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First principles study on structural, electronic and optical properties of $Ga_{1-x}B_xP$ ternary alloys ($x = 0$, 0.25, 0.5, 0.75 and 1)

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ABSTRACT

The structural, electronic and optical properties of GaP, BP binary compounds and their ternary alloys $Ga_{1-x}B_xP$ ($x = 0.25$, 0.5 and 0.75) have been studied by full-potential linearized augmented plane wave (FP-LAPW) method within the framework of density functional theory (DFT) as implemented in WIEN2k package. Local density approximation (LDA) and generalized gradient approximation (GGA) as proposed by Perdew–Burke–Ernzerhof (PBE), Wu–Cohen (WC) and PBE for solid (PBESol) were used for treatment of exchange-correlation effect in calculations. Additionally, the Tran–Blaha modified Becke–Johnson (mBJ) potential was also employed for electronic and optical calculations due to that it gives very accurate band gap of solids. As B concentration increases, the lattice constant reduces and the energy band gap firstly decreases for small composition x and then it shows increasing trend until pure BP. Our results show that the indirect–direct band gap transition can be reached from $x = 0.33$. The linear optical properties, such as reflectivity, absorption coefficient, refractive index and optical conductivity of binary compounds and ternary alloys were derived from their calculated complex dielectric function in wide energy range up to 30 eV, and the alloying effect on these properties was also analyzed in detail.

1. Introduction

Until nowadays, III–V semiconductor compounds always have gained immense attention of scientific community due to their unique chemical and physical properties. One of the most interesting member is gallium phosphide (GaP), it has been applied in optical devices, light-emitting diodes (LEDs), photo cells [1]. At ambient conditions, GaP crystallizes in zincblende-type structure of space group $F\bar{4}3m$ whose lattice constant is 5.451 (Å) [2], previous theoretical studies have shown that GaP has indirect band gap [3,4], which limits so much its technological applicability.

Otherwise, the modification of conventional properties of materials to find out new ones with desired properties is one of the most important task of materials science. This can be solved by combining two or more compounds. In case of GaP, the ternary alloys $Ga_{1-x}In_xP$ have been experimentally prepared in thin film [5] and nanowires [6] and the indirect–direct band gap transformation has been observed.

Beside the experimental area, theoretical one is employed to obtain better understanding on physical properties of materials, which would serve to predict and design new ones. For examples, using different methods based on density functional theory (DFT), several authors have investigated the ternary alloys formed by replacing Ga atom in crystalline lattice of GaP by other IIIA-group atoms with different concentrations, such as Al [7,8] and Tl [9]. Recently, Zhang et al. [10] studied structural, electronic and mechanical properties of $Ga_{1-x}B_xP$ ternary alloys ($x = 0$, 0.25, 0.5, 0.75 and 1) using the plane-wave pseudopotential technique as implemented in the CASTEP package, and found that unlike binary compounds (GaP and BP), ternary alloys have direct band gap and they are brittles and mechanically stables. This is the only work devoted to $Ga_{1-x}B_xP$ alloys that we could find, so a deeper knowledge about physical properties of these materials is still needed.

In this paper, we study theoretically the structural, electronic and optical properties of $Ga_{1-x}B_xP$ ($x = 0$, 0.25, 0.5, 0.75 and 1) mixed crystals in zinc-blende structure using FP-LAPW method. Our work aims to predict new ternary alloys based on GaP and BaP with promising properties for technological applications.

2. Computational details

All calculations were performed using FP-LAPW method as implemented in WIEN2k code [11]. We used the local density approximation (LDA) [12] and generalized gradient approximation (GGA) as proposed by Perdew et al. [13], Wu et al. [14] and PBE for solid [15] functionals to treat the exchange-correlation effect. Ad-

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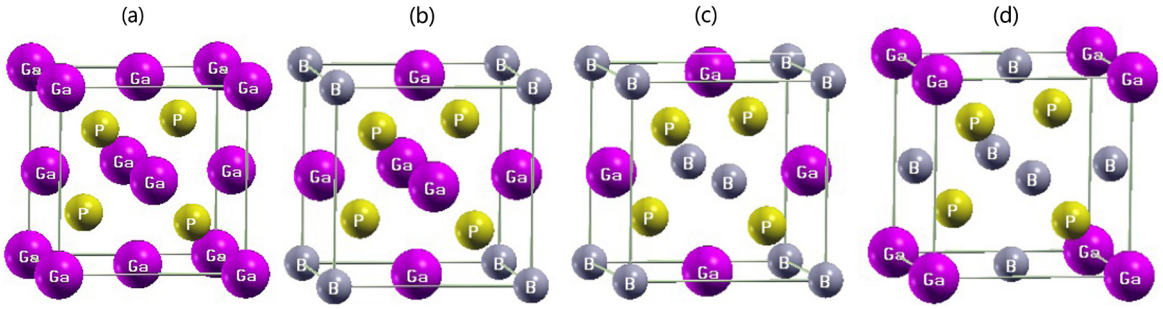

Fig. 1. Crystal structure of $Ga_{1-x}B_xP$ at different concentrations: (a) $x = 0$; (b) $x = 0.25$; (c) $x = 0.5$ and (d) $x = 0.75$.

ditionally, we also employed Tran–Blaha modified Becke–Johnson potential (mBJ) for the studies of electronic and optical properties. The mBJ potential has been proven to give very accurate band gap of a lot of types of solid, such as wide band gap insulators, *sp*-semiconductors and strongly correlated *3d* transition-metal oxides [16,17]. It is a modified version of potential introduced by Becke–Johnson [18] to improve the band gaps calculated by DFT. It is important to mention that mBJ potential just considers exchange effect, hence, we choose PBE potential for the correlation (mBJ-PBE).

In zinc-blende structure of $F\bar{4}3m$ space group, Ga and P atoms are located at *4a* (0; 0; 0) and *4c* (0.25; 0.25; 0.25) positions, respectively [2]. When Ga atoms are replaced by B atoms forming ternary alloys, these have simple cubic structure of space group $P\bar{4}3m$. The unit cells of $Ga_{1-x}B_xP$ for $x = 0$, 0.25, 0.5 and 0.75 are shown in Fig. 1, the crystal structure of binary BP ($x = 1$) is identical to that of GaP compound ($x = 0$). For the structure optimization, we calculated total energy for 11 points from $-0.1V_0$ to $0.1V_0$, where V_0 is experimental volume in case of binary compounds and optimized volume of GaP for ternary alloys, then obtained data were fitted to the Birch–Murnaghan equation of state [19] to find the volume with lowest energy.

The linear optical properties of materials can be studied by means of the frequency dependent complex dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$. The imaginary part $\epsilon_2(\omega)$ was calculated using the method described in detail by Ambrosch-Draxl et al. [20], while the real part $\epsilon_1(\omega)$ can be obtained from computed imaginary part using the Kramers–Kronig relationship [21]. The optical responses as optical conductivity, refractive index, absorption coefficient, and reflectivity can be derived from the dielectric function of material as continuation:

$$\sigma(\omega) = \frac{\omega}{4\pi}\epsilon_2 \tag{1}$$

$$n(\omega) = \sqrt{\frac{(\epsilon_1^2 + \epsilon_2^2)^{1/2} + \epsilon_1}{2}} \tag{2}$$

$$\alpha(\omega) = \frac{2k\omega}{c} \tag{3}$$

$$R(\omega) = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \tag{4}$$

where, the extinction coefficient:

$$k(\omega) = \sqrt{\frac{(\epsilon_1^2 + \epsilon_2^2)^{1/2} - \epsilon_1}{2}} \tag{5}$$

For performing calculations, a k-mesh $8 \times 8 \times 8$ in the first Brillouin zone has been used and to separate core states from valence states, the cut-off energy is set to -6 Ryd. The maximum quantum number (l_{max}) for atomic wave functions inside the atomic spheres is 10, and the cut-off energy for plane wave expansion of wave functions in the interstitial region is taken to be $K_{max} = 7/R_{MT}$, where R_{MT} is the muffin-tin radius. The self-consistent calculations are considered to be converged when the total energy of system is stable within 10^{-4} Ryd. It is important to mention that in the optical calculations, we used the k-mesk much denser than that in structural and electronic calculations.

3. Results and discussions

3.1. Structural properties

The structural parameters such as lattice constant and bulk modulus of GaP and BP binary compounds and their ternary alloys obtained by LDA, PBE, WC and PBESol functionals are listed in Table 1 along with other available theoretical results and experimental data. It is well known that PBE functional usually gives optimized lattice constant higher than that of LDA one and a contrary trend is observed for bulk modulus, and the results of structural optimization of WC and PBESol are very similar, as seen in Table 1. Otherwise, our results agree well with other theoretical and experimental ones for binary systems but for ternary alloys, our optimized lattice constants are from 1% to 3% higher than those obtained in work [10]. It can be seen that the lattice constant decreases as the composition x increases, this diminution is due to that the ionic radius of B is lower than that of Ga. The order of bulk modulus is GaP < $Ga_{0.75}B_{0.25}P$ < $Ga_{0.5}B_{0.5}P$ < $Ga_{0.25}B_{0.75}P$ < BP, this result indicates that as the composition x increases, the compressibility of compound decreases, this is due to that the mass of B atom is lower than that of Ga atom.

Usually, in ternary alloy problems, it is assumed that the atoms are located at the ideal lattice sites and the lattice constant varies linearly with the composition x as Vegard's law [23]:

$$a(A_xB_{1-x}C) = xa_{AC} + (1-x)a_{BC} \tag{6}$$

where a_{AC} and a_{BC} are the equilibrium lattice constants of the binary compounds AC and BC, respectively, and $a(A_xB_{1-x}C)$ is the alloy lattice constant. However, the deviation from Vegard's law has been observed in semiconductor alloys both experimentally [24] and theoretically [25,26]. Hence, other relation has been proposed:

$$a(A_xB_{1-x}C) = xa_{AC} + (1-x)a_{BC} - x(1-x)b \tag{7}$$

where b is the bowing parameter. Based on this idea, the calculated lattice constants are fitted to a quadratic equation en function of composition x, which is:

$$a(x) = 5.4003 - 0.4851x - 0.4069x^2 (LDA) \tag{8}$$

$$a(x) = 5.5127 - 0.4839x - 0.4629x^2 (PBE) \tag{9}$$

$$a(x) = 5.4495 - 0.4961x - 0.4171x^2 (WC) \tag{10}$$

$$a(x) = 5.4476 - 0.4838x - 0.4274x^2 (PBESol) \tag{11}$$

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