First-principles investigation of structural and electronic properties of \( \text{Tl}_x\text{Al}_{1-x}\text{P} \) ternary alloys

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ABSTRACT
In this study, the structural and electronic properties of semiconductor \( \text{Tl}_x\text{Al}_{1-x}\text{P} \) alloys were derived from minimum total energy by using Density Functional Theory with Local Density Approximation. A 16 atom supercell was used to model the ternary \( \text{Tl}_x\text{Al}_{1-x}\text{P} \) alloys. The lattice constant, electronic band gap energies and bowing parameters was examined. The lattice constant of the \( \text{Tl}_x\text{Al}_{1-x}\text{P} \) alloys comply well with Vegard’s law. Also, the polynomial equation of concentration dependent electronic band gap energy of the \( \text{Tl}_x\text{Al}_{1-x}\text{P} \) is \( E_g(x) = 2.02693x^2 - 2.17819x - 1.15118x + 1.29644 \) (eV). Electronic band gap bowing parameters vary depending on the Thallium concentration value. It was concluded that the average bowing parameter of \( \text{Tl}_x\text{Al}_{1-x}\text{P} \) alloys was \( b = 1.1649 \) eV.

1. Introduction

Although naive Thallium is toxicological [1], Thallium-containing alloys have been committed as encouraging materials for implementations in the optical communication system [2]. Thallium-containing alloys status for nanotechnological applications were investigated with experimental and theoretical studies [3–7]. There are many studies in the literature on the suitability of Ti-containing alloys as photo detectors [8–11]. Alloys composed of III-V compounds containing thallium are alternative materials for photodetectors operating in the infrared region [7,12,13]. Thallium is used in bearing shafts as it has good wear resistance. Thallium-containing alloys are important materials in the electronics industry for soldering materials, rectifiers and bearing [14]. Schilfgaarde et al. [7] and Krishnamurthy et al. [15] conducted studies on \( \text{TlInP} \), \( \text{TlInAs} \) and \( \text{TlInSb} \). Yamamoto et al. [12] produced \( \text{TlGaAs} \) and \( \text{TlInAs} \) by the molecular beam epitaxy method. Said-Houat et al. [2] and Dantas et al. [3] revealed theoretical studies on \( \text{AlInN} \), \( \text{GaInN} \), \( \text{TIP} \), \( \text{TIN} \), \( \text{TiAs} \), \( \text{TiSb} \) and \( \text{TIBi} \) studies were carried out using density functional theory [16–19]. Mankefors and Svensson [13] investigated ab initio calculations of \( \text{Ga}_{1-x}\text{Tl}_x\text{As} \) alloys. They examined the dependence of lattice constant, electronic band gap and bowing parameter on Thallium concentration. Koh et al. [5] studied photoconductivity measurement and temperature changes of band gap energies for \( \text{TlInP} \), \( \text{TlGaP} \) and \( \text{TlInGaP} \). Gulebaglan et al. [20] calculated the structural and electronic properties of zincblende new semiconductor \( \text{Tl}_x\text{Ga}_{1-x}\text{As}_{y}\text{P}_{1-y} \) quaternary alloys. Bilege Akyuz et al. [21] investigated bowing parameter of \( \text{Tl}_x\text{Ga}_{1-x}\text{As} \) ternary alloys. Yildiz Tunali et al. [22] reported the structural and electronic properties of zincblende \( \text{Ga}_x\text{Th}_{1-x}\text{P} \) alloys. Meynoian et al. experimentally investigated the electro-optical properties of “Thallium aluminium-codoped zinc oxide” materials [23]. Salem and Abdulwahed prepared single crystals thallium bismuth diselenide and declared electrical properties of \( \text{TlBiSe}_2 \) [24]. Khon et al. experimentally investigated and reported the electronic, thermal and transport properties of the \( \text{TlPbSbTe} \) alloy [25].

Investigations using density functional theory can be used to support experimental studies. Apart from this, even if a compound or alloy has not been synthesized yet, it can be a source for experimental or engineering studies by determining many properties. For this reason, some properties of \( \text{Tl}_x\text{Al}_{1-x}\text{P} \) alloys, which have not been synthesized yet, have been investigated.

Density functional theory is a method used to determine the properties of atoms, molecules, and crystal structures. The discovery of new materials or in the design of materials knowledge of the properties of the material that provide the calculation time and budget savings. So it is important to have knowledge about crystal structures before working in the laboratory. The approximations used to define the exchange and correlation term in calculations using density functional theory are local density approximation (LDA) [26] and generalized gradient approximation (GGA) [27]. The structural and electronic properties of many crystals
have been investigated using these approximations [28–31]. However, the approximations used in the studies made with the density functional theory have been tried to be developed by the researchers. For example, local density approximation plus the multi-orbital mean-field Hubbard model (LDA+U) and Fermi-Löwdin orbital self-interaction correction (Flo-SIC) approach. There are studies in which studies are conducted using the approximations developed in the literature [32–34]. With these developed approximations, studies examining the electronic properties of crystal structures have been brought to the literature [35–37].

In this present work, the structural and electronic properties of the TiAl−xP have been studied using density functional theory. The plan of the current study is as follows: A description of the computational method is given in Section 2. Then, the lattice constant and energy band structures and bonding parameters of TiAl1−xP alloys are examined in Section 3. Finally, a short result of this study is given in Section 4.

2. Computational method

In preparing this study, structural and electronic properties of TiAl1−xP alloys in Zincblende structure were investigated by using Local Density Approximation [26] with Quantum Espresso program [38]. Electron-ion interactions were identified by ultrasoft pseudopotentials and the cut-off energy was tested with these pseudopotentials. The wave functions were selected as a cut off 60 Ry on a plane wave basis. This cut-off energy value was used in the TiAl1−xP alloys performed using the standard special k-points technique of Monkhorst and Pack [39]. This a 12 × 12 × 12 lattice was used during the investigations. The selected plane-wave cut-off energy and k-point number were carefully checked to ensure the minimum of total energy. Supercell containing 16 atoms were used for TiAl1−xP alloys. 2 × 2 × 2 classical Zincblende cubic cells corresponding to the 16 atom supercell were applied. There are different atomic configurations which need to be structurally optimized. Similar results were obtained by calculating the electronic band gap energy for entire configuration. In this way, the average effect of the doped was examined. Starting with the maximum AIP clustered configuration, the Aluminum atoms were removed from the clusters one at a time and Thallium atoms were added one by one to produce a clustered alloy. Atomic coordinates for each Thallium percentage were relaxed. In addition, Ti (4f145d106s26p1), Al (3s2 3p1) and P (3s2 3p3) orbitals as valence electrons, it was discussed. Spin-orbital interactions were not insert account in the calculations. The mean error value of the energy obtained during the calculations process is lower than 10.10−8 Ry. This ensures high accuracy results.

3. Results and discussion

First, the structural and electronic properties of the compounds of TIP and AIP were examined. The ground states of the binary compounds TIP and AIP are the structure in Zincblende (B3) and the space group is F43m (216). The total energies of TIP and AIP were calculated as a function of volume in the Zincblende phase using plane wave pseudopotentials. The energy volume curve is fit to the Vinet [40] equation. Then the lattice constants and bulk modulus are obtained for TIP and AIP. All investigated values are in good agreement with the previous calculations. These values are given in Table 1.

The calculated lattice constant value of TIP and AIP are 5.933 and 5.41 Å, respectively. According to these results, it was seen that there is a difference of 0.11% and 0.7% between lattice parameters calculated with other theoretical results [41,43] for TIP and AIP compounds, respectively. This difference is acceptable. The value of the lattice parameter calculated for AIP compound is very close to the experimental value [43]. Since TIP has not yet been synthesized, it has not been experimentally compared. The electronic properties calculations give an electronic band gap of 1.42 eV for AIP and 0.0 eV for TIP. The result of AIP is in agreement other theoretical and experimental results and the result of another compound, TIP, is agreement other theoretical results. The experimentally obtained electronic band gap of the TIP compound is not yet available. These values are given in Table 2. The investigated electronic band structures are plotted in Figures 1 and 2 for TIP and AIP, respectively.

The atomic coordinates of AIP compound in the Zincblende phase are Al (0.0 0.0 0.0) and P (0.25 0.25 0.25). If the AIP compound is grown to 2 × 2 × 2, a super cell of 16 atoms is obtained. This structure continues to preserve the Zincblende structure. The crystal structure of the TiAl1−xP alloys formed, when Thallium is

| a (Å) | B (GPa) | B′ |
|-------|---------|----|
| TIP (Present Work) | 5.933 | 60.23 | 4.87 |
| TIP (41) | 6.001 | 53.3 | 4.5 |
| TIP (42) | 5.747 | 71.3 | 4.847 |
| AIP (Present Work) | 5.41 | 88.469 | 4.025 |
| AIP [43][Exp.] | 5.451 | 86 | |
| AIP [44] | 5.436 | 89 | 4.14 |

| AIP | TIP |
|-----|-----|
| Present Work | 1.42 | ~0.0 |
| Ref.[45] | 1.594 | |
| Exp.[46] | 2.5 | ~0.0 |
| Ref.[16] | ~0.0 | |
| Ref.[20] | ~0.0 | |
added to the material, the addition is made at the ratio of the number of Thallium atoms placed. In this case, starting from Vegard’s law \([47]\), the lattice constants of Tl\(_x\)Al\(_{1-x}\)P alloys can be expressed in relation to the Thallium doped ratio \((x)\). For this reason, calculations were made based on Vegard’s law for Tl\(_x\)Al\(_{1-x}\)P alloys in the ground state. The lattice constant of the Tl\(_x\)Al\(_{1-x}\)P alloys can be calculated by Vegard’s law as follows:

\[
a(x) = xa_{\text{TIP}} + (1 - x)a_{\text{AlP}}
\]

where \(a(x)\) is the lattice constant of Tl\(_x\)Al\(_{1-x}\)P, \(a_{\text{TIP}}\) is the lattice constant of TIP and \(a_{\text{AlP}}\) is the lattice constant of AlP.

The calculation was made for the case where the Thallium addition as a percentage was 0%, 12.5%, 25%, 37.5%, 50%, 62.5%, 75%, 87.5% and 100%.

The lattice constants of Zincblende Tl\(_x\)Al\(_{1-x}\)P alloys have been found to be almost directly proportional to the additive ratio \((x)\) to the alloy are shown in Figure 3.

For different concentration percentages, bond lengths between T1 and P atoms and bond lengths between Al and P atoms were calculated using the XCRYSDEN computer program \([48]\). These calculated values are listed in Table 3.

The electronic band gap energy of Tl\(_x\)Al\(_{1-x}\)P:

\[
E_g(x) = xE_g,\text{TIP} + (1 - x)E_g,\text{AlP} - bx(1 - x)
\]

can be expressed.

Here, \(E_g,\text{TIP}\) is the electronic band gap energy of TIP, \(E_g,\text{AlP}\) is the electronic band gap energy of AlP \(E_g(x)\) is the electronic band gap energy depending on the doped ratio of Tl\(_x\)Al\(_{1-x}\)P, and \(b\) is the electronic band gap bowing parameter of Tl\(_x\)Al\(_{1-x}\)P alloys.

Table 4 shows that a large reduction in the electronic band gap of the AlP is observed, depending on the concentration of Thallium. In addition, electronic energy band gap diagram of Tl\(_x\)Al\(_{1-x}\)P is shown in Figures 4–9.

First of all, it should be noted that the electronic properties of the AlP compound will be affected by the Tl doping. In this case, the electronic band gap will change. One of the aims of this study is to examine this change.

The electronic bowing parameter values obtained from each concentration are shown in Figure 10 and an average band gap bowing parameter of 1.1649 eV calculated from Equation (3) to 0 < \(x\) < 100. The result of the study showed that the Thallium concentration decreases, the electronic band gap of Tl\(_x\)Al\(_{1-x}\)P...
decreases. If the density of Thallium is high, the electron concentration in the alloy is higher, which further reduces the edge of the conduction band. The electronic band gap energy of the AlP binary structure is 1.415 eV, while 50% Thallium is added, which reduces the electronic band gap of the Tl\textsubscript{0.5}Al\textsubscript{0.5}P alloy to 0.5076 eV. As the doped percentage increased, the electronic band gap was calculated as 0.0 eV.

The electronic band gap value of the Tl\textsubscript{x}Al\textsubscript{1-x}P alloys’ structure decreases with the addition of Thallium as in the structure of Tl\textsubscript{x}Al\textsubscript{1-x}As. That is, the AlAs and AlP crystal structures react similar to Thallium doped [49]. These alloy materials are thought to be very useful in the construction of infrared optical devices.
Furthermore, it is recognized that the ternary alloys have a parabolic composition structure for the electronic band gap. The size of the parabolic factor is known as the bowing parameter. It is possible to define the linear bowing function from these results. This curve has the minimum value and the maximum value. Figure 10 shows the variation of the bowing parameter depending on the concentration ratio. As seen in Figure 10, the bowing parameter suddenly increases at $x = 0.25$ Thallium concentration. Shi et al. [50] investigated the variation of the concentration-dependent bowing parameter of the Tl$_x$Al$_{1-x}$N ternary alloys in the Wurtzite crystal structure. According to these results, if the value of the bowing parameter in the $x = 0.25$ Thallium contribution is compared with the value in the $x = 0.375$ Thallium contribution, an increase in the bowing parameter value is observed. However, when the bowing parameter value of $x = 0.375$ Thallium contribution and the value of the bowing parameter are compared with the $x = 0.5$ Thallium contribution, a decrease is observed in the value of the bowing parameter. This decrease continues as the Thallium doping value increases. In the Tl$_x$Al$_{1-x}$P alloys whose properties are predicted, it is thought that this shot and decrease in the bowing parameter is due to the electron concentration, as in the Tl$_x$Al$_{1-x}$N ternary alloys [42]. It is thought that Tl$_x$Al$_{1-x}$P alloy can be used in the design of optoelectronic devices.

Bowing parameter function $b(x)$,

$$b(x) = \frac{x E_{\text{g,TIP}} + (1-x) E_{\text{g,AlP}} - E_g(x)}{x(1-x)}$$  \hspace{1cm} (3)

can be expressed.

In order to understand the physical origins of the band gap and the bowing parameter depending on the doped quantity, it is necessary to physically divide $b$ into three parts. The bowing parameter is defined as the sum of these three parts:

$$b = b_{\text{VD}} + b_{\text{CE}} + b_{\text{SR}}$$  \hspace{1cm} (4)

Table 5. Changes of $b$, $b_{\text{VD}}$, $b_{\text{CE}}$ and $b_{\text{SR}}$ depending on Thallium concentration.

| $x$   | 12.5% | 25%  | 37.5% | 50%  | 62.5% | 75%  | 87.5% |
|-------|-------|------|-------|------|-------|------|-------|
| $b$   | 0.5397| 1.6253| 0.6484| 0.7996| 1.3974| 1.5266| 1.6170|
| $b_{\text{VD}}$ | -0.7406| -0.4664| -0.4627| -0.4516| -0.4379| -0.3325| -0.008 |
| $b_{\text{CE}}$ | 1.0021| 2.0918| 1.1111| 1.2512| 1.8354| 2.219| 1.6182|
| $b_{\text{SR}}$ | 0.2762| -0.0001| 0.0| 0.0| -0.0001| -0.3628| 0.0068|

The parts of this parameter are called volume deformation ($b_{\text{VD}}$), charge transfer ($b_{\text{CE}}$) and structural relaxation ($b_{\text{SR}}$). The term $b_{\text{VD}}$ refers to the response of AlP(TlP) from the equilibrium lattice constant $a_{\text{AlP}}(a_{\text{TIP}})$ to the alloy value $a(x)$ relative to the hydrostatic pressure. The second term $b_{\text{CE}}$ represent the charge transfer in AlP and TlP. The third term $b_{\text{SR}}$ describes the change of band gap in the transition from the non-relax alloy state to the relax alloy state.

$$b(x)$$ to calculate the doped ratio of the parts

$$b_{\text{VD}} = \frac{E_{\text{TIP}}(a_{\text{AlP}}) - E_{\text{TIP}}(a)}{1 - x} + \frac{E_{\text{AlP}}(a_{\text{AlP}}) - E_{\text{AlP}}(a)}{x}$$  \hspace{1cm} (5)

$$b_{\text{CE}} = \frac{E_{\text{TIP}}(a) - E_{\text{AlP}}(a)}{1 - x} + \frac{E_{\text{AlP}}(a) - E_{\text{TIP}}(a)}{x(1 - x)}$$  \hspace{1cm} (6)

$$b_{\text{SR}} = \frac{E_{\text{TIP}}(a) - E_{\text{TIP}}(a_{\text{eq}})}{x(1 - x)}$$  \hspace{1cm} (7)

The bowing parameter and its components ($b_{\text{VD}}$, $b_{\text{CE}}$, $b_{\text{SR}}$) are listed in Table 5.

4. Conclusion

Using the numerical simulation program with first-principles calculations, lattice constants of TIP and AlP binary compounds and Tl$_x$Al$_{1-x}$P alloys in Zincblende structure were calculated. The results for TIP and AlP are consistent with other results in the literature. The electronic band structure of Tl$_x$Al$_{1-x}$P alloys at different concentrations was calculated. The lattice constant of the alloy was found to be compatible with Vegard's law. According to the simulation results, the electronic energy band gap of the Tl$_x$Al$_{1-x}$P alloys is calculated by the third-order polynomial equation, such as $E_g(x) = 2.02693x^3 - 2.17819x^2 - 1.15118x + 1.29644$ (eV). The bowing parameter of the energy band gap was found to be strongly dependent on the doped ratio. The average bowing parameter of Tl$_x$Al$_{1-x}$P alloys was calculated as 1.1649 eV. It is anticipated that the TlAlP alloy may be suitable for use in the design of optoelectronic devices. It is believed that these results will direct experimental and theoretical studies.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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