

Ab initio investigation of a new boron nitride allotrope

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A new allotropic superhard and superdense structure of sp³-bonded boron nitride (hP3-BN) is proposed. Geometric, electronic, elastic, and optical properties of the structure are investigated by density functional theory-generalized gradient approximation (DFT-GGA) calculations. It is shown that the structure is an insulator with a band gap of 5.06 eV; its density is 5.03% higher than that of cubic boron nitride (c-BN)

and its bulk modulus is 2.25% higher than that of c-BN. The calculated hP3-BN refractive index in the range 200–800 nm is significantly higher than the indexes of diamond and all known carbon allotropes, except for the analogous carbon h-P3 structure, and it has a large optical dispersion. In the range above 800 nm the refractive index changes from 2.60 to 2.35.

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1 Introduction In recent years, with development of technology the interest in theoretical design and experimental synthesis of new superhard materials has increased. Such materials are in great demand in material science, electronics, optics, and even jewelry. Diamond is the most frequently used hard material and has the best strength properties. Unfortunately, diamond has insufficient thermodynamic stability and burns in air at 850–1000 °C. Also, diamond cannot be used in the treatment of iron alloys due to its interaction with iron and formation of iron carbides.

Another frequently used superhard material is cubic boron nitride (c-BN) with a sphalerite lattice. Its hardness is almost identical to diamond, but it has much better thermal stability. It withstands heating in air up to 1100–1300 °C.

Boron nitride has various allotropes, which are similar to structural modifications of carbon. Hexagonal boron nitride (h-BN) is a graphite-like layered structure of the ABAB type, where each layer is rotated with respect to the previous one [1]. h-BN has mechanical strength similar to graphite, but its band-gap width is $\approx 4\text{--}6$ eV, so h-BN is an insulator [2]. Also, there is a range of phases, usually referred to as turbostratic boron nitride (t-BN) [8, 12], which are located between highly ordered h-BN and an amorphous material. These phases have longer distance between the basal planes (3.33 Å) [13] and small curvature of the planes.

Rhombohedral boron nitride (r-BN) [3–5] is also composed of layers of sp²-linked atoms which form hexagons, but the layers are stacked in a three-layer sequence (ABCABC) [6]. This structure is a semiconductor [7]. Like the carbon lonsdaleite structure having $P63/m$ space group and mechanical properties similar to diamond, there is an analogous form of boron nitride – wurtzite-kind boron nitride (ω -BN) [8]. The atoms in the ω -BN structure are sp³-hybridized and grouped into tetrahedrons with different angles between adjacent tetrahedrons [9]. This phase is metastable at ambient conditions, but stable at high pressure (> 12 GPa) in the temperature range 500–3200 K [10]. As opposed to the carbon lonsdaleite phase, ω -BN is a conductor [7]. The c-BN structure is closely related to the structure of diamond. It has the sphalerite structure, where atoms are tetrahedrally coordinated and have sp³-bound states. c-BN has exceptional hardness slightly inferior to diamond only; it has very high thermal conductivity and wide band gap (6–6.4 eV) [11]. Together with these modifications, Sheng et al. [19] presented another possible modification of carbon: T-carbon phase. This structure was obtained by replacing each atom in the diamond by the tetrahedron of the carbon atoms. T-carbon is about one-third softer than diamond, but its parameters are comparable to c-BN ones: the density and hardness of this phase are 1.50 g cm⁻³ and 61.1 GPa,

respectively. It is a semiconductor with a band-gap width of about 3.0 eV and a bulk modulus of 169 GPa.

In addition to carbon nanostructures, boron nitride can also form nanotubes [14] or even fullerenes [15, 16]. Zhu et al. [17] proposed new superdense allotropic modifications of carbon: hP3, tI12, and tP12 phases. All these phases contain carbon atoms in the sp^3 -hybridization state. In the hP3 structure atoms occupy the same positions as the silicon atoms in the β -quartz structure. The analogue of the carbon tP12 phase is keatite and the tI12 modification is similar to a SiS2 phase, obtained at high pressure, where all atomic positions of silicon and sulfur atoms are occupied by carbon atoms. The hP3 and tI12 phases are the most dense carbon structures at ambient temperature. They are semiconductors with band gaps of 3.0 and 5.5 eV, respectively. The tP12 phase is an insulator with a band gap of 7.3 eV, which is the highest value among all allotropes of carbon. All new carbon phases have high hardness and bulk elastic modulus. The hP3 phase compressibility is even smaller than that of diamond. In comparison with diamond, all three forms have a high refractive index and large light dispersion, which means that they should have a high gloss and strong color reflections. Based on the fact that carbon and boron nitride allotropes are similar, it is interesting to investigate the hP3 phase of boron nitride as the only possible one among all of the new carbon modifications (hP3, tI12, tP12, and T-carbon) proposed by Zhu et al., as this structure only allows alternating boron and nitrogen atoms.

2 Technical details Calculations were carried out using VASP 5.2 (Vienna *ab initio* simulation package) [20]–[22] in the framework of density functional theory (DFT) [23] using the plane wave basis set and the projector augmented wave (PAW) method [24, 25]. Exchange-correlation effects were taken into account in the generalized gradient approximation (GGA) by the Perdew–Burke–Ernzerhof (PBE) functional [26]. The cutoff energy value E_{cutoff} in the calculations was equal to 400 eV.

At the first stage, the geometrical and electronic structures of the hP3-BN unit cell, containing 12 boron and 12 nitrogen atoms, were calculated. During structural optimization we let all degrees of freedom relax, i.e., the complete set of atomic positions and the unit-cell parameters. During relaxation atoms were shifted until forces acting on them became less than $0.01 \text{ eV } \text{\AA}^{-1}$. The first Brillouin zone (1BZ) was sampled by a $4 \times 4 \times 4$ grid using the Monkhorst–Pack scheme [27]. For a precise density of states (DOS) calculation, a $6 \times 6 \times 6$ grid was used.

3 Results and discussion After the hP3-BN unit-cell geometry optimization the unit-cell parameters are given by $a = b = 5.190 \text{ \AA}$, $c = 5.802 \text{ \AA}$. The geometry of the optimized cell is shown in Fig. 1.

The calculated binding energy of the hP3-BN structure is equal to -15.551 eV per formula unit (two atoms), while the corresponding binding energies of the c-BN and h-BN phases are equal to -17.918 and -17.840 eV , respectively.

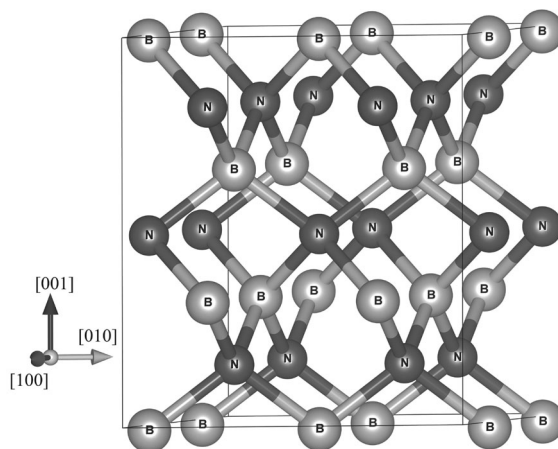


Figure 1 hP3-BN crystal structure.

Although the binding energy of the hP3-BN phase is higher than the energies above, it is hoped that the hP3-BN phase can be obtained at nonzero temperatures, when the hP3-BN Gibbs energy may be lower than the c-BN Gibbs energy due to the phonon entropy contribution. Also, the hP3-BN phase existence may be analogous to the case of graphite and diamond coexistence when the diamond is metastable. The calculated hP3-BN density is 3.655 g cm^{-3} , which is 5.03 and 3.80% more than c-BN [28] and diamond [17] densities, respectively. The static elastic tensor of hP3-BN is determined by performing six finite distortions of the lattice with 0.015 \AA magnitude and deriving the elastic moduli from the strain–stress relationship [18]. The nonzero elastic constants in Voigt notation are given by $C_{11} = 966.70$, $C_{12} = 185.74$, $C_{13} = 133.33$, $C_{22} = 967.33$, $C_{23} = 134.57$, $C_{33} = 1089.59$, $C_{44} = 371.50$, $C_{55} = 372.00$, and $C_{66} = 389.73 \text{ GPa}$. Also, the hP3-BN bulk modulus K was calculated by isotropic change of unit-cell vectors using the relation

$$K \times \ln(V) = -P, \quad (1)$$

where V is the unit-cell volume and P is the pressure. The dependence slope is equal to K . Using seven different volumes in the range $[-9 \text{ to } +9\%]$ from the equilibrium volume, after the slope is calculated, the hP3-BN bulk modulus is equal to 396.18 GPa , which is larger than the c-BN bulk modulus 387.28 GPa [29]. However, the hP3-BN bulk modulus is smaller than the elastic moduli of diamond and the new carbon allotrope hP3-C, which are 431.1 and 432.7 GPa , respectively [17]. The calculated hP3-BN electron density of states (DOS) and the band structure designated along lines connecting the 1BZ points D (0, 0, 0), A (0, 0, 0.5), H (1/3, 1/3, 0.5), K (1/3, 1/3, 0), T (0, 0, 0), M (0.5, 0, 0), and L (0.5, 0, 0.5) ($\times \pi/a$) are shown in Fig. 2.

The figure shows that the hP3-BN crystal is an insulator with a band gap of 5.056 eV . One can see that the conduction-band minimum and the valence-band maximum correspond to the Γ point, so the material has a direct band gap. Also, the frequency-dependent refractive-index tensor $n_{i,j}(\omega)$, as

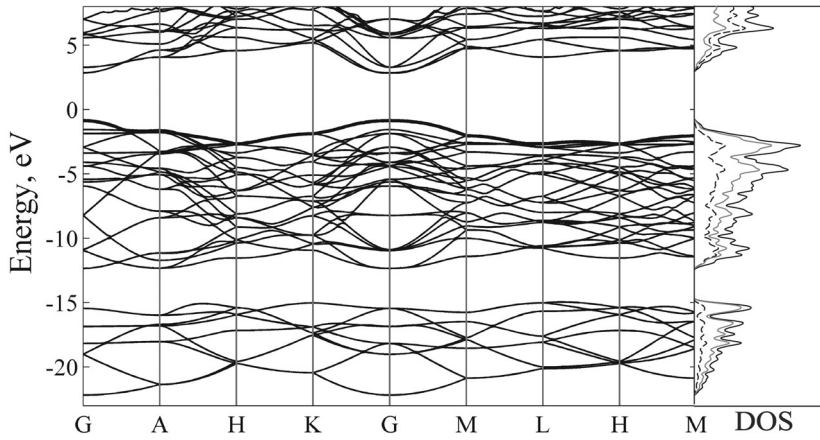


Figure 2 hP3-BN band structure (left) and DOS (right). Thick line represents the total DOS, gray line corresponds to the partial DOS of N atoms, dotted line corresponds to the partial DOS of B atoms.

well as the absorption coefficient tensor $\alpha_{i,j}(\omega)$, has been calculated by the formulas

$$n_{i,j}(\omega) = \sqrt{\frac{\sqrt{(\epsilon_{i,j}^1(\omega))^2 + (\epsilon_{i,j}^2(\omega))^2} + \epsilon_{i,j}^1(\omega)}{2}},$$

$$\alpha_{i,j}(\omega) = \sqrt{\frac{\sqrt{(\epsilon_{i,j}^1(\omega))^2 + (\epsilon_{i,j}^2(\omega))^2} - \epsilon_{i,j}^1(\omega)}{2}}. \quad (2)$$

The frequency-dependent macroscopical dielectric tensor $\epsilon_{i,j}(\omega)$ has been determined using density functional perturbation theory after the electronic ground state calculation. The method is explained in detail in Ref. [30]. The imaginary part $\epsilon_{i,j}^2(\omega)$ has been computed by a summation over unoccupied states using the equation

$$\epsilon_{\alpha\beta}^2(\omega) = \lim_{q \rightarrow 0} \frac{4\pi^2 e^2}{\Omega q^2} \sum_{c,v,k} 2\Theta_{v,k} \delta(\epsilon_{c,k} - \epsilon_{v,k} - \omega) \times \langle u_{c,k+e_{\alpha}q} | u_{v,k} \rangle \langle u_{c,k+e_{\beta}q} | u_{v,k} \rangle^*, \quad (3)$$

where the indexes c and v refer to the conduction- and valence-band states, respectively, and $u_{c,k}$ is the cell periodic part of the orbitals at the k -point k .

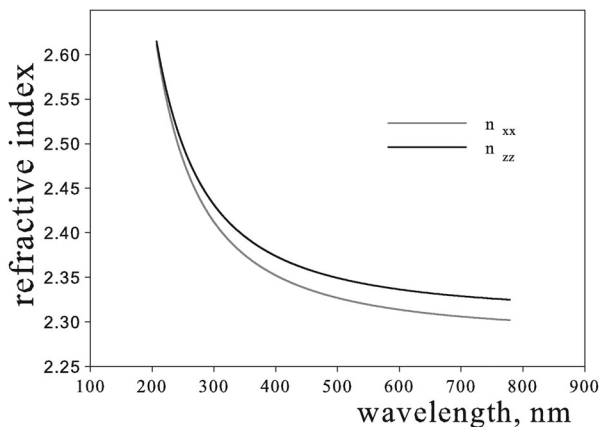


Figure 3 Frequency-dependent hP3-BN refractive index.

The real part of the dielectric tensor $\epsilon_{\alpha\beta}^1(\omega)$ was obtained by the Kramers–Kronig transformation:

$$\epsilon_{\alpha\beta}^1(\omega) = 1 + \frac{2}{\pi} P \int_0^{\infty} \frac{\epsilon_{\alpha\beta}^2(\omega') \omega'}{(\omega')^2 - \omega^2 + i\eta} d\omega', \quad (4)$$

where P denotes the integral principal value and η is the infinitesimal value. The calculated frequency-dependent refractive indexes (n_{xx} and n_{zz} components) and corresponding absorption coefficients in the visible and near-UV region are shown in Figs. 3 and 4.

This dependence shows that hP3-BN has significantly greater refractive index than the diamond index changing from 2.30 to 2.25 in the 300–800 nm range, but less than the index of the carbon hP3-C phase, which changes from 2.85 to 2.66 in this range, see [17]. hP3-BN light dispersion is significantly larger than dispersion of diamond and hP3-C, so this material can have good jewelry properties. Also, the phonon dispersion curves and phonon density of states (PDOS) were calculated using Phonopy – a software package for phonon calculations. This package is based on the supercell approach.

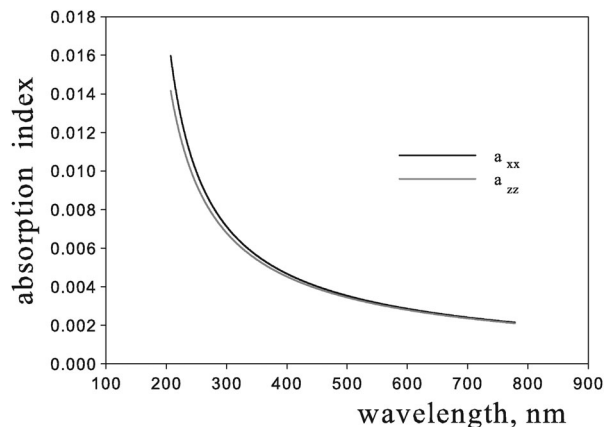


Figure 4 Frequency-dependent hP3-BN optical absorption coefficient.

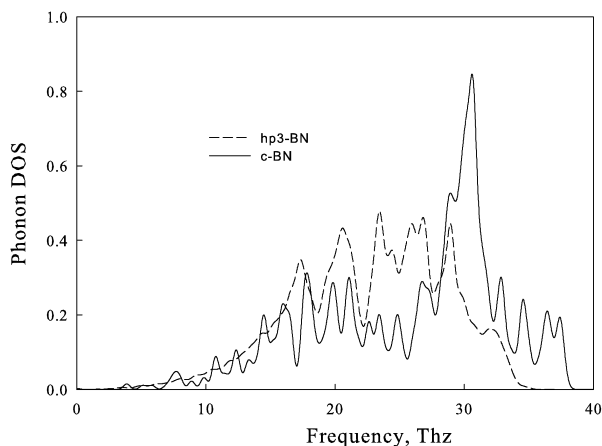


Figure 5 Phonon DOS for the hp3-BN structure.

Phonons for different wave numbers \mathbf{q} in the supercell of $2 \times 2 \times 2$ unit cells were calculated by the frozen phonon method [31], when interatomic force constants were calculated from the derivatives of total energy with respect to small displacements of 0.02 Å of every atom. The PDOS for the hp3-BN structure is shown in Fig. 5 by a dotted line. For comparison, the PDOS for the c-BN structure is shown by a solid line.

One can see that the PDOS of hp3-BN is significantly greater than that of c-BN in the range 20–30 THz, but is significantly less above 30 THz. Because of that, both curves are similar enough below 20 THz. We guess that this difference is a result of the contribution of the highest-frequency vibrations.

4 Conclusions In this work, a new boron nitride (hp3-BN) structure analogous to the new carbon superhard hp3 phase is proposed. Geometrical, electronic, optical and elastic properties of this phase were investigated by the DFT-GGA approach. It was shown that this structure is an insulator with a band gap of 5.06 eV; its density is 5.03% higher than the c-BN density and its bulk modulus is 2.25% higher than that of c-BN. The calculated h-BN refractive index n in the range 200–800 nm is significantly higher than that of diamond and all known carbon allotropes except for the analogous carbon h-P3-C structure. In the range above 800 nm, the refractive index changes from 2.60 to 2.35.

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