Cubic $(BN)_x C_{2(1-x)}$ ordered alloys: a first-principles study of the structural, electronic, and effective mass properties

Cubic $(BN)_x C_{2(1-x)}$ ordered alloys: a first-principles study of the structural, electronic, and effective mass properties

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Abstract

We apply a first-principles method based on the density functional theory within the generalized gradient approximation, and the full-potential linear augmented plane-wave method, to calculate the structural and electronic properties of cubic $(BN)_x C_{2(1-x)}$ ordered alloys. We investigate the equilibrium lattice parameters, the bulk moduli, the density of states, the band-gap energies and the effective masses of the conduction and valence bands along the [111], [100] and [110] directions. The obtained results are used to provide effective-mass and Luttinger parameters, and to give an important guideline to the material's design for optoelectronic devices, we link the first-principles band calculations with effective mass theory.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Diamond (C) and cubic boron nitride (c-BN) have attracted both scientific and technological interest in recent years. Their fascinating mechanical properties, such as hardness, high melting point (>3000 K), high thermal conductivity (200 W m^{-1} K^{-1}), and large bulk moduli (442 and 369 GPa for C and BN, respectively) make them useful for protective coatings, high-speed cutting, and polishing of ferrous alloys [1–6]. Their electronic properties, characterized by large band-gap energies (5.5 and 6.1 eV for C and BN, respectively) and low dielectric constants, indicate potential device applications in ultraviolet optics and high-temperature electronics [7–9]. The alloying between c-BN and C, producing $(BN)_x C_{2(1-x)}$ alloys, leads to the possibility to obtain new super-hard and super-abrasive materials by controlling the composition. In addition, these alloys are expected to be thermally and chemically more stable than diamond, and harder than c-BN [9, 11]. The promising potentialities of these materials have motivated extensive experimental [2–6] and theoretical [7–19] studies. With respect to the theoretical studies, some electronic-structure calculations have been published

for compounds based on c-BN and C with cubic structure. Most of the results of electronic-structure calculations are addressed to the question of the band-gap behaviour, the energy formation, the phase stability, and the structural properties such as bulk modulus and pressure dependence of the band-gap energies [7–19]. In spite of these works, comprehensive control of device characteristics of these materials remains a technological challenge and still requires detailed understanding of their physical and chemical behaviour. In particular, although the effective-mass approximation is used extensively throughout the literature, the actual electron and hole effective masses for the alloys in the whole range of x are unknown. The transport and optical phenomena are usually governed by the band structures in the immediate vicinity of the Brillouin zone centre. Thus, the effective-mass approximation turns out to be an appropriate method to make an analysis of the electronic properties of materials. The aim of the present paper is to present a systematic study of the structural and electronic properties of cubic $(BN)_x C_{2(1-x)}$ ($x = 0.00, 0.25, 0.50, 0.75, 1.00$) ordered alloys on the basis of first-principles band calculations, and to derive valence-band and conduction-band effective masses, as well as the Luttinger parameters. Therefore, we focus on the electronic structures around the valence-band maximum and the conduction-band minimum, and we obtain the effective-mass parameters (electron effective mass and hole effective masses), or, equivalently, the Luttinger parameters. As a result, we predict significant parameters of these materials, which can be used for the design of optoelectronic devices.

2. Theoretical framework

We carry out self-consistent and first-principles calculations using the full-potential linear augmented plane-wave (FP-LAPW) method (Wien2k code [20]) within the local density functional theory (DFT) [21] in the generalized gradient approach (GGA) [22]. The exchange–correlation potential within the generalized gradient approximation is calculated using the parameterization scheme of Perdew *et al* [22]. All core and valence states are treated self-consistently. We have included scalar-relativistic effects for all valence states. Core states are calculated fully relativistically, retaining only the spherical part of the potential. We do not consider spin–orbit coupling. The charge density was self-consistently determined using 32 k-points in the irreducible symmetry wedge of the Brillouin zone. The maximum spherical harmonic l-value of partial waves inside the atomic spheres were set equal to 10. The muffin-tin sphere radius was assumed to be 0.74 Å for all atoms. The basis set size was fixed by choosing $Rk_{max} = 7.0$. Self-consistency was achieved by demanding the convergence of both the total energy and the eigenvalues to be smaller than 10^{-6} eV.

In figure 1, we show the supercell (space group $P1$) containing eight atoms used in order to simulate the ordered alloys with cubic phase and compositions $x = 0.00, 0.25, 0.50, 0.75, 1.00$. In the substitution process we applied the consideration made by Tateyama *et al* [9], who predicted that the most stable $(BN)_x C_{2(1-x)}$ structures have no B–B or N–N bonds, and maximize the number of C–C and B–N bonds connections with C–B bond disfavoured.

3. Results and discussion

3.1. Structural properties

The equilibrium lattice parameters, a, were determined by means of the total energy and force calculations by relaxing the unit-cell volume without relaxing its internal structure, and the bulk moduli, B_0, were obtained by fitting the data to the Murnaghan equation of states [23].
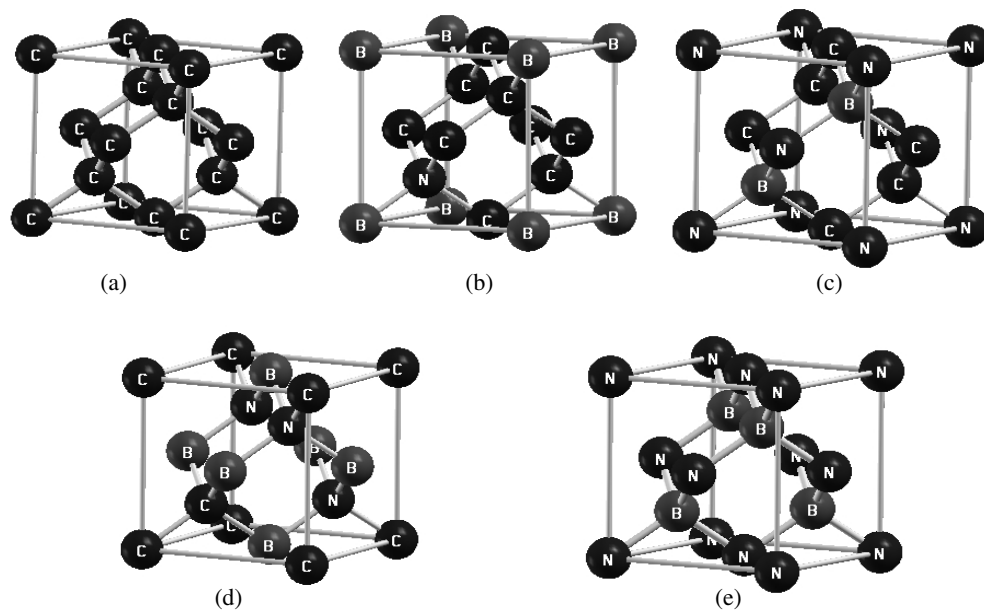
Figure 1. Supercell used to simulate the $(BN)_x C_{2(1-x)}$ ordered alloys with compositions (a) $x = 0.0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1.0$.
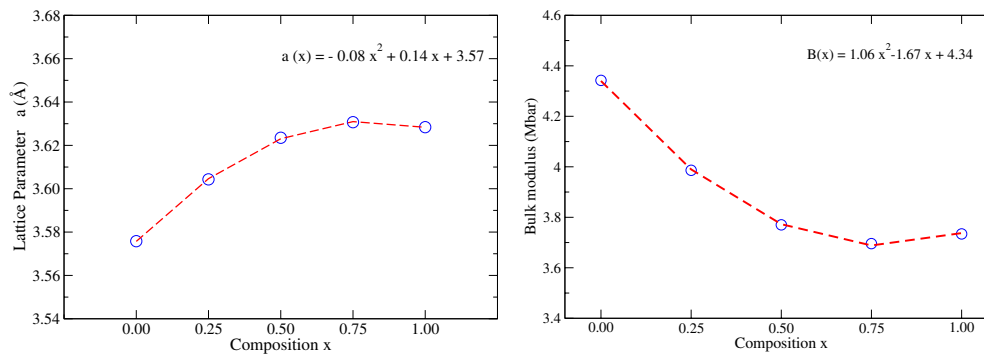
Figure 2. Composition dependence of the calculated equilibrium lattice parameters (a) and bulk modulus (b) of $(BN)_x C_{2(1-x)}$ ordered alloys.

The values for binary compounds and their alloys, compared to experimental data and previous calculations, are shown in table 1. Our results for a and B are in good agreement with the available experimental data and other theoretical obtained from plane-wave pseudopotential (PWPP) and linear-muffin-tin-orbital (LMTO-ASA) calculations. The differences encountered between experimental data and our results were less than 0.5% for lattice parameter and less than 2% for bulk modulus, which is the accuracy normally achieved within the GGA [30]. Figures 2(a) and (b) show the variation of the calculated equilibrium lattice parameters and bulk moduli with composition for $(BN)_x C_{2(1-x)}$ ordered alloys, respectively. The trends, which can be observed from figure 2, are the following. (i) The variation of the lattice parameters with composition exhibits a small deviation from Vegard's law with upward bowing parameters equal to -0.08 Å, obtained by fitting the calculated values with a quadratic polynomial

Table 1. Calculated lattice parameters, a, and bulk modulus, B_0, for $(BN)_x C_{2(1-x)}$ ordered alloys, compared to experimental data and previous calculations.

x	Lattice parameters a (Å)			Bulk modulus B_0 (GPa)		
	This work	Expt.	Other cal.	This work	Expt.	Other cal.
0.00	3.576	3.567[a]	3.53[b], 3.56[c] 3.561[d], 3.546[e] 3.539[f], 3.571[g]	4.34	4.42[h], 4.43[a]	4.80[b], 4.38[c] 4.64[d], 4.426[e] 4.574[f], 4.47[g]
0.25	3.604			3.99		
0.50	3.623	3.602[a], 3.642[i]	3.577[d], 3.583[f] 3.591[g], 3.60[j]	3.77	2.82[i]	4.38[d], 3.997[f] 4.19[j]
0.75	3.631			3.69		
1.00	3.628	3.615[k], 3.617[a] 3.572[d], 3.596[e] 3.594[f], 3.623[g] 3.63[o]	3.606[l], 3.58[b]	3.73	4.65[m], 2.90[n] 3.66[d], 3.525[e] 3.932[f], 3.68[g] 3.86[o]	3.67[l], 4.12[b]

[a] Reference [3].
[b] LMTO-ASA within LDA [7].
[c] Reference [24].
[d] PWPP within LDA from [9].
[e] PWPP within GGA from [11].
[f] PWPP within LDA from [12].
[g] FP-LAPW within GGA from [16].
[h] From elastic constants measured by Brillouin scattering [25].
[i] Reference [5].
[j] FP-LAPW within GGA from [26].
[k] Reference [27].
[l] PWPP within LDA from [28].
[m] Interpreted using empirical relations for the elastic constants [24].
[n] From estimated elastic constants [6].
[o] FP-LAPW within GGA from [29].

function. The physical origin of this small upward bowing parameter may be due to the small mismatches of the lattice parameters of BN and C. (ii) The composition dependence of the bulk modulus shows a significant deviation from linear composition dependence, with downward bowing equal to 1.06 Mbar. The large bowing values is rooted in the significant mismatch of the bulk modulus of BN and C. (iii) The bulk modulus has just the opposite behaviour to the lattice parameter, as was to be expected.

3.2. Electronic properties

For the $(BN)_x C_{2(1-x)}$ ordered alloys, the calculations of the band structures for all composition gave an indirect band gap, with the valence-band maximum at the Γ point and conduction-band maximum at the X point. The behaviour of the calculated band-gap energies with the composition for $(BN)_x C_{2(1-x)}$ ordered alloys is given in figure 3. In order to observe these changes in band-gap energies we show the total density of states in figure 4. The density of states for the $(BN)_x C_{2(1-x)}$ ordered alloys lies mainly in three energy regions: (i) the lowest region, stemming mainly from N 2s states, (ii) the region at the top of the valence band, mainly due to C states mixed with some N 2p states, and (iii) the region just above E_F, dominated by unoccupied BN states with a significant B component because of the cation nature of the latter. The reduction of band-gap energy, observed in figure 4, can be assigned to the shift of the C states to high energy in the valence band and to an analogue
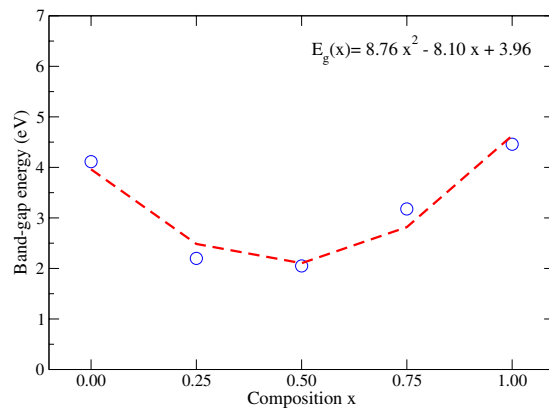
Figure 3. Composition dependence of the calculated band gap for $(BN)_x C_{2(1-x)}$ ordered alloys.
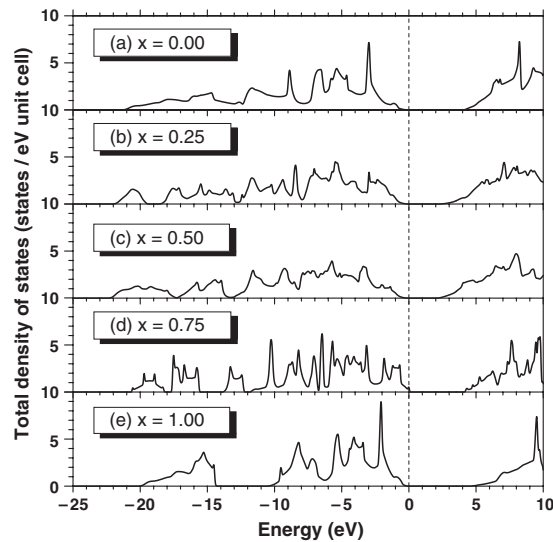
Figure 4. Total density of states for the $(BN)_x C_{2(1-x)}$ ordered alloys. The vertical line denote the position of the Fermi energy, which has been chosen to be 0.0 eV.

lowering of the states in the conduction band. The shifting of the energies of the C states and the consequent reduction of the band gap can be correlated to: (i) the fact that the atomic energy levels of C are between those of B and N [7, 8], and (ii) a certain weakening of C–C bonds in $(BN)_x C_{2(1-x)}$ ordered alloys. A large composition dependence of band-gap energy is clearly visible with upward bowing parameter equal to 8.77 eV, obtained by fitting to a parabola the curves of band-gap energies versus composition. This value can be compared with that estimated from other theoretical works [7, 8, 16]. Lambrecht and Segall [7, 8], using the LMTO-ASA method and local density approach, investigated the electronic properties of $(BN)_x C_{2(1-x)}$ ($x = 0.0, 0.25, 0.50, 0.75, 1.00$) alloys; the band-gap bowing parameter estimated from their results is 7.97 eV. Zaoui and Hassan [16], using the FP-LAPW method, studied the electronic structure and disorder effects in $(BN)_x C_{2(1-x)}$ ($x = 0.0, 0.5, 1.0$) alloys; the band-gap bowing parameter estimated from their results is 10.01 eV. The values of band-

Table 2. Band-gap energy, E_g, of cubic $(BN)_x C_{2(1-x)}$ ordered alloys at equilibrium lattice parameter, in eV.

	E_g (eV)		
x	This work	Other cal.	Expt.
0.00	4.11	4.11[a], 3.51[b]	5.50[c]
0.25	2.20	2.30[a]	
0.50	2.05	2.51[a], 1.98[b]	
0.75	3.18	3.29[a]	
1.00	4.46	4.69[a], 4.84[b]	6.40[c]

[a] LMTO-ASA within LDA [7, 8].
[b] LAPW within GGA [16].
[c] Reference [31].

gap energy of cubic $(BN)_x C_{2(1-x)}$ alloys at equilibrium lattice parameter are depicted in table 2. Considering that the GGA tends to underestimate the band-gap energies, our results are in good agreement with the experimental and other theoretical values. Comparing our results with these calculations, one can deduce that the band-gap bowing parameter and band-gap energy are directly related to the variation of the composition and the atomic arrangement in the unit cell. Besides the band-gap energy, the effective masses at the valence-band maximum and the conduction-band minimum are also of vital importance in electrical properties. Therefore, we focus on the electronic structure around the valence-band maximum and the conduction-band minimum, and we obtain the electron effective masses, hole effective masses, and, equivalently, the Luttinger parameter [32, 33]. We calculated heavy-hole (hh) and light-hole (lh) effective masses in the [111], [100], and [110] directions, and the electron effective mass. The heavy-hole and light-hole effective masses were obtained by fitting to a parabola the curves of energy versus **k** in the range from -0.04 $(2\pi/a)$ to 0.04 $(2\pi/a)$, along the [111], [100], and [110] directions. The electron effective masses were obtained in a similar way by the energy curves starting from the conduction-band minimum at the X point. The corresponding effective masses for binary compounds and their alloys are given in table 3. There is a general agreement between our results and those available in the literature. By using the following expressions:

$$\gamma_1 = \frac{1}{2}\left(\frac{1}{m_{lh}^{[100]}} + \frac{1}{m_{hh}^{[100]}}\right),$$

$$\gamma_2 = \frac{1}{4}\left(\frac{1}{m_{lh}^{[100]}} - \frac{1}{m_{hh}^{[100]}}\right),$$

$$\gamma_3 = \frac{1}{4}\left(\frac{1}{m_{lh}^{[100]}} + \frac{1}{m_{hh}^{[100]}} - \frac{2}{m_{hh}^{[111]}}\right).$$

(1)

and the calculated values for the effective masses, we obtained values for the Luttinger parameter, γ_i, which are shown in table 4. The literature is scarce in experimental and first-principles calculated values of the effective masses for the materials studied in this work. According to our first-principles calculations, the hole masses have non-negligible k-directional dependence, which is important when designing devices. In addition, the Luttinger parameters are very important for the calculation of other systems, such as quantum wells and superlattices that need these parameters as input [29, 33]. The calculated effective masses of the light-hole along the [100] direction are bigger than the calculated masses along the [111] and [110] directions, which are coincident. On the other hand, the calculated effective masses of the

Table 3. Effective masses for electrons (e), heavy-holes (hh) and light-holes (lh) (in units of the free electron mass m_0), along the [111], [100], and [110] directions for cubic $(BN)_x C_{2(1-x)}$ ordered alloys.

x	m_e	$m_{hh}^{[100]}$	$m_{lh}^{[100]}$	$m_{hh}^{[111]}$	$m_{lh}^{[111]}$	$m_{hh}^{[110]}$	$m_{lh}^{[110]}$
0.00	0.4726	0.5113	0.3040	0.6961	0.1761	0.3001	0.2112
0.25	0.4859	0.4361	0.3276	0.7911	0.2046	0.2848	0.2678
0.50	0.3237	0.4117	0.3912	0.9115	0.2716	0.4424	0.3898
0.75	0.8702	0.4734	0.4462	0.9451	0.2392	0.3613	0.3174
1.00	0.9290	0.5358	0.5043	1.2637	0.2437	0.5355	0.2799
	0.94[a]	0.53[a]	0.51[a]	1.26[a]	0.33[a]	1.09[a]	0.35[a]
	0.75[b]	0.37[b]	0.15[b]	0.93[b]	0.11[b]		

[a] LAPW within GGA [29].
[b] Landolt-Börnstein tables [27].

Table 4. Luttinger parameter of cubic $(BN)_x C_{2(1-x)}$ ordered alloys.

x	γ_1 This work	γ_1 Other cal.	γ_2 This work	γ_2 Other cal.	γ_3 This work	γ_3 Other cal.
0.00	2.62		0.33		0.59	
0.25	2.67		0.19		0.70	
0.50	2.49		0.03		0.70	
0.75	2.18		0.03		0.56	
1.00	1.92	1.92[a]	0.02	0.02[a]	0.57	0.56[a]

[a] LAPW within GGA [29].

heavy-hole along the [111] direction are bigger than the masses along the [100] direction, which are also almost coincident. This behaviour may be due to the alignment of the band energy in BN (conduction-band minimum) and diamond (valence-band maximum). In table 4 we can see that the Luttinger parameters increase as the BN composition decreases.

4. Conclusion

In summary, we have obtained the structural, electronic, and effective mass properties of $(BN)_x C_{2(1-x)}$ ordered alloys ($x = 0.0, 0.25, 0.50, 0.75, 1.0$) using the FP-LAPW method and the GGA. For the binary compounds we find that the lattice parameters are 0–1% larger, the bulk moduli 1–2% smaller, and the band-gap energies approximately 20–30% smaller as compared to the experimental results. The lattice parameters and bulk moduli are in good agreement with other calculations and experimental data, where they are available. The lattice parameter of $(BN)_x C_{2(1-x)}$ ordered alloys exhibits a small deviation from Vegard's law with upward bowing parameters equal to −0.08 Å. On the other hand, the bulk modulus shows a significant deviation from linear concentration dependence, with downward bowing equal to 1.06 Mbar. We found a strong composition dependence of the band-gap energy of $(BN)_x C_{2(1-x)}$ ordered alloys. Our results suggest that the bowing of $(BN)_x C_{2(1-x)}$ ordered alloys has a remarkable contribution from the structural effect. The electron effective mass, hole effective masses, or equivalently, the Luttinger parameters were derived from the calculated band structures near the conduction-band minimum and the valence-band maximum. From the analysis of our results, we observe a strong dependence of the structural and electronic properties with the composition, and deduce that the atomic arrangement of these materials used in the calculations are critical for the results.

Acknowledgments

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