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Pressure dependent ultrasonic characterization of nano-structured w-BN

Chandreshvar Prasad Yadav*, Dharmendra Kumar Pandey

Department of Physics, P.P.N. (P.G.) College, Kanpur 208 001, India

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ABSTRACT

The work includes evaluation of elastic constants of wurtzite Boron nitride (w-BN) at different particle-size (5–40 nm) and pressure (0–60 GPa) at 300 K using potential model approach. Size and pressure dependent thermo-physical and ultrasonic parameters are also calculated using evaluated elastic constants. It is found that the elastic constants, ultrasonic velocities and Debye temperature of nanostructured w-BN enhance with increase in pressure and reduction in particle size. The size variation of thermal relaxation time resembles the dependency of thermal conductivity with size. The thermal conductivity of nanostructured w-BN is found to increase with reduction in nanoparticle size.

1. Introduction

Boron nitride is low porosity white solid ceramic material that may possess different types of crystal structures (cubic boron nitride (c-BN), hexagonal boron nitride (h-BN), rhombohedral (r-BN), turbostratic boron nitride (t-BN) and wurtzite boron nitride (w-BN)) depending upon the arrangement of boron and nitrogen atoms. The h-BN is the stable phase under ambient conditions while c-BN and w-BN were synthesized from h-BN at high temperature and high pressure [1,2]. The w-BN phase is metastable phase in nature. The keen interest for the study of this material is due to its technological features like extreme hardness, high melting point, interesting dielectric and thermal behaviour. Several works on structural, mechanical, electronic and acoustical properties of BN were done using first-principles calculations, X-ray diffraction, pseudo-potential, DFT methods [3–8]. Thermal properties of h-BN, c-BN, t-BN, r-BN and its composites were reported elsewhere [1,2,9,10]. This material has important applications in electronics as an insulator, substrate for semi-conductors, coating for refractory molds, fabrication of nanotransistors, robust nanocomposites, conducting polymers, storage components and field emission sources [11]. Being ceramic material, it has also application in the field of cosmetics [12]. Since reduction in particle size causes enhancement in effective surface area thus size dependent study of BN are useful in encapsulating cosmetics actives.

Very few works on pressure and size dependent structural and thermo-physical of nanostructured w-BN were reported in literature [12–17]. The experimental study of thermal conductivity of different nanostructures of boron nitrides are reported in literature [18]. Both the pressure and size affect the thermo-physical properties of the material. Thus the essential characteristics of boron nitride under influence of different pressure and size are required to enhance its applicability at room temperature. Therefore the present study is focused on elastic, thermal and ultrasonic characterization of nanostructured w-BN as the function of pressure. The present work incorporates theoretical evaluation of elastic, thermo-physical and ultrasonic properties of nanostructured w-BN as function of pressure (0–60 GPa) and nanoparticles size (5–40 nm) at 300 K.

1.1. Theory of elastic constants

The higher order elastic constants of wurtzite structured materials are the function of lattice parameters (a and c) under the potential model approach of evaluation [19,20]. The second order elastic constants can be determined with the following expressions [20].

$$\left.\begin{array}{l} C_{11} = 24.1\ \mathrm{p}^4 C' \quad C_{12} = 5.918\ \mathrm{p}^4 C' \\ C_{13} = 1.925\ \mathrm{p}^6 C' \quad C_{33} = 3.464\ \mathrm{p}^8 C' \\ C_{44} = 2.309\mathrm{p}^4 C' \quad C_{66} = 9.851\ \mathrm{p}^4 C' \end{array}\right\} \tag{1}$$

Here $\mathrm{p} = \mathrm{c/a}$; $C' = \chi\ \mathrm{a} / \mathrm{p}^5$; $\chi = (1/8)[\{nb_0\ (n - m)\}/\{\mathrm{a}^{\mathrm{n}+4}\}]$; m, n = integer quantity; b_0 = Lennard Jones parameter. The lattice parameters of w-BN are the function of pressure [13].

$$a/a_0 = 1.000 - 9.230 \times 10^{-4}P + 5.580 \times 10^{-6}P^2 - 3.817 \times 10^{-8}P^3 \tag{2a}$$

$$c/c_0 = 1.000 - 9.076 \times 10^{-4}P + 5.689 \times 10^{-6}P^2 - 4.140 \times 10^{-8}P^3 \tag{2b}$$

Here a_0 and c_0 are the lattice parameters at zero pressure. The several studies of nanostructured materials [21,22] reveal that lattice parameter reduces at nanoscale. These studies indicate that the percent

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* Corresponding author.
E-mail address: cpy99physics@gmail.com (C.P. Yadav).

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of average change in lattice parameters at nanoscale follows the expression.

$$\Delta y = 0.174 + 1.582\exp(-x/5.377) \tag{3}$$

Here, y is lattice parameter and x is size of nanoparticles. So, second order elastic constants of nanostructure w-BN as function of pressure and nanoparticle size can be evaluated using Eq. (1) after determination of lattice parameters of w-BN at different pressure and nanoparticle size.

1.2. Theory of ultrasonic velocity

The ultrasonic longitudinal and shear wave velocities (V_L and V_S) in hexagonal structured crystal for wave propagation along unique axis are given by expressions [23].

$$V_L = \sqrt{C_{33}/d} \tag{4a}$$

$$V_S = \sqrt{C_{44}/d} \tag{4b}$$

The density of hexagonal structured material can be determined by following expression [24].

$$d = 2Mn/(3\sqrt{3}\,a^2cN_A) \tag{5}$$

where M, N_A and n are molecular weight, Avogadro number and number of atoms per unit cell respectively.

Debye average velocity is an important parameter in the low temperature physics as it is related to elastic constants through ultrasonic velocities. The Debye average velocity (V_D) is defined as [23].

$$V_D = \left[\frac{1}{3}\left(\frac{1}{V_L^3} + \frac{2}{V_S^3}\right)\right]^{-1/3} \tag{6}$$

Debye temperature (T_D) is indirectly related to elastic constants through Debye average velocity [23].

$$T_D = \hbar V_D(6\pi^2 n_a)^{1/3}/K_B \tag{7}$$

Here, $\hbar = h/2\pi$; K_B: Boltzmann Constant; n_a: atomic concentration. By the propagation of ultrasonic wave, the energy distribution of thermal phonons is disturbed. It comes in equilibrium through relaxation mechanism. The re-establishment times of thermal phonons after propagation of ultrasonic wave is termed as thermal relaxation time (τ) which is directly co-related with thermal conductivity (k), specific heat (C_V) and Debye average velocity [23,25].

$$\tau = 3k/C_V V_D^2 \tag{8}$$

The thermal conductivity of material can be obtained by following expression [26].

$$k = AMT_D^3\delta^3/\gamma^2 Tn^{2/3} \tag{9}$$

where A is a constant; M is the molecular weight; δ^3 is volume per atom; γ is Grüneisen number; T is the temperature. The constant 'A' is depends on the Grüneisen number and is given by following expression.

$$A = 2.43 \times 10^{-8}/\,(1 - 0.514/\gamma + 0.228/\gamma^2) \tag{10}$$

2. Results

The lattice parameters of w-BN at different pressure and size are evaluated with help of Eqs. (2) and (3) using zero pressure lattice parameters [7] and are given in Table 1. The pressure and size dependent densities of w-BN are calculated using Eq. (5) and are presented in Table 1. The value of m and n for wurtzite boron nitride are taken 6 and 7 respectively. Lennard Jones constant b_0 for w-BN is determined under equilibrium condition and is 7.44×10^{-65} erg cm^7. The pressure and size dependent second order elastic constants are calculated using evaluated lattice parameters, m, n, b_0 and Eq. (1). The pressure and size dependent bulk modulus (B) is calculated using second order elastic constants and literature [19]. The obtained second order elastic constants and bulk modulus at different pressure and size are given in Table 2.

Table 1
Lattice parameters and density of w-BN at different nanosize and pressure at 300 K.

Size parameter	Pressure (GPa)	5 nm	10 nm	20 nm	40 nm	Bulk
a (Å)	0	2.530	2.539	2.545	2.546	2.550
	20	2.490	2.499	2.505	2.506	2.510
	40	2.460	2.470	2.475	2.476	2.480
	60	2.440	2.450	2.455	2.456	2.460
c (Å)	0	4.166	4.182	4.191	4.193	4.200
	20	4.117	4.133	4.141	4.143	4.150
	40	4.067	4.083	4.091	4.093	4.100
	60	4.028	4.043	4.051	4.053	4.060
d (10^3 kg/m^3)	0	3.597	3.556	3.534	3.530	3.512
	20	3.758	3.715	3.691	3.687	3.668
	40	3.896	3.852	3.827	3.823	3.803
	60	3.999	3.953	3.928	3.923	3.904

Table 2
Elastic constants of w-BN at different nanosize and pressure at 300 K.

Size parameter	Pressure (GPa)	5 nm	10 nm	20 nm	40 nm	Bulk
C_{11} (GPa)	0	887	856	836	832	816
	20	1036	999	976	972	952
	40	1169	1123	1100	1096	1074
	60	1271	1220	1196	1191	1167
C_{12} (GPa)	0	218	210	205	204	200
	20	254	245	240	239	234
	40	287	276	270	269	264
	60	312	300	294	292	287
C_{13} (GPa)	0	192	185	181	180	177
	20	226	218	213	212	208
	40	255	245	240	239	234
	60	276	265	260	259	254
C_{33} (GPa)	0	938	905	884	880	863
	20	1112	1072	1047	1043	1022
	40	1255	1205	1181	1176	1153
	60	1354	1300	1274	1269	1243
C_{44} (GPa)	0	230	222	217	216	212
	20	271	262	255	242	249
	40	306	294	288	287	281
	60	332	318	312	311	304
C_{66} (GPa)	0	348	336	328	326	320
	20	406	392	383	381	374
	40	459	440	432	430	421
	60	499	479	469	467	458
B (GPa)	0	435	420	410	408	400
	20	511	492	481	479	469
	40	576	553	542	540	529
	60	625	600	588	585	573

The ultrasonic velocities are evaluated with the help of Eq. (4). The Debye average velocity at different pressure and size are calculated using Eq. (6). The obtained velocities V_L, V_S, V_D are reported in Table 3. The Debye temperature of w-BN is calculated with the help of Eq. (7) at different pressure and size at 300 K which is shown in Table 3.

The specific heat at constant volume (C_V) and energy density (E_0) are obtained with help of Debye temperature and literature [25]. The evaluated values of C_V and E_0 at different nanosize, zero pressure and at 300 K are shown in Fig. 1. The calculated thermal conductivity of w-BN at zero pressure and different size at 300 K are presented in Fig. 2. The size dependent thermal relaxation time is determined with the help of Eq. (8) using k, C_V and V_D at zero pressure and 300 K and is presented in Fig. 3.

Table 3
Ultrasonic velocities, Debye average velocity and Debye temperature of w-BN at different nanosize and pressure at 300 K.

Size parameter	Pressure (GPa)	5 nm	10 nm	20 nm	40 nm	Bulk
V_L (km/sec)	0	16.15	15.95	15.81	15.79	15.68
	20	17.20	16.99	16.84	16.82	16.69
	40	17.95	17.69	17.57	17.54	17.41
	60	18.40	18.13	18.00	17.98	17.84
V_S (km/sec)	0	8.00	7.91	7.84	7.83	7.77
	20	8.50	8.39	8.32	8.31	8.24
	40	8.86	8.74	8.68	8.66	8.60
	60	9.11	8.97	8.91	8.90	8.83
V_D (km/sec)	0	8.98	8.88	8.80	8.79	8.72
	20	9.54	9.42	9.34	9.32	9.26
	40	9.95	9.81	9.74	9.73	9.65
	60	10.22	10.07	10.00	9.99	9.91
T_D (K)	0	1491	1467	1452	1449	1436
	20	1606	1580	1563	1560	1546
	40	1696	1665	1650	1647	1632
	60	1757	1725	1709	1706	1691

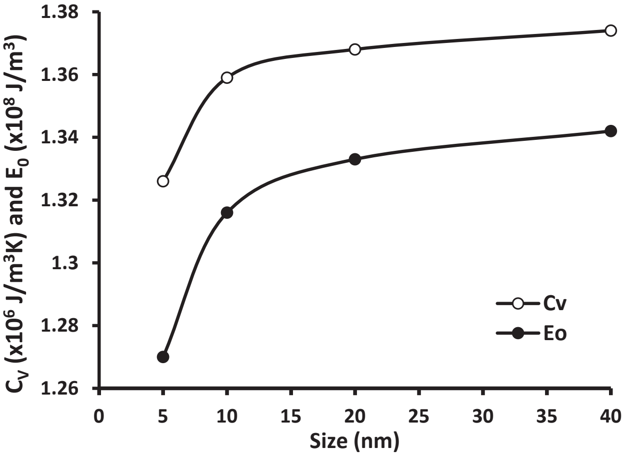

Fig. 1. C_V and E_0 vs size for w-BN crystal.

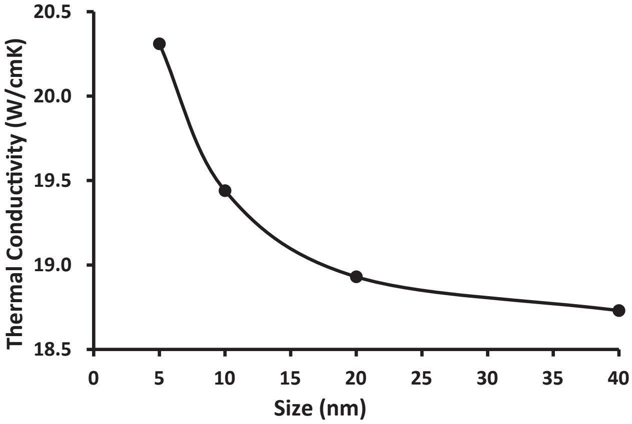

Fig. 2. Thermal conductivity vs size for w-BN crystal.

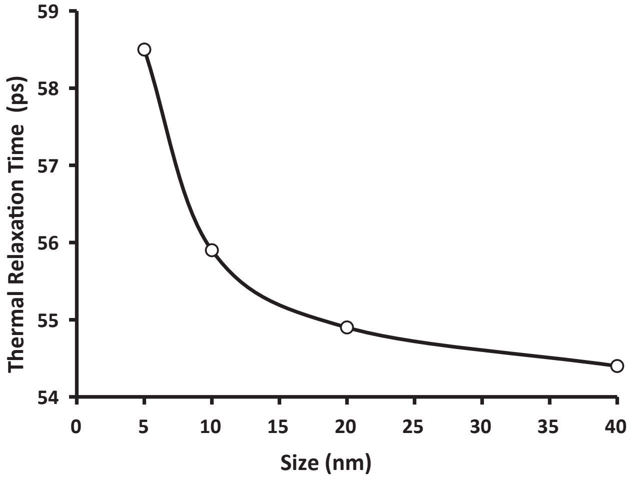

Fig. 3. Thermal relaxation time vs size for w-BN crystal.

3. Discussion

A perusal of Table 2 indicates that the second order elastic constants and bulk modulus rise with increase in pressure and decrease in nanoparticle size of w-BN. Due to increase in pressure and decrease in particle size, the lattice parameter of w-BN is found to reduce (Table 1). This causes reduction in inter-atomic distance. Therefore the inter-atomic force increases with enhancement in pressure and reduction in particle size. This results the growth in stress bearing capacity of material. Therefore increase in elastic constants is obtained by increasing pressure and reducing particle size of w-BN.

Bulk modulus of w-BN has been reported 400 GPa at 300 K elsewhere [6]. The present bulk modulus at zero pressure and 300 K is exactly same with reported value. Thus present elastic constants of w-BN at different pressure/particle size under potential model approach are justified. The maximum increase in elastic constants of w-BN is found 9% with reduction in particle size from bulk scale to 5 nm. It is also obtained that elastic constants enhance by 43% with increase in pressure from 0 to 60 GPa. Therefore pressure is more effective than the size of nanoparticle towards the enhancement in elastic behaviour of w-BN. The elastic constants of w-BN are found too large in comparison to same group nitrides [19]. Therefore the mechanical behavior will be better than the same group nitrides and refines under the external pressure.

The density of hexagonal wurtzite structured material is inversely proportional to a^2c(Eq. (5)) and the lattice parameters is found to decrease with pressure and reduction in particle size (Table 1). Hence the density of w-BN is found to increase with pressure and reduction in particle size (Table 1). The present value of density of w-BN at zero pressure and 300 K is 3.512 gm cm^{-3} and the density given in literature is 3.487 gm cm^{-3} [1,2]. Therefore our evaluated densities are justified.

Yet, the reduction in particle size and increase in pressure cause the rise in elastic constants and density of w-BN but the elastic constants play dominating role towards the enhancement in ultrasonic velocity. It is obtained that ultrasonic velocity enhances by 14% with increase in pressure from 0 to 60 GPa and is enhances by maximum 3.0% with reduction in particle size from bulk scale to 5 nm.

Debye temperature of w-BN is found to rise with increasing pressure and reducing particle size (Table 3). The lattice parameters/bond length of chosen material is received to decrease with pressure and reducing particle size. This causes growth in Brillion zone and therefore Debye frequency and Debye temperature increases. The reported Debye temperature of w-BN at 300 K in literature is 1400 K [1,7] while present value is 1436 K (Table 3) at bulk scale. The first principle calculation reports that the Debye temperature of w-BN increases with pressure and it changes by 15.14% under 40 GPa pressure [13]. The present study also found increase in Debye temperature by 13.64% under pressure of 40 GPa. The similarity between present and reported Debye temperature reveals its justification. Fig. 1 indicates that specific heat and thermal energy density of w-BN decrease as particle size decreases. The atoms of crystal come closer due to reduction in particle size. Therefore energy or momentum transfer becomes easy among the atoms. Hence to increase the temperature by one degree, less amount of energy is required. Due to this reason, reduction in C_V is obtained with decreasing particle size.

It is obvious from Figs. 2 and 3 that the thermal conductivity and thermal relaxation time of w-BN increases with reducing particle size at zero pressure and 300 K. The experimental thermal conductivity of boron nitride nano-ribbon is reported to increase with reduction in size and has its value in range 17.0–20.0 W/cm K [27]. This justifies our evaluation of size dependent thermal conductivities of w-BN. The particle size variation of thermal relaxation time exactly resembles the characteristics of thermal conductivity. The transfer of momentum among atoms becomes fast with reduction in particle size due to reduction in atomic separation. Therefore the re-establishment time (τ) for thermal phonons is found to reduce with particle size at constant temperature and pressure. Quantity τ for w-BN is order of pico-second which is same as reported for same group nitrides in literature [19].

4. Conclusion

Above discussion reveals that our theoretical approach for evaluation of elastic, thermo-physical and ultrasonic parameters is justified. It is obtained that elastic constants, ultrasonic velocities, thermal conductivity and thermal relaxation time of w-BN increase with increase in pressure or reduction in particle size. It can also be concluded that the actual nanoscale range of w-BN lies between 5 and 40 nm because after this range, all the parameters become approximately same with bulk scale values.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultras.2019.01.008.

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