First principles calculations of structural, electronic and optical properties of BAs\textsubscript{1-x}P\textsubscript{x} alloy.

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Abstract

We present first principles calculations of the structural, electronic and optical properties of boron ternary alloy BAs\textsubscript{1-x}P\textsubscript{x}, using a hybrid full-potential (linear) augmented plane wave plus local orbitals (L/APW +lo) method within the density-functional theory (DFT). The generalized gradient approximation (GGA) was used as well as the Engel-Vosko GGA formalism to calculate the band gap. We investigated the effect of composition on lattice constants, bulk modulus and band gap. Deviations of the lattice constants from Vegard’s law and the bulk modulus from linear concentration dependence (LCD) were observed for the alloy. Using the approach of Zunger and co-workers, the microscopic origins of the gap bowing were explained. For the optical properties, the compositional dependence of the refractive index and the dielectric constant was studied.

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1. Introduction

Boron compounds have attracted increasing research interest over the past few years, as wide gap semiconductors. These materials are of great technological interest for high temperatures, electronic and optical applications [1-9]. The electronic valence configuration is 1s\textsuperscript{2}2s\textsuperscript{2}2p\textsuperscript{1} for boron atoms and ns\textsuperscript{2}np\textsuperscript{3} for the group V elements. They crystallize at low pressure in the four-fold coordinated zinc-blende structure. Semiconductor alloys, which are solid solutions of two or more semiconducting elements, have important technological applications, especially in the manufacture of electronic and electro-optical devices [10]. One of the easiest ways to change artificially the electronic and optical properties of semiconductors is by forming their alloys; it is then interesting to combine two different compounds with different optical band gaps and different rigidities in order to obtain a new material formulation with intermediate properties.

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Several studies have been devoted to BSb, BP and BAs such structural, electronic and optical properties. Using the plane-wave basis sets and pseudopotential approximation (PWPP) within LDA, the ground state and the high-pressure properties have been calculated by Wentzcovich et al. [2, 3] for BP and BAs, and by Ferhat et al. [5] and Zaoui et al. [8]. A comparative study of the structural and electronic properties of the series BP, BAs and BSb has been presented by Bouhafs et al. [4, 7] using the same approach. Using the FP-LAPW method and LDA approximation for the exchange correlation potential, the optical properties under hydrostatic pressure of these compounds have been reported by Zaoui et al. [9]. Recently Elhajhassan et al. [11, 12] have calculated the structural, electronic and thermodynamic properties of boron ternary alloys using the FP-LAPW method. Hence, in order to exploit fully these materials for new optical devices, the structural, electronic and optical properties of these alloys need to be investigated in more detail. Therefore, the purpose of this paper is to study the structural, electronic and optical properties by using full-potential (linear) augmented plane wave plus local orbitals (LAPW +l0) method. The physical origins of gap bowing were investigated by following the approach of Zunger et al. [13]. In this approach, the alloy is studied in an ordered structure (we used a cubic supercell of eight atoms) designed to reproduce the most important pair correlation functions of a random (disorder) alloy and where the chemical and structural effects are captured very well.

The paper is organized as follows. In section 2, we describe the computational details. Results and discussion concerning the structural, electronic and optical properties are presented in section 3. Paper is concluded in section 4.

2. Calculations

In the present work, first-principles calculations of structural, electronic and optical properties of boron ternary alloy BAs1−xPx have been performed using the Vienna package wien2k [14]. This is an implementation of a hybrid full-potential (linear) augmented plane wave plus local orbitals (LAPW +l0) method within the density-functional theory [15, 16]. This new approach is shown to reproduce the accurate results of the LAPW method, but using a smaller basis set size. Due to the smaller basis set and faster matrix set up, “APW +l0” offers a shorter run time and uses less memory than LAPW.

The APW +l0 method expands the Kohn-Sham orbitals in atomic like orbitals inside the atomic muffin-tin (MT) spheres and plane waves in the interstitial region. The details of the method have been described in the literature [17-19]. For the exchange and correlation potential, we use the generalized gradient approximation (GGA) with a parameterization of Perdew-Burke- Ernzerhof [20]. For the electronic properties, in addition to the GGA correction, Engel-Vosko’s (EVTGG) formalism [21] was also applied. Basis functions, electron densities and potentials were expanded inside the muffin-tin spheres in combination with spherical harmonic functions with a cut off ℓmax = 10, and in Fourier series in the interstitial region. We use a parameter RMT Kmax = 8 which determine matrix size, where RMT denotes the smallest atomic sphere radius and Kmax gives the magnitude of the largest K vector in the plane wave expansion. The charge density was Fourier expanded up to Gmax = 14. All of the calculations were carried out at the theoretical equilibrium lattice constants. The muffin-tin radii of B, As, and P were chosen equal 1.5, 2.0 and 2.0 a.u. respectively. A mesh of 55 special k-points for binary compounds and 27 special k-points for alloy were taken in the irreducible wedge of the brillouin zone for the total energy calculation.

3. Results

3.1. Structural properties

In this section, we compute the structural properties of the binary compounds BP and BAs and their ternary alloy using the GGA scheme. Then, we model the alloy at some selected compositions with ordered structures described in terms of periodically repeated supercells with eight atoms per unit cell, for the the compositions x = 0.25, 0.5, 0.75. The calculated total energies at many different volumes around equilibrium were fitted by the Murnaghan’s equation of state [22] in order to obtain the equilibrium lattice constant and the bulk modulus for the binary compounds and their alloy. Table 1 summarizes the results of our calculations and compares them with other experimental and theoretical predictions. Considering the general trend that the GGA usually overestimates the lattice parameters [8], our GGA results of binary compounds are in reasonable agreement with the experimental and
other theoretical calculated values. Usually in the treatment of alloys, it assumed that the atoms are located at the ideal lattice sites and the lattice constant vary linearly with composition \( x \) according to the Vegard’s law [24]. However, violation of this linear law has been reported in semiconductor alloy both experimentally [25] and theoretically [26]. The variation of the lattice parameter versus P concentration is seen to be non linear. We display in Fig.1 the variation of the calculated equilibrium lattice constant versus concentration of the alloy under investigation which exhibits a visible deviation from Vegard’s law with an upward bowing parameter equal to \( -0.027 \) Å. The physical origin of this small deviation should be mainly because of the weak mismatches of the lattice constants of the binary compounds.

Figure 2 shows the bulk modulus as a function of \( x \) for the alloy. A significant deviation from LCD (linear concentration dependence) with downward bowing equal to 3.428 GPa was observed. Our results show that the bulk modulus increases with increasing the P concentration ( \( 0 \leq x \leq 1 \) ). This suggests that as \( x \) increases from \( x = 0 \) (BAs), to \( x = 1 \) (BP), BAs\(_{1-x}\)P\(_x\) becomes generally more compressible.

3.2. Electronic properties

The calculated band structures energies of binary compounds and their alloy using both GGA and EVGGA schemes indicate an indirect band gap near \( X \rightarrow \Delta_{\text{min}} \) in the whole range of concentrations. The results are presented in Table 2. The values obtained for the band gap of binary compounds within EVGGA are in better agreement with available experimental results in comparison with the values calculated by GGA. It is well known that GGA usually underestimates the energy gap [30, 31]. This is mainly due to the fact that the functionals within this approximation have simple forms that are not sufficiently flexible to accurately reproduce both exchange-correlation energy and its charge derivative. Considering this shortcoming, Engel and Vosko constructed a new functional form of GGA that is able to reproduce better exchange potential at the expense of less agreement in exchange energy. This approach which is called EVGGA yields a better band splitting and some other properties which mainly depend on the accuracy of exchange-correlation potential. On the other hand, in this method, the quantities which depend on an accurate description of \( E_s \) such as equilibrium volumes and bulk modulus are in poor agreement with experiment.

Figure 3 shows the composition dependence of the calculated band gaps using GGA and EVGGA schemes. We calculated the gap bowing by fitting the non linear variation of the calculated band gaps versus concentration with quadratic function. The results are shown in Fig.3 and obey the following variations:

\[
\begin{align*}
\text{BAs}_{1-x}\text{P}_x &\Rightarrow \\
E_{\text{GGA}}^G(x) &= 1.201 + 0.093x - 0.041x^2 \\
E_{\text{EVGGA}}^G(x) &= 1.819 + 0.098x - 0.041x^2
\end{align*}
\]

(1)

The calculated band gap bowing parameter exhibits a weak composition dependence. In order to better understand the physical origins of the gap bowing in our alloy, we follow the procedure of Bernard and Zunger [32], and decompose the bowing parameter \( b \) into physically distinct contributions. By considering the fact that the bowing dependence on the composition is marginal, the authors limited their calculations to \( x = 0.5 \) (50%-50% alloy). The overall gap bowing at \( x = 0.5 \) measures the change in band according to the reaction:

\[
\text{AB}(\text{a}_{\text{AB}}) + \text{AC}(\text{a}_{\text{AC}}) \rightarrow \text{AB}_{0.5}\text{C}_{0.5}(\text{a}_{\text{eq}})
\]

(2)
Fig 1: Composition dependence of the calculated lattice constant of BAs$_{1-x}$P$_x$ alloy (filled squares) compared with Vegard's law (dotted line).

Fig 2: Composition dependence of the calculated bulk modulus of BAs$_{1-x}$P$_x$ alloy (filled squares) compared with the linear composition dependence prediction (dotted line).

Table 1: Calculated lattice parameter (a) and bulk modulus (B) for BAs$_{1-x}$P$_x$ alloy and its binary compounds. Available experimental and theoretical data from the literature are also included for comparison.

<table>
<thead>
<tr>
<th>( x )</th>
<th>Lattice constant ( a ) (Å)</th>
<th>Bulk Modulus B (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This work</td>
<td>Experiment</td>
</tr>
<tr>
<td>1</td>
<td>4.554</td>
<td>4.538$^*$</td>
</tr>
<tr>
<td>0.75</td>
<td>4.624</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>4.690</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>4.752</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>4.812</td>
<td>4.777$^g$</td>
</tr>
</tbody>
</table>

$^* \text{Ref [23]}, ^b \text{Ref [8]}, ^f \text{Ref [6]} \text{ and } ^g \text{Ref [7]}.$

where \( a_{AB} \) and \( a_{AC} \) are the equilibrium lattice constants of the binary compounds AB and AC, respectively; and \( a_{eq} \) the alloy equilibrium lattice constant. We now decompose reaction (2) into three steps:
The first step measures the volume deformation (VD) effect on the bowing. The corresponding contribution to the total gap bowing parameter \( b_{VD} \) represents the relative response of the band structure of the binary compounds AB and AC to hydrostatic pressure, which here arises from the change of their individual equilibrium lattice constants to the alloy value \( a = a(x) \) (from Vegard’s rule). The second contribution, the charge-exchange (CE) contribution \( b_{CE} \) reflects a charge transfer effect which is due to the different (averaged) bonding behaviour at the lattice constant \( a \). The final step measures changes due to the structural relaxation (SR) in passing from the unrelaxed to the relaxed alloy by \( b_{SR} \). Consequently, the total gap bowing parameter is defined as:

\[
b = b_{VD} + b_{CE} + b_{SR}
\]

\[
b_{VD} = 2\left[ E_{AB}(a_{AB}) - E_{AB}(a) + E_{AC}(a_{AC}) - E_{AC}(a) \right]
\]

\[
b_{CE} = 2\left[ E_{AB}(a) + E_{AC}(a) - 2E_{AC}(a) \right]
\]

\[
b_{SR} = 4\left[ E_{ABC}(a) + E_{AC}(a) - E_{ABC}(a_{eq}) \right]
\]

Where \( \varepsilon \) is the energy gap which has been calculated for the indicated atomic structures and lattice constants. Energy gaps terms in Eqs (7)-(9) are calculated separately with self-consistent band structure approach FP-LAPW and the results are given in Table 3.

The total gap bowing is found to be marginal for the BA\(_{1-x}P_x\). The small \( b_{CE} \) value is due to the weak ionicity mismatch of BP and BAs (f \( = 0.006 \) and 0.002 for BP and BAs respectively). In the same way, the weak contribution of \( b_{VD} \) can be correlated to the small mismatch of the lattice constants of the corresponding binary compounds. Finally, it is clearly seen that the GGA and EVGGA values for the bowing parameter are almost identicals.

### 3.3. Optical properties

Optical properties of a solid are usually described in terms of the complex dielectric function \( \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \). The imaginary part of the dielectric function in the long wavelength limit has been obtained directly from the electronic structure calculation, using the joint density of states and the optical matrix elements. The real part of the dielectric function can be derived from the imaginary part by the Kramers-Kronig relationship. The knowledge of both the real and the imaginary parts of the dielectric function allows the calculation of important optical functions. In this paper, we also present and analyse the refractive index \( n(\omega) \), given by

\[
n(\omega) = \sqrt{\frac{E_1(\omega)}{2} + \sqrt{\frac{E_1^2(\omega) + E_2^2(\omega)}{2} + \gamma^2}}
\]

At low frequency (\( \omega=0 \)), we get the following relation:

\[
n(0) = \varepsilon_0^{1/2}(0)
\]

A few empirical relations [33, 34] relate the refractive index to the energy band gap for a large set of semiconductors. The following models are used:

1. The Moss formula [33] based on atomic model:

\[
E_g n^4 = k
\]
Table 2: Indirect band gap energy $E_g$ (in eV) for $\text{Ba}_{1-x}\text{P}_x$ at various x compositions.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$E_g$ (eV)</th>
<th>This work</th>
<th>Experiment</th>
<th>other calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>GGA</td>
<td>EVGGA</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.254</td>
<td>1.877</td>
<td>2.44</td>
<td>1.12$^a$, 1.14$^d$</td>
</tr>
<tr>
<td>0.75</td>
<td>1.247</td>
<td>1.867</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>1.238</td>
<td>1.861</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0025</td>
<td>1.221</td>
<td>1.839</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.201</td>
<td>1.820</td>
<td>0.67$^j$</td>
<td>1.06$^c$, 1.25$^e$</td>
</tr>
</tbody>
</table>

$^a$Ref [27], $^b$Ref [7], $^c$Ref [28], $^d$Ref [29] and $^e$Ref [1]

Table 3: Decomposition of optical bowing into volume deformation (VD), charge exchange (CE) and structural relaxation (SR) contributions compared with the optical bowing obtained by a quadratic interpolation (all values are in eV).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Calculation</th>
<th>Quadratic fits</th>
<th>other works</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GGA</td>
<td>EVGGA</td>
<td>GGA</td>
</tr>
<tr>
<td>$b_{VD}$</td>
<td>-0.061</td>
<td>-0.034</td>
<td></td>
</tr>
<tr>
<td>$b_{CE}$</td>
<td>0.042</td>
<td>0.013</td>
<td></td>
</tr>
<tr>
<td>$b_{SR}$</td>
<td>-0.024</td>
<td>-0.031</td>
<td></td>
</tr>
<tr>
<td>$b$</td>
<td>-0.043</td>
<td>-0.052</td>
<td>-0.041</td>
</tr>
</tbody>
</table>

$^a$Ref [11]

where $E_g$ is the energy band gap and $k$ a constant. The value of $k$ is given to be 108 eV by Ravindra and Srivastava [33].

2. Herve and Vandamme’s empirical relation [34]

$$n = \left[ 1 + \left( \frac{A}{E_g + B} \right)^2 \right]^{1/2}$$

(13)

with $A=13.6$ eV and $B=3.4$ eV.

In Table 4, we summarize the calculated values of the refractive index for the alloy under investigation for some compositions, $x$, obtained by using the L/APW +lo method and the different models. Comparison with the available data has been made where possible.
It is clear that the values of the refractive index obtained from full potential calculations agree well with those obtained from the other models. Figure 5 shows the variation of the calculated refractive index versus concentration for the alloy. Through Figure 4, one can notice that the refractive index decreases monotonically with increasing P content over the entire range of 0-1 for both L/APW+Lo and models used. The calculated refractive indices versus concentration were fitted by a polynomial equation. The results are summarized as follows:

\[ n(x) = 3.121 - 0.087x - 0.029x^2 \quad (L/APW+Lo) \]  
\[ n(x) = 3.078 - 0.057x + 0.025x^2 \quad (relation\,12) \]  
\[ n(x) = 3.120 - 0.054x + 0.022x^2 \quad (relation\,13) \]

Form these equations, we can note the weak nonlinear dependence of the refractive index of the alloy with concentration \( x \). Interestingly, we note on going from BAs to BP, the band gap of BAs\(_{1-x}\)P\(_x\) increases (see Figure 3) whereas, the refractive index decreases, therefore indicating that the ternary system BAs\(_{1-x}\)P\(_x\), shows that the smaller band gap material has a large value of the refractive index as generally many other groups III-V compound semiconductors alloys do [37].

The dielectric function has been estimated according to expression (11). The results are given in Table 5. Qualitatively, the compositional dependence of the dielectric function of the alloy has the same trend as that of the refractive index. This is not surprising as the dielectric function is directly calculated from relation (11).

![Figure 4](image)

**Table 4:** Refractive indices of BAs\(_{1-x}\)P\(_x\) for different compositions \( x \).

<table>
<thead>
<tr>
<th>Composition</th>
<th>( n ) (calculated using L/APW+Lo method)</th>
<th>( n ) (calculated from relation 12)</th>
<th>( n ) (calculated from relation 13)</th>
<th>Other works</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.120</td>
<td>3.079</td>
<td>3.120</td>
<td>3.35(^a)</td>
</tr>
<tr>
<td>0.25</td>
<td>3.104</td>
<td>3.066</td>
<td>3.108</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>3.063</td>
<td>3.056</td>
<td>3.098</td>
<td></td>
</tr>
<tr>
<td>0.75</td>
<td>3.044</td>
<td>3.050</td>
<td>3.092</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3.004</td>
<td>3.046</td>
<td>3.088</td>
<td>3.25(^a), 3.1(^b)</td>
</tr>
</tbody>
</table>

\(^a\) Ref [35]. \(^b\) Ref [36]

**Table 5:** Optical dielectric constants of BAs\(_{1-x}\)P\(_x\) for different compositions \( x \).

<table>
<thead>
<tr>
<th>Composition</th>
<th>( \varepsilon ) (calculated using L/APW+Lo method)</th>
<th>( \varepsilon ) (calculated from relation 12)</th>
<th>( \varepsilon ) (calculated from relation 13)</th>
<th>Other works</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>9.740</td>
<td>9.480</td>
<td>9.737</td>
<td>11.19(^c)</td>
</tr>
<tr>
<td>0.25</td>
<td>9.639</td>
<td>9.404</td>
<td>9.660</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>9.386</td>
<td>9.337</td>
<td>9.595</td>
<td></td>
</tr>
<tr>
<td>0.75</td>
<td>9.269</td>
<td>9.303</td>
<td>9.562</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>9.030</td>
<td>9.280</td>
<td>9.539</td>
<td>10.55(^c), 11.0(^c)</td>
</tr>
</tbody>
</table>

\(^c\) Ref [23]. \(^d\) Ref [36]
4. Conclusion

We have studied the structural, electronic, thermodynamic and optical properties of BAs$_{1-x}$P$_x$ ternary alloy using the L/APW +l method. A summary of the key findings follows.

The lattice constant of the alloy exhibits a small deviation from Vegard’s law with bowing parameter equal to -0.027 Å.

A significant deviation of the bulk modulus from LCD was found for the alloy. As the P content increases, BAs$_{1-x}$P$_x$ becomes generally less compressible.

The gap bowing is found to be marginal for BAs$_{1-x}$P$_x$ alloy. This should be expected since there is a weak lattice mismatch and a weak ionicity difference between BP and BAs compounds.

A weak non-linear dependence of the refractive index and the dielectric constant has been observed.

References