Heat Capacity of BN and GaN binary semiconductor under high Pressure-Temperature (PT) from First-principles

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Abstract: *In this paper, we have calculated the molar heat capacity for cubic zinc blende (cZB) BN and GaN binary semiconductors at high pressure-temperature (PT). For the calculation of heat capacity, we firstly obtained the Debye temperature (Θ_D) variation with temperature and at higher temperature it becomes constant with temperature in quasi-harmonic approximation limits. We have also calculated the static Debye temperature (Θ_D) from elastic constant for the both BN and GaN binary semiconductors. The elastic constants are calculated from the energy-strain relation using plane wave method in DFT approach. All the calculated results are well consistence with experimental and reported data.*
Keywords: *Debye temperature, DFT, LDA, PDOS, QHA, USPP etc.*

I. INTRODUCTION

The III-V group of nitrides have attracted due to their potential applications in the fields of optoelectronic such as wide band gap, light sources, super hardness properties, uses at high temperature and pressure, high density data storage capacity and high power conversion efficiency[1-2]. The hardest natural materials we have ever known as diamond. Cubic boron nitride (cBN) is a second promising hardest material that contains many important physical and chemical properties in high temperature-pressure range after diamond. cBN has been utilized in many industrial applications as cutting tools and abrasives[3]. The binary compound cBN and cGaN crystallizes in a zinc blend structure which closely resembles that of diamond, each atom being tetragonally linked to four neighboring boron or nitrogen atoms by strong covalent bonds. Charge accumulates strongly between the atoms due to the strong interatomic interaction of s and p orbital's. Moreover, because of its wide band gap and good thermal conductivity, cBN and cGaN also has the potential application for the high-temperature, high-power electronic applications and utilized from visible spectrum to the ultraviolet spectrum by varying its wide bandgap[4-5]. These two are also very prominent binary compounds for extreme condition as high pressure-temperature. Therefore, experimental and theoretical investigations are of a great interest to physicists and researchers community. Earlier work [6-8] explored more information with improved accuracy about the characteristics of cBN and cGaN. It was found that cBN and cGaN were thermodynamically stable at ambient environment but still the structural phase and its thermodynamic stability of cBN and cGaN under high temperature -pressure remain uncertain.

In the present work, we investigate the heat capacity at high PT of cBN and cGaN by using a first-principles plane wave method in the frame of quasi-harmonic approximation with local density approximation (LDA). We have also calculated the elastic constants from which other thermal and mechanical properties like Debye temperature (Θ_D) and bulk modulus (B_0) have been calculated. We have also proposed a mathematical model for calculation of heat capacity approximating that Debye temperature is varying with temperature. The results obtained are in good agreement with the available experimental results and other reported theoretical methods.

II. COMPUTATIONAL METHODS

First principles total energy calculations were performed using quantum-espresso code [9]. The interaction between ions and valence electrons were described by the USPP method [10] for the both binary semiconductor. The exchange and correlation effects were treated by the local density approximation of Perdew and Zunger[11]. The k mesh was sampled according to a Monkhorst-Pack scheme as 4 4 4 with a spacing of 0.5 / Å [12].The electronic configurations for B, Ga and N are $[He]2s^2 2p^1$, $[Ar]3d^{10}4s^2 4p^1$ and $[He]2s^2 2p^3$ respectively. The valence electrons are taken as 3, 13 and 5 respectively for B, Ga and N. The $3d^{10}$ electrons have taken in valence because to see the non localized effect of d shell in Ga atom. The energy cutoff in the plane wave expansion was 65Ry and cutoff for charge density was 720 Ry for the both cBN and cGaN. Convergence of relative energies with respect to the k mesh and energy cutoff was found to be better than 1 meV/atom. The cutoff of plane wave expansion is taken as high due to hard pseudo-potential of N atom. The equation of states (EOS) is used to determine equilibrium lattice parameter for cBN and cGaN. Debye

temperature and heat capacity at equilibrium lattice parameter have calculated in the frame of quasi-harmonic approximation (QHA) by fitting the thermal EOS.

III.   RESULTS AND DISCUSSION

3.1 Structural properties

To calculate the structural properties we take the local density approximation (LDA) pseudo-potential for the cBN and cGaN in zinc-blend structure. The graph between total energy verses lattice parameter are plotted for cBN and cGaN in Figure 1. The calculated equilibrium lattice parameters are 3.582Å and 4.467Å for cBN and cGaN respectively from Figure 1. The calculated equilibrium lattice parameters are underestimated due to inherent property of LDA. The obtained equilibrium lattice parameter results are compared with available experimental and reported data given in Table 1. The lattice parameter in terms of volume verses pressure is calculated for two different ambient temperatures 0K and 1500K for cBN and cGaN shown in Figure 2. Figure 2 is showing that at higher pressure volumes are very less deviates from each other regardless of any temperatures range for the case of cBN but shows much deviation for cGaN as the pressure increased also the temperature will play a major role in variation of volumes verses temperature. The general behavior of volume verses pressure is decreasing in nature as pressure increased also shown in Figure 2. We have also calculated the volume variations with respect to wide temperature range at two different extreme pressures (0GPa, 150GPa) for cBN and (0GPa, 50GPa) for cGaN. From the obtained results, it is observed that volume varies with respect to temperature significantly at low pressure but very less varying at higher pressure which is true for both cBN and cGaN. The simulated results have been shown in Figure 3.

3.2 Debye temperature (Θ_D) calculation using Elastic constants

The Debye temperature can be calculated using Elastic constants [13] whereas elastic constants are calculated at equilibrium (P=0, T=0) lattice parameter for cBN and cGaN. The stiffness constants are defined as

$$C_{ij} \equiv c_{\alpha\beta\gamma\delta} = \frac{1}{V_0}\frac{\partial^2 E_{total}}{\partial \varepsilon_{\alpha\beta}\partial\varepsilon_{\gamma\delta}}$$
(1)

where $U=E_{total}/V_0$ is the total energy per unit volume. $\sigma_{\alpha\beta}$ and $\varepsilon_{\alpha\beta}$ (α, β = x,y,z) are the components of the stress and strain tensors respectively. Due to the symmetry of cubic crystals, the stiffness constants using Voigt indices' are C_{11}, C_{12} and C_{44} [14]. For the calculation of the stiffness constant, we used the periodic DFT method to calculate the energies of cBN and cGaN crystals for the applied strain. We applied three independent strains 0, ±0.015, ±0.010, ±0.005 and fitted the stiffness constants to the energy-strain relation $U = \frac{1}{2}C_{11}\varepsilon_{xx}^2$, $U = (C_{11} + C_{12})\varepsilon_{xx}^2$ and $U = 2C_{44}\varepsilon_{yz}^2$ for the calculation of C_{11}, C_{12} and C_{44} respectively. The Total energy $E_{total}(\varepsilon)$ were fitted to polynomial equation

$$E_{total}(\varepsilon) = V_0U(\varepsilon) = A_0 + A_1\varepsilon + A_2\varepsilon^2 + A_3\varepsilon^3$$
(2)

where A_0, A_1, A_2 and A_3 are the fitting parameters. A_1 corrects inaccuracies in the variable cell optimization and A_3 corrects for anharmonic terms [15]. The 3rd term A_2 is the important for calculation of stiffness constants which is related by A_2/V_0 is equal to $C_{11}/2$ for strain ε_{xx}, $(C_{11}+C_{12})$ for strain $\varepsilon_{xx}=\varepsilon_{yy}$ and $2C_{44}$ for strain ε_{yz}. The calculated stiffness constants are given in Table 1. The obtained values of stiffness constants are in good agreement for cBN cGaN with the reported and available experimental data. The results shows overestimation of stiffness constants for cBN and cGaN from the experimental values. The Debye temperature, Θ_D, defined as a measure of the cutoff frequency by $\theta_D = \hbar\omega_D/k_B$, is then proportional to the Debye sound velocity υ_D:

$$\theta_D = \frac{\hbar}{k_B}\left(\frac{6\pi^2 N}{V}\right)^{1/3}\upsilon_D$$
(3)

And

$$\upsilon_D = k(\nu)\sqrt{\frac{B}{\rho}}$$
(4)

The bulk modulus B and Poisson ratio ν of a polycrystalline material is estimated from the single crystal elastic constants by the Voigt–Reuss–Hill (VRH) approximation [16].

Θ_D and $k(\nu)$ can be given in more usable format in terms of atomic weight M and Poisson ratio ν as:

$$\theta_D = k(\nu)\frac{\hbar}{k_B}\left(\frac{6\pi^2\rho}{M}\right)^{1/3}\sqrt{\frac{B}{\rho}}$$
(5)

And

$$k(\nu) = \left[\frac{1}{3}\left[\left[\frac{1+\nu}{3(1-\nu)}\right]^{3/2} + 2\left[\frac{2(1+\nu)}{3(1-2\nu)}\right]^{3/2}\right]\right]^{-1/3}$$
(6)

Θ_D can be further rewritten as:

$$\theta_D = k(\nu)\frac{\hbar}{k_B}(48\pi^5)^{1/6}\sqrt{\frac{r_0 B}{M}}$$
(7)

In this expression, r_0 is the equilibrium Wigner–Seitz radius, which is defined by $4\pi r_0^3/3 = V/N = M/\rho$. Where V is the equilibrium volume, N is the number of atoms per unit cell. The Debye temperature (Θ_D) obtained from the elastic constants using Eq. (7) are compared with the calculated value of Θ_D in frame of quasi-harmonic approximation (QHA) at equilibrium (T=0, P=0) are given in Table 1 and also compared with the available experimental value which are in good agreement with some allowable error. The Debye temperatures vary between 1540 K (expanded BN) and 1740 K (compressed BN) for cBN [17] and 867 for cGaN[26]. These calculated values are deviated from the experimental values of due to error in bulk modulus which is varying from 2% to 10% from their experimental value.

3.3 Debye temperature (ƟD) variation with temperature and heat capacity in quasi-harmonic approximation (QHA)

Quantum mechanical effects are very important in understanding the thermodynamic properties below the Debye temperature. The Debye temperature variation with respect to temperature below its melting temperature is also shown in Figure 4 at the equilibrium (T=0, P=0) lattice constant for cBN and cGaN in quasi-harmonic approximation. Heat capacity at constant volume C_V can be calculated directly from the phonon DOS under the harmonic approximation. Heat capacity at constant volume under the Debye approximation is expressed as

$$C_V = 9N_A k_B (T/\theta_D)^3 \int_0^{\theta_D/T} (h\nu/k_B T)^2 W(h\nu/k_B T) d\nu \tag{8}$$

where $W(h\nu/k_B T)$ is weighting factor and again Eq.(8) can be rewritten as

$$C_V = rN_A k_B \int_0^\infty g(\nu) W(h\nu/k_B T) d\nu \tag{9}$$

where $g(\nu)$ is phonon density of states (PDOS).

We have plotted the calculated total phonon DOS (PDOS) and each elemental phonon DOS in Figure 5 for cBN and in Figure 6 for cGaN at 0 K using the static equilibrium geometry obtained from the first principles. There some important observations from Figure 5 and Figure 6 are as follows: From Figure 5, Below 800 cm^{-1} frequency, equal contributions from atom B and atom N are observed in total phonon DOS of cBN and above 800 cm^{-1} frequency, B atom contributions is much larger compare to N atom in total phonon DOS of cBN. Two gaps are shown in Figure 6 around the frequency 350cm^{-1} to 530 cm^{-1} and 675cm^{-1}. Below 350cm^{-1}, the total phonon DOS are mixed vibrations of atom Ga and atom N mainly dominated by Ga atom. Above 530cm^{-1}, the total phonon DOS is mainly originated from the N atom vibrations and very small vibrations are originated from the Ga atom. The difference between C_P and C_V was given by a relationship $C_P-C_V=VT\beta^2 B_0$. V, T, β and B_0 are molar volume, absolute temperature, volume thermal expansion coefficient and isothermal bulk modulus respectively. 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. The molar heat capacity at constant pressure is shown in Figure 7 at two extreme different pressure 0GPa and 150GPa for cBN, 0GPa and 50GPa for cGaN. As the pressure increases, the heat capacity does not deviate much from the Dulong-Petit limit. At high temperature, heat capacity will become constants due to constant value is obtained for the Debye temperature as shown in Figure 4 and if the temperature increase, the heat capacity at constant pressure C_P increases almost linearly with temperature. For higher temperatures, the anharmonic approximations of the Debye model is used here in which the anharmonic effect on C_V is suppressed, and C_V is very close to the Dulong-Petit limit to 3R, where R (8.3144621 J/mol.K) represents the molar gas constant. It is more informative to plot the heat capacity data(C_P) C_P/T^3 vs. temperature as shown in Figure 8 and according to the Debye T^3 model, the lattice vibration to C_P/T^3 should approach constant value at lower temperature. If C_P/T^3 vs. temperature deviated from constant value, it means others factors like electronics, magnetic etc have contributed in heat capacity (C_P). It is well known that the contributions due to optical phonons do not obey the Debye T^3 model. From Figure 8, it has been observed in cBN that optical phonons are less dominated compare to the cGaN in C_P/T^3 vs. temperature graph at extreme pressure.

IV. CONCLUSIONS

In summary, we have performed first-principles calculations for cBN and cGaN, including the equilibrium lattice parameters, volume variations at extreme conditions, Debye temperature variation with temperature, elastic constants, Debye temperature using elastic constant, total phonon DOS with phonon DOS of individual elements of cBN and cGaN and heat capacity. All the obtained results are well consistent with the previous experimental and reported results from others workers.

REFERENCES

[1]   I.Vurgaftman, J. R. Meyer and L. R. Ram-Mohan, JAP 89 (2001) 5815-5875.
[2]   G. Chris, Van de Walle, Jorg Neugebauer, JAP 95 (2004) 3851-3879.
[3]   Tetsuya Tohei, Akihide Kuwabara, Fumiyasu Oba, and Isao Tanaka, Phys. Rev. B 73 (2006) 064304.
[4]   Hao Yan-Jun, Cheng Yan,Wang Yan-Ju, and Chen Xiang-Rong, Chin. Phys. Soc. 16(1) (2007).

[5]   G Will and P G Perkins, Diamond Relat. Mater. 10 (2001) 2010.
[6]   E. Ĺopez-Aprezaa , J. Arriagaa , and D. Olgúınb , Rev. Mex. F´ıs, 56 (3) (2010) 183–194.
[7]   H Sachdev, R Haubner, B Lux and H Noth , Diamond Relat. Mater. 6 (1997) 286.
[8]   V L Solozhenko, J. Hard Mater. 6 (1995) 51.
[9]   P. Giannozzi et al., J. Phys.:Condens. Matter 21 (2009) 395502.
[10]   D. Vanderbilt, Phys. Rev. B 41 (1990) 7892-7895.
[11]   J. P. Perdew and A. Zunger, Phys. Rev. B 23 (1981) 5048.
[12]   H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13 (1976) 5188.
[13]   Q. Chen and B. Sundman, Acta mater. 49 (2001) 947–961.
[14]   E. Dieulesaint, D. Royer, Elastic Waves in solids. Wiley, chichester, 1980.
[15]   E. Menendez-Proupin, S. Cervantes-Rodriguez, R.Osorio-Pulgar, M. Franco-Cisterna, H.
        Camacho-Montes, M.E. Fuentes, JMBBM 4 (2011) 1011-1020.
[16]   R. Meister, and L. Peselnick, J. Appl. Phys., 37 (1966) 4121.
[17]   Won Ha Moona, Myung Sik Sonb, Ho Jung Hwanga, Physica B 336 (2003) 329–334.
[18]   U.Rössler, Group IV Elements, IV-IV and III-V Compounds,41A1 of Landolt Börnstein, Group III Condensed Matter, Springer-
        Verlag, Berlin, 2001.
[19]   Y. S. Touloukian, R. K. Kirby, R. E. Taylor, and T. Y. R. Lee, Thermal Expansion: Nonmetallic Solids, Vol. 13 of Thermophysical
        Properties of Matter IFI-Plenum, New York, 1977.
[20]   R. H. Wentorf, Jr., J. Chem. Phys. 26 (1957) 956.
[21]   P. Rodriguez-Hern!ndez, M. Gonz!lez-Diaz, A. Munoz,aa, Phys. Rev. B 51 (1995) 14705.
[22]   M. Grimsditch, E.S. Zouboulis, A. Polian, J. Appl. Phys.76 (1994) 832.
[23]   P.J. Gielisse, S.S. Mitra, J.N. Plendl, R.D. Griffis,L.C. Mansur, R. Marshall, E.A. Pascoe, Phys. Rev. 155 (1967) 1039.
[24]   G.A. Slack, S.F. Bartram, J. Appl. Phys. 46 (1975) 89.
[25]   W. Sekkal, B. Bouhafs, H. Aourag, M. Certier, J. Phys., Condens. Matter 10 (1998) 4975.
[26]   D. Gerlich, S.L.Dole and G.A. Slack, J. Phys. Chem.Solids 47 (1986) 437.
[27]   J. Petalas, S. Logothetidis, S. Boultadakis, Phys. Rev. B 52 (1995) 8082.
[28]   A. Trampert, O. Brandt, K.H. Ploog, Acad. Press, 50 1998.
[29]   S. Berrah, H. Abid, A. Boukortt, M. Sehil, Turk J Phys., 30 (2006) 513-518.
[30]   S. Q. Wang and H. Q. Ye., J. Phys., Condens. Matter,14 (2002) 9579.
[31]   Donald T. Morelli, Glen A. Slak, HTCM, (2006) 37-68.
[32]   J. Petalas, S. Logothetidis, S. Boultadakis, Phys. Rev. B 52 (1995) 8082.
[33]   D. Sedmidubsk, J. Leitner, P. Svoboda, Z. Soferand, J. Macháek , J. Thermal Analysis and Calorimetry, 95 2 (2009) 403–407.
[34]   D. Gerlich, S.L.Dole and G.A. Slack, J. Phys. Chem.Solids,47 (1986) 437.

Figure 1 Total energy (Ry) variation with lattice parameters in Bohr (a.u) are plotted for zinc-blende cBN and cGaN for obtaining the equilibrium(P=0,T=0) lattice parameters.
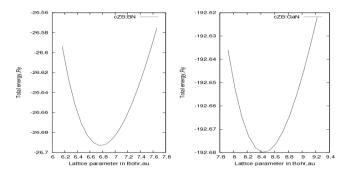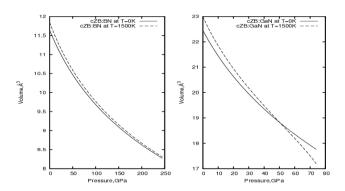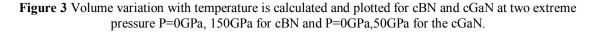

Figure 2 Volume variation with pressure is calculated and plotted for cBN and cGaN at two extreme temperature T=0K, 1500K.
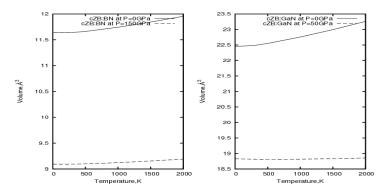
Figure 3 Volume variation with temperature is calculated and plotted for cBN and cGaN at two extreme pressure P=0GPa, 150GPa for cBN and P=0GPa,50GPa for the cGaN.

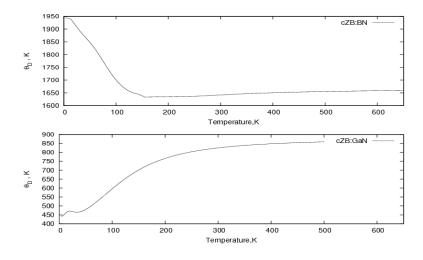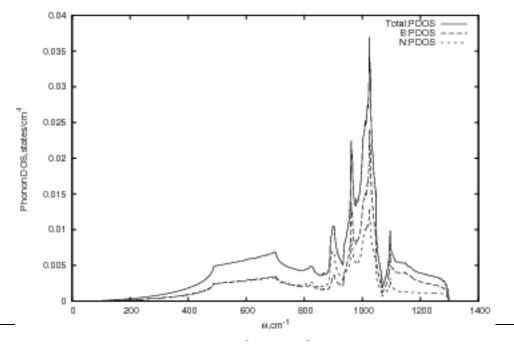**Figure 4** Debye temperature variations with temperature for cBN and cGaN at equilibrium lattice parameters.

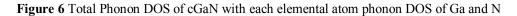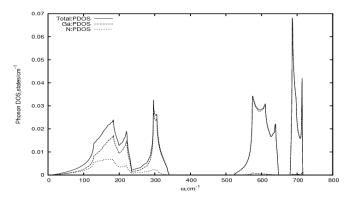**Figure 5** Total Phonon DOS of cBN with each elemental atom phonon DOS of B and N

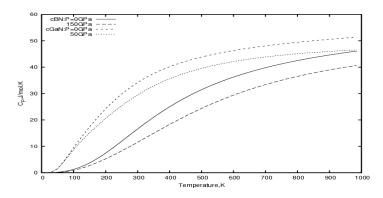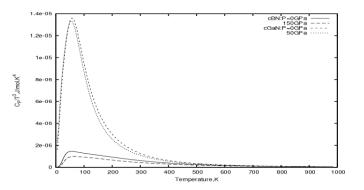**Figure 6** Total Phonon DOS of cGaN with each elemental atom phonon DOS of Ga and N

Figure 7 Heat capacity Cp at two extreme pressure P=0GPa,150GPa for cBN and P=0GPa,50GPa for cGaN are shown.

Figure 8 C_p/T^3 verse T graph at two extreme pressure P=0GPa,150GPa for cBN and P=0GPa,50GPa for cGaN are shown.

Table 1 All the calculated properties are tabulated and compare with experimental and results obtained from others workers for cBN and cGaN.

Parameters	Our Work		Others		Experimental	
	cBN	cGaN	cBN	cGaN	cBN	cGaN
a_0(Å)	3.582	4.467	3.582[a]	4.475[l], 4.335[m]	3.615[e]	4.52[k]
B_0(GPa)	390.45	196.5	391[a] at 300K	205.38[l], 207[m]	369–465[c]	190[k]
$B_0^{'}$	3.77	4.57	3.18[b],3.94[j]	4.8[l], 4.182[m]		
V_0(Å^3/atom)	5.747	22.279	5.745[a]		5.905[e]	
C_{11}(GPa)	820.39	287.84	844[f], 754[b]		820[g]	

C_{12}(GPa)	192.853	158.67	190[f], 179[b]	190[g]
C_{44}(GPa)	475.013	160.07	480[f], 433[b]	480[g]
B_0(GPa) (C_{ij})	402.032	201.73	377[b]	
Poisson's ratio(v)	0.12486	0.26738		
v_R	0.13063	0.28621		
v_V	0.11909	0.24855		
Θ_D(K)	1530.46	496.38		390[n]
Θ_D(K) QHA	1665.33	833.09	1710[b]	823[p],600-800[o],867[q] 1700[h]

[a]Reference[1]   [b]Reference[17]   [c]Reference[18]
[d]Reference[19]   [e]Reference[20]   [f]Reference[21]
[g]Reference[22]   [h]Reference[23]   [i]Reference[24]
[j]Reference[25]   [k]Reference[28]   [l]Reference[29]
[m]Reference[30]   [n]Reference[31]   [0]Reference[32]
[p]Reference[33]   [q]Reference[34]