Band gap behavior of thallium phosphide and gallium phosphide binary compounds and Ga$_x$ Tl$_{1-x}$ P ternary alloys

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Abstract. Full-potential linear muffin-tin orbitals method has been implanted within density functional theory and within local density approximation. The structural and electronic properties of GaP and TlP binary compounds and their ternary alloys Ga$_x$ Tl$_{1-x}$ P ($x=0.25$, 0.5 or 0.75) in the zinc-blende structure were investigated and calculations obtained results gave reasonable agreements with other published data.

1. Introduction

III–V semiconductor compounds have been extensively studied theoretically and experimentally during the last half century. Over many years, this family of semiconductors has demonstrated its potential for applications in optoelectronic devices (light-emitting diodes, laser diode, gas captors, solar cells), and devices in hostile environments (high temperatures, high frequency) with high performances [1–17].

The III–phosphide binary compounds appear as promising materials among the family of III–V semiconductors. At ambient conditions, these compounds crystallize in the zinc-blende structure and have an indirect band gap [18–32] apart from InP [33]. However, the weak optical transition in indirect gap materials, such as GaP, is a major limitation for their use in optical devices. The radiative transition in these materials is accompanied by phonon emission and the oscillator strength of such transitions is, therefore, inferior compared to the direct band-gap semiconductors such as GaAs [34]. Thus, the investigation about new materials, allowing the design and the construction of new optoelectronic devices, motivates our work with the aim of proposing new materials. These new semiconductor alloys exhibit a range of unexpected characteristics. Particularly, We have aimed to combine GaP to TlP since they possess different structural and electronic properties, in order to obtain new materials consisting in Ga$_x$ Tl$_{1-x}$ P ternary alloys with intermediate properties.

It is expected that TlP crystallizes most probably in the zinc-blende (B3), with a semi-metallic behavior in this phase [35]. However, GaP may have an indirect band gap in the zinc blende (B3) phase [36].

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In order to take full advantage of the properties of these compounds for possible technological applications, a theoretical investigation of the structural and electronic properties is necessary. For this purpose, we used the first-principles method to investigate the structural and electronic properties of the binary compounds GaP and TlP and their ternary alloys Ga<sub>x</sub>Tl<sub>1-x</sub>P (x = 0.25, 0.5 or 0.75) in the zinc-blende structure, using the state of the art Full-Potential Linear Muffin-Tin Orbital (FP-LMTO) method, in the framework of the Density Functional Theory (DFT), within the Local Density Approximation (LDA) for the exchange correlation functional.

In the following, we briefly describe the used method and the detailed calculations, and results of the structural and electronic properties of the studied binary and ternary compounds are then presented and discussed.

2. Calculation methodology

The calculations reported in this work were carried out using the FP-LMTO method [37, 38]. It consists in an implementation of the DFT, which is a universal quantum mechanical approach for many-body problems. In the latter, the quantum many-body problems of interacting electrons and nuclei can be mapped onto a system of one-electron equations called Kohn-Sham equations [39, 40]. In this method, the space is divided into an interstitial region (IR) and non-overlapping (MT) spheres centered at the atomic sites. In the IR region, the basis set consists of plane waves. Inside the MT spheres, the basis set is described by radical solutions of the one particle Schrödinger equation (at fixed energy) and their energy derivatives multiplied by spherical harmonics.

In order to achieve energy eigenvalues convergence, the charge density and potential inside the muffin-tin spheres are represented by spherical harmonics up to l<sub>max</sub>=6. The exchange-correlation potential is treated within the local density approximation developed by Perdew–Wang [41]. The self-consistent calculations are considered to be converging when the total energy of the system is stable within 10<sup>-5</sup> Ry. The k integration over the Brillouin zone is performed using the tetrahedron method [42].

3. Results and discussion

3.1. Structural properties

The majority of III-V compound semiconductor materials have a zinc blende crystal lattice structure. The zinc blende structure consists of two interpenetrating face centered cubic (FCC) sub-lattices, one containing group III atoms and the other containing group V atoms. The two sub-lattices are shifted relative to each other by (a/4,a/4,a/4) where a is the cubic lattice constant. In this subsection, we calculate the structural properties of the compounds GaP and TlP and their alloys in the cubic structure. The considered semiconductor ternary alloys are of the type B<sub>x</sub>A<sub>1-x</sub>C having the basic cubic cell as the unit cell, in which there are four C anions and three A and one B, two A and two B, or one A and three B cations (respectively for x = 0.25, 0.50 or 0.75). We have started our FP-LMTO calculations of the structural properties with the zinc-blende structure and let the calculation forces to move the atoms to their equilibrium positions.

For the considered structures, we perform the structural optimization by calculating the total energies for different volumes around the equilibrium cell volume V<sub>0</sub> of the binary GaP and TlP compounds and their alloys. The calculated total energies are fitted to the Birch's equation of state [43] to determine the ground state properties such as the equilibrium lattice constant a<sub>0</sub>, the bulk modulus B<sub>0</sub> and its pressure derivative B<sub>0</sub>′. The calculated equilibrium parameters (a<sub>0</sub>, B<sub>0</sub> and B<sub>0</sub>′ are given in table 1). We remark that our results for GaP and TlP agree well with literature values; however, comparison was not always possible for ternary alloys phase because of the lack of data in the literature.
3.2. Electronic properties

The calculated band structure energies of binary compounds as well as their alloys using the FP-LMTO method within the LDA approximation along the higher symmetry directions of Brillouin zone are shown in figures 1 and 2. From these figures, we remark an indirect band gap at the $\Gamma$-X point for GaP and a negative band gap for TlP. For Ga$_{0.75}$Tl$_{0.25}$P and Ga$_{0.5}$Tl$_{0.5}$P, both valence band maximum (VBM) and the conduction Band minimum (CBM) are located at the $\Gamma$ point, predicting a direct transition. Nevertheless, for Ga$_{0.25}$Tl$_{0.75}$P, one can clearly see the semi metallic nature of this compound. The important features of the band structure (main band gaps) are given in table 1.

Table 1. Calculated lattice constants $a_0$, bulk modulus $B_0$ first derivatives $B'_0$ and gap energies $\Delta E$ for Ga$_x$Tl$_{1-x}$P compounds for $x = 0.25, 0.50$ or $0.75$.

| $x$ | $a_0$ (Å)          | $B_0$ (GPa)  | $B'_0$ | $\Delta E$ (eV) | Transition type |
|-----|--------------------|-------------|--------|----------------|----------------|
| 0   | Calculated         | Literature  | Calculated | Literature | | |
|     | 6.3                | 6.12        | 42     | 46.75        | 4.67           | -              |
|     | [35]               | [35]        |        |              |                |                |
| 0.25| 5.9                | 58.42       | 3.98   |              |                | -              |
| 0.5 | 5.78               | 59          | 4.27   |              | 0.37           | Direct ($\Gamma$- $\Gamma$) |
| 0.75| 5.61               | 66.15       | 4.4    |              | 0.87           | Direct ($\Gamma$- $\Gamma$) |
| 1   | 5.43 [36]          | 91.15 [36]  | 3.6    | 3.6          | 1.5            | Indirect ($\Gamma$-X) |

Figure 1. Band structure along the symmetry lines of the Brillouin zone at the equilibrium lattice constant for the (B3) structure for the binary alloys GaP (left graph) and TlP (right graph). The horizontal blue line shows the position of the Fermi level.
Figure 2. Band structures along the symmetry lines of the Brillouin zone at the equilibrium lattice constant for the (B3) structure for the Ga\textsubscript{x} Tl\textsubscript{1-x} P ternary alloys (a) Ga\textsubscript{0.25} Tl\textsubscript{0.75} P, (b) Ga\textsubscript{0.5} Tl\textsubscript{0.5} P and (c) Ga\textsubscript{0.75} Tl\textsubscript{0.25} P. The horizontal blue line shows the position of the Fermi level.

4. Conclusions

Full-potential linear muffin-tin method was used to investigate structural and electronic properties of the ternary alloys Ga\textsubscript{x} Tl\textsubscript{1-x} P. The lattice constants of these ternary alloys is correlated with increasing Tl concentration, but the bulk modulus is correlated inversely with increasing Tl concentration. Moreover, the gap energies of GaP and TlP binary compounds and their ternary alloys Ga\textsubscript{x} Tl\textsubscript{1-x} P are decreasing rather linearly as Tl concentration increases. When compared with other published data, our calculated results gave an impetus for further application studies in optoelectronics, light-emitting diodes, laser diode, gas captors and solar cells.

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