13] as well as thallium - phosphide (TlP) compound [17].

At p = 0 and T = 0 K, the obtained value of B_T is 376.8 GPa, while at pressure of 100 GPa and temperature of 1000 K, B_T increases to the value 689.1 GPa. At p = 0 and T = 0 K, the value of B_T is in total agreement with the experimental value (369 GPa) reported by Knittle *et al.* [22].
The analytical relationships for the pressure dependence of BT (where both the pressure p and BT are expressed in GPa) have been given by the following a quadratic fits:

$$B_T = 377.6 + 3.67\,p - 3.03 \times 10^{-3}p^2 (\text{at } T = 0K) \quad (2)$$
$$B_T = 373.8 + 3.69\,p - 3.02 \times 10^{-3}p^2 (\text{at } T = 300K) \quad (3)$$
$$B_T = 361.1 + 3.68\,p - 2.57 \times 10^{-3}p^2 (\text{at } T = 600K) \quad (4)$$
$$B_T = 341.7 + 3.59\,p - 1.24 \times 10^{-3}p^2 (\text{at } T = 1000K) \quad (5)$$

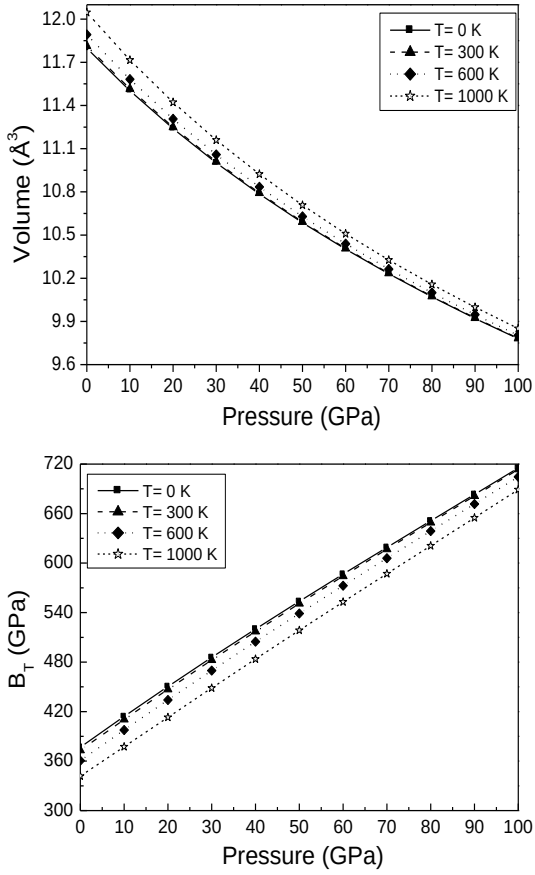


Figure 1: *Volume* of the *primitive unit cell* and the bulk modulus B_T of BN compound in B3 phase versus pressure and temperature.

In the quasi-harmonic approach, the Debye temperature (θ_D) of an isotropic solid can be expressed by the following formula [16]:

$$\theta_D = \frac{\eta}{k_B}\left[6\pi^2 V^{1/2} n\right]^{1/3} f(\delta)\sqrt{\frac{B_s}{M}} \tag{6}$$

Where M is the mass of the unit cell, BS is the adiabatic bulk modulus, and δ is the Poisson ratio.

$$f(\delta) = \left\{3\left[2\left(\frac{2}{3}\frac{1+\delta}{1-2\delta}\right)^{3/2} + \left(\frac{1}{3}\frac{1+\delta}{1-\delta}\right)^{3/2}\right]^{-1}\right\}^{1/3} \tag{7}$$

Fig. **2** illustrates the variations of the isothermal bulk modulus B_T as a function of temperature at zero pressure, as well as the Debye temperature θ_D of *c*-BN compound in relation to pressure and temperature.

The obtained results clearly demonstrate that B_T decreases with increasing temperature. Specifically, at room temperature (T = 300 K), the isothermal bulk modulus B_T takes the 373.1 GPa value, whereas at T = 1000 K, it decreases to 341.8 GPa.

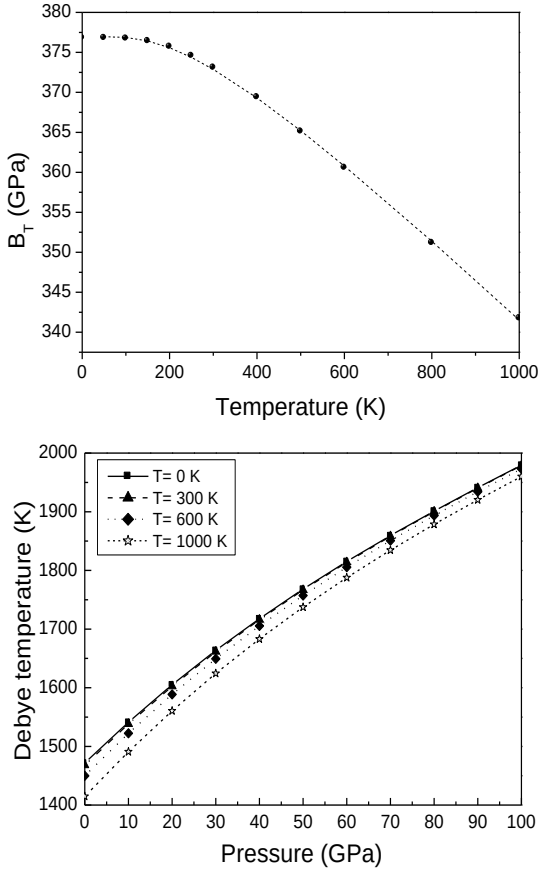


Figure 2 : Isothermal bulk modulus B_T of BN compound versus temperature at zero-pressure, and Debye temperature (θ_D)of BN versus pressure and temperature.

The temperature dependence of B_T is described by an exponential relationship, as clearly shown in the following expression [13, 23]:

$$B(T) = B_0 - bTe^{-T_0/T} \tag{8}$$

Here in, B_0 denotes the bulk modulus at absolute zero, b and T_0 are the two specific parameters of the compound.
The fitted parameters from our present results for BN compound are : 376.95 GPa, 5.343 × 10^{-2} GPa/K, and 410.92 K for B_0, b and T_0, respectively.

Based on the results presented in Figure **2**, it can be observed that the Debye temperature θ_D gradually increases with increasing pressure up to 100 GPa. This behavior is consistent with observations in cubic zinc-blende BSb compounds [13], in cubic zinc-blende thallium-phosphide (TlP) [17], in both PtThSn and NiThSn Half-Heusler ternary thermoelectric materials [23], in cubic rock-salt calcium oxide (CaO) binary compound [24] and cubic rock-salt cadmium oxide (CdO) semiconducting compound [25].

At zero-pressure and zero-temperature, we obtained value of θ_D is 1471.8 K, while at pressure of 100 GPa and temperature of 1000 K, the Debye temperature of BN compound increases to the value 1960 K. At zero-pressure and T = 300 K, the value (1468 K) of the Debye

temperature is lower than the experimental value (1613 K) reported by Adachi.[26].The relationships for the pressure dependence of θ_D have been given by the following a quadratic fits:

$$\theta_D = 1475.1 + 6.71\,p - 1.7 \times 10^{-2} p^2 (\text{at } T = 0K) \quad (9)$$
$$\theta_D = 1471.4 + 6.77\,p - 1.73 \times 10^{-2} p^2 (\text{at } T = 300K) \quad (10)$$
$$\theta_D = 1453.4 + 7\,p - 1.83 \times 10^{-2} p^2 (\text{at } T = 600K) \quad (11)$$
$$\theta_D = 1418.4 + 7.38\,p - 2 \times 10^{-2} p^2 (\text{at } T = 1000K) \quad (12)$$

The pressure *p* herein is expressed in GPa while the Debye temperature θ_D is expressed in K. The constant volume heat capacity C_V can be predicted using this expression $C_V = (\partial U / \partial T)_V$, where U is internal energy [16]. Fig. **3** shows the variations of the isochoric heat capacity C_V and entropy S as functions of temperature at different pressures for the boron nitride semiconductor.

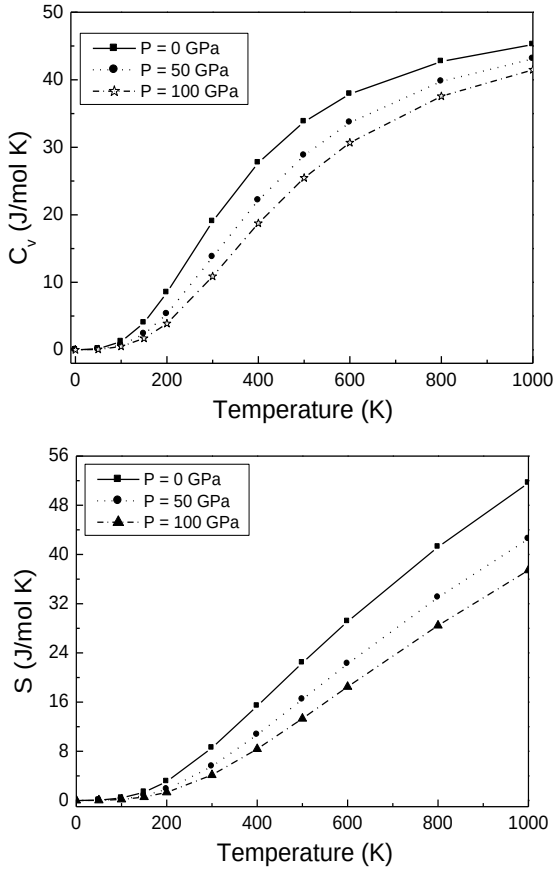


Figure 3 : Isochoric heat capacity C_V and the entropy S versus temperature at different pressures for BN

At low temperatures, C_V exhibits a clear T^3 dependence, consistent with the Debye model. As the temperature increases, C_V raises rapidly on account of enhanced anharmonic effects. It eventually approaches the classical Dulong-Petit limit at higher temperatures [13, 27]. Additionally C_V increases with temperature at a given pressure and decreases slightly with increasing pressure at a fixed temperature. These behaviors are also observed in cubic zinc-blende BSb compounds [13] and in InP, InN binaries and $InN_{0.5}P_{0.5}$ ternary alloy [27].

3.2 Dynamical properties

The phonon dispersion curve for Boron Nitride (BN) in the zincblende (ZnS) phase is given in figure 4. It depicts the vibrational frequencies of *c*-BN as a function of the wave vector (k) along high-symmetry directions in the Brillouin zone.

The phonon dispersion curve of *c*-BN provides valuable information about its lattice dynamics and vibrational properties. Plotting the dispersion relation along the high-symmetry in the Brillouin zone reveals distinct acoustic and optical branches, which are characteristic of a diatomic crystal structure.

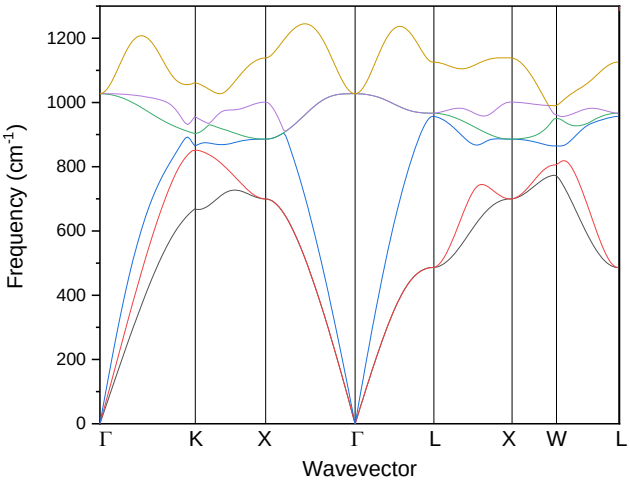


Figure 4 : Phonon dispersion curve of BN (ZnS phase)

At the Gamma point, the longitudinal (LO) and transverse (TO) optical modes are degenerate, though slight splitting may occur due to the polar nature of the B-N bonds. The optical branches appear at higher frequencies (approximately 600–1200 cm^{-1}), reflecting the strong covalent bonding between boron and nitrogen. In contrast, the acoustic branches (approximately 0–400 cm^{-1}) demonstrate the expected linear behaviour near the Γ point, which is typical of sound-wave-like atomic displacements.

Notably, the dispersion shows anisotropy in phonon group velocities, particularly along the path from the Γ point to the X point compared to the path from the Γ point to the L point, suggesting directional variations in thermal and mechanical properties. Flat regions in the optical branches near the X and L points suggest the presence of localised vibrations that could impact thermal conductivity by reducing phonon propagation efficiency.
The absence of imaginary frequencies confirms the dynamical stability of zinc-blende boron nitride (BN). A comparative study in Ref. [28] for BN, AlN and GaN exhibit approximately similar behaviour with differences in values due the method and conditions of calculation.

4. Conclusion

All in all, we have investigated the thermodynamic properties of the cubic zinc blende boron nitride semiconducting compound using the quasi-harmonic approach under high pressures up to 100 GPa and temperatures ranging from 0 to 1000 K. The findings of our undertaking

reveal that both the isothermal bulk modulus and the Debye temperature of the BN semiconducting compound decline with rising temperature and increase with escalating pressure. Conversely, the unit cell volume, constant-volume heat capacity and entropy exhibit an increase with temperature and a decrease with pressure. This demonstrates that temperature and pressure exert opposing effects on the thermodynamic properties of boron nitride. Although, the phonon diagram indicates that *c*-BN is a stable dynamic material with a rigid crystalline structure with strong covalent bonds, and distinct polar optical modes. These characteristics make *c*-BN a promising candidate for use in thermal insulation materials, electronic substrates or protective films.

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