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Band Gap Characterization of Ternary $BBi_{1-x}N_x$ Alloys: A First-Principles Study

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III–V based alloys and heterostructures have got much attention due to their great device applications as well as for the development of electronic, optic and optoelectronic devices. Because of this reason, the present study reports an investigation about the band gap properties of $BBi_{1-x}N_x$ ($0 \leq x \leq 1$) ternary alloy in zinc-blende phase. The results of studied binary (BN and BBi) and ternary $BBi_{1-x}N_x$ alloy structures are presented by means of density functional theory within the Wu–Cohen exchange correlation potential based on generalized gradient approximation. We have implemented geometric optimization before the volume optimization calculations for all studied alloys structure. The obtained equilibrium lattice constants of studied binary compounds are in coincidence with experimental works. The band gap character (direct/indirect or negative) of ternary $BBi_{1-x}N_x$ alloys is also investigated.

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1. Introduction

The alloys of III–V zinc-blende semiconductor compounds are of vital importance because these materials are potentially good for application of optoelectronic and high-speed electronics [1]. The development in the metal-organic vapour phase epitaxy (MOVPE) and the molecular beam epitaxy (MBE) have opened a way to research bismuth and nitrogen compounds/alloys (III–Bi(N)). Tixier et al. [2] have reported band gaps of dilute quaternary alloys $GaN_xAs_{1-x-y}Bi_y$ ($x < 1.6\%$, $y < 2.6\%$) lattice matched to GaAs at room temperature by MBE. Gottschalch [3] observed a small influence of the boron concentration on the band gap energies by the help of MOVPE growth of $B_xGa_{1-x}As$, $B_xGa_{1-x-y}In_yAs$ and $B_xAl_{1-x}As$ alloys on (001) GaAs substrate.

In this study, for ground-state total energy calculation, the first principles density functional theory (DFT) [4, 5] performed with the WIEN2k [6] code. The Wu–Cohen (WC) [7] calculation based on generalized gradient approximation (GGA) was used for the total energy calculations. The rest of the paper is organized as follows. In Sect. 2, the computational method used in the present work is described. Results and their discussion are presented in Sect. 3. Finally, a conclusion of the work is given in Sect. 4.

2. Method of calculation

In the current study, all calculations are implemented into WIEN2k software package which is based on the full-potential (linearized) augmented plane wave and local-orbitals method (FP-(L)APW+lo) to solve the Kohn–Sham equations. The WC–generalized gradient approximation (GGA) exchange-correlation functional is used for electron–electron interactions.

We use an energy cut-off parameter $RK_{\max}$ (R is the average radius of the muffin-tin (MT) spheres and $K_{\max}$ is the cut-off for the wave function basis) of 6. The cut-off energy is set to -6 Ry for separating core from valence states. Inside the MT spheres, the angular momentum expansion is expanded up to $l_{\max} = 10$. Magnitude of the largest vector G is equal to 12 $\mathrm{Ry}^{1/2}$ in charge density Fourier expansion. For a well force, charge convergence of crystal system is stable within less than 0.001e. In the total energy between self-consistency cycles (SCF) was $< 10^{-4}$ Ry. In the considered alloy structure, free coordinates of atoms were relaxed using the quantum-mechanical forces so residual forces on the ions were < 1 mRy/bohr.

For accurate Brillouin zone (BZ) integrations, the standard special k-points technique of Monkhorst and Pack (MP) [8] was used. The k-mesh sizes was a $3 \times 3 \times 3$ MP special points (14 special k-points in the irreducible wedge of the BZ) for each considered 8-atom $1 \times 1 \times 1$ supercell. The k-meshes and basis sets are chosen to be good enough such that the obtained results are well converged.

3. Results and discussions

As in the first step in the present work, structural properties of binary (BN and BBi) and ternary ($BBi_{1-x}N_x$) compounds have been performed for $x = 0.25$, 0.50, and 0.75 compositions. $1 \times 1 \times 1$ supercell with 8 atoms in zinc-blende (ZB) phase is used for the crystal structure of studied materials. The calculated total energies are fitted with the Murnaghan [9] equation of state in order to get structural properties such as the equilibrium lattice constants (a_0) and the static bulk modulus (B_0). The obtained structural results of studied materials are

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TABLE I

The calculated equilibrium lattice parameter and bulk modulus of binary BBi, BN compounds and their ternary alloys $BBi_{1-x}N_x$. The present results are compared with previous experimental and theoretical calculations.

Material	a_0 [Å]	B_0 [GPa]	Ref.
BBi	5.462	84.370	this work
	5.531	66.846	GGA [12]
	5.529	72.209	GGA [13]
	5.416	86.27	LDA [13]
$BBi_{0.75}N_{0.25}$	5.013	111.056	this work
$BBi_{0.50}N_{0.50}$	4.607	150.776	this work
$BBi_{0.25}N_{0.75}$	4.353	186.252	this work
BN	3.61	372.881	this work
	3.615	369	exp. [10, 11]
	3.627	375.923	GGA [12]
	3.57	398.74	LDA [14]

summarized in Table I. As is shown in Table I, the predicted structural properties significantly depend on x. The lattice parameters for binary compounds BN and BBi are found to be 3.61 Å and 5.46 Å, respectively. The calculated a_0 value within the WC potential for BN (3.61 Å) and experimental lattice constant (5.615 Å) [10, 11] are within about 0.1% of each other. BBi compound for which no experimental results are listed in Table I has not yet been synthesized in the laboratory. However, calculated lattice parameter of BBi is in accordance with available theoretical works [12, 13]. The small differences between the two GGA [12, 13] calculations are due to the different $R_{\mathrm{MT}}K_{\mathrm{MAX}}$ value. The lattice parameters of $BBi_{1-x}N_x$ ternary alloys are found as 5.013 Å, 4.607 Å and 4.353 Å for $x = 0.25$, 0.50 and 0.75, respectively. Unfortunately, there are no experimental and theoretical results for $BBi_{1-x}N_x$ ternary alloys to check the validity of this calculation. Therefore it is hoped that the obtained results can be used to cover the lack of data in the literature for $BBi_{1-x}N_x$ ternary alloys.

On the other hand, the bulk moduli of considered structure are also presented in Table I. The calculated B_0 of BN is 1% larger than the value of 369 GPa obtained within experimental study [10, 11]. One can see that the calculated bulk modulus of binary BN compound is 0.7% and 7% larger than other theoretical GGA [12] and LDA [14] method, respectively, due to lattice constant differences between these approaches. The calculated B_0 of BBi is larger than the GGA [12, 13] method due to underestimation of the calculated lattice constant.

TABLE II

The calculated high symmetry point energies of binary BBi, BN compounds and their ternary alloys $BBi_{1-x}N_x$. The present WC results are compared with previous experimental and theoretical calculations (all energies are in eV).

	BBi	$BBi_{0.75}N_{0.25}$	$BBi_{0.50}N_{0.50}$	$BBi_{0.25}N_{0.75}$	BN
this work					
$\Gamma-\Gamma$	0.3821	0.5656	0.4181	1.2366	8.84
$\Gamma-X$	0.9701	−0.7996	−2.2983	0.3136	4.36
other					
$\Gamma-\Gamma$	−0.085 [13], 0.13 [16]	–	–	–	–
$\Gamma-X$	–	–	–	–	4.45 [19]
exp.					
$\Gamma-X$	–	–	–	–	6 [18]

On the other hand, the electronic band structures for considered structures along the high symmetry directions in the BZ are obtained by using their equilibrium lattice parameters calculated with WC calculations. The energy level differences at different high symmetry points are also listed in Table II. It is clearly seen that BBi has a direct band gap with a value of 0.3821 eV at Γ point. That value is found to be 0.13 eV (direct) by Madouri and Ferhat [15] by using semi-local (GGA) function calculation. The disagreements between these studies are fundamentally originating from used calculation methods. Recently, Ferhat and Zaoui [13] have investigated the ground state properties for III–Bi (BBi, AlBi, GaBi and InBi) compounds. By using semi-local function calculations they also have concluded that BBi compound shows negative band gap of −0.085 eV. This underestimation of the band gaps is mainly due to the fact that the simple form of GGA does not take into account the quasiparticle self-energy correctly [16] which makes them not sufficiently flexible to accurately reproduce both exchange and correlation energy and its charge derivative [17]. As shown in Table II, BN compound is an indirect semiconductor material (4.36 eV at X point) compared with experimental [18] and semi-local calculation [19].

From Table I it is clearly seen that ternary semiconductor alloy $BBi_{0.25}N_{0.75}$ has an indirect band gap at X point while both ternary alloys $BBi_{0.50}N_{0.50}$ and

$BBi_{0.75}N_{0.25}$ show metallic behavior due to the crossovers of valance and conduction bands at Fermi level.

4. Conclusion

In this study, the structural and electronic properties of binary BBi and BN compounds and ternary alloys $BBi_{1-x}N_x$ have been studied using Wu–Cohen GGA within the density functional theory as implemented in the WIEN2k. The obtained structural results of binary compounds are in good agreement with experimental and available theoretical studies. By means of the calculated equilibrium lattice parameter the electronic band structures of studied alloys are investigated.

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