Existence or absence of bandgap bowing in II-VI ternary alloys: comparison between common-anion and common-cation cases

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Abstract. The common-anion and common-cation II-VI ternary alloys of the family Cd(Zn)Se(Te) are theoretically investigated based on two different methods. Within the virtual-crystal approximation (VCA), both the sp³s*-tight-binding method, with the inclusion of spin-orbit coupling, and the first-principle full-potential linear augmented plane waves (FP-LAPW) technique are employed to determine the alloy constituents' charge states (ionicities) and degree of bond polarity. The results show that: (i) in the common-cation ternary alloys (i.e., CdSe₀.₅Te₀.₅ and ZnSe₀.₅Te₀.₅), the anions alter a strong competition in trapping more charge. Such a competition builds up a compromised effect yielding the bowing behaviour. Whereas, (ii) in the common-anion ternary alloys (i.e., Cd₀.₅Zn₀.₅Te and Cd₀.₅Zn₀.₅Se), the absence of such competition would cause the complete absence of bandgap bowing behaviour. The variation of the bandgap is found to be rather close to linear. The obtained good agreement between our theoretical results and the recently available photoluminescence data does further corroborate our claims.

1. Introduction
The recent advent in growth techniques of semiconductor nanostructures has paved the way for a technological revolution extending the field of applications from the Si-based microelectronics to the GaAs-based telecommunications. Among the produced nanostructures, the II-VI alloys find a broad field of applications in optoelectronics industry [1] (e.g., laser diodes emitting in the visible range, light detectors and emitters, and solar cells). There are already many new device structures which are commercially available and many more at the advanced research stage [1].

Understanding the chemical and physical properties of compound semiconductor alloys is important in making any future progress in their technological applications. One among the approaches is to give priority to focus on understanding the properties of the common-cation and common-anion ternary alloys. From there, one can proceed toward studying the properties of more complex alloys such as quaternary alloys and beyond [2]. However, despite decades of extensive studies, there are no commonly accepted explanations for the diverse observed behaviours of the bandgap versus composition (to name few, for instance, the bowing [2-4], linearity [2-4], band anti-crossing [2] and anomalous behaviours [5]).

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2. Computational Methods

The present investigation focuses on finding the origins of the observed bowing in the common-cation and the linearity in the common-anion ternary alloys, members of the Zn(Cd)Se(Te) family. For such task we employ two different computational methods. The $sp^3s^*$ tight-binding (TB) method [6], which includes the spin-orbit coupling, is used to evaluate the partial density of states (PDOS), the atomic electronic charge and alloy-bandgap energy to simulate the photoluminescence (PL) data. On the other hand, the first-principle full-potential linear augmented plane waves (FP-LAPW) technique [7], which is famous to be reliable in accurately predicting the ground-state properties, is used to calculate the electron charge-density contour plots aiming to corroborate our TB results.

3. Results and Discussions

3.1. Charge distribution

Figure 1 displays the TB-results of atomic charges versus composition for the 2 cases: (a) the common-cation CdSe$_x$Te$_{1-x}$ and (b) the common-anion Cd$_{1-x}$Zn$_x$Te ternary alloys. In both panels, the charges of cations (Cd and Zn) vary around 2 electrons while the charges of anions (Se and Te) vary around 6 electrons as the compounds considered are all from the II-VI group. In Figure 1a, by focusing on the alloy’s regime $0.25 \leq x \leq 0.75$, the anions Se and Te are shown to strongly compete with each other in trapping the charge. While in the binary states, $x=0$ and 1, one can clearly notice that $q_{\text{Te}} < q_{\text{Se}}$, in the alloy regime the charges of these two anions become comparable, and Te is even a bit more charged than Se. It is believed that this competition would make a compromise to cause the bandgap bowing behaviour (see below for further details). In Figure 1b, the cations Cd and Zn are shown to be robust to change their charge states (the variation is slow if not nil). It is shown that $q_{\text{Cd}} < q_{\text{Zn}}$ which is consistent with the fact that the former is more electro-positive than the latter. As a matter of fact, such charge behaviours reveal the lack of competition of cations in trapping/losing the charge which, in turn, is the main reason for a complete absence of the bowing character (see below for further details).

![Figure 1. The TB-calculated atomic charge variation of alloy constituents versus composition in (a) the common-cation CdSe$_x$Te$_{1-x}$ and (b) the common-anion Cd$_{1-x}$Zn$_x$Te ternary alloys](image-url)
Figure 2. The electron charge density contour plots on the (110) plane obtained by the FP-LAPW as applied to CdSe$_{x}$Te$_{1-x}$ and Cd$_{1-x}$Zn$_x$Te ternary alloys

Figure 2 shows the FP-LAPW-obtained electron charge density contour plots on the (110) plane for the two alloys: (a) CdSe$_x$Te$_{1-x}$ and (b) Cd$_{1-x}$Zn$_x$Te, with $x=0.5$. In both panels of Figure 2, the horizontal and vertical sides correspond to the $\langle 001 \rangle$ and $\langle 110 \rangle$ crystallographic directions, respectively. It is also important to mention that all four binary compounds (CdSe, CdTe, ZnSe and ZnTe) in their bulk zinc-blende (ZB) structures are found to be covalent with partial ionic character (i.e. polar materials). In the left panel of Figure 2, both Se and Te are shown to attract electrons as both are electronegative. In contrast to the TB predictions of Figure 1a, Se looks a bit stronger in electronegativity than Te; which is consistent with their well-known chemical properties. However, in the case of common-anion ternary alloy (CdZnTe, which is shown on the right panel of Figure 2), the Zn-Te and Cd-Te bonds are shown to be similarly populated with charge. These bonds reveal the lack of competition between cations in changing their charge states in consistency to what was predicted by TB results in Figure 1b.

3.2. Modelling of photoluminescence data

Figure 3 shows our TB-theoretical modeling to various PL-data on the four alloys of interest. The figure shows the variation of the alloy bandgap versus lattice constant at low temperatures ($T \leq 15K$). The PL data shown correspond to: (a) PL1: on CdSeTe alloys from reference [8]; (b) PL2: on ZnSeTe alloys from reference [4]; (c) PL3: on CdZnTe alloys from reference [9]; and (d) PL4: on CdZnSe alloys from reference [10]. The curves correspond to our TB-results fitting using either a linear function for the common-anion or a quadratic function for the common-cation ternary alloys, respectively. The theoretical results (curves) are in excellent agreement with the various PL data, which in turn corroborate our theoretical findings mentioned above. The results of bowing parameters are listed in Table 1.

Figure 3. TB-theoretical modeling of PL data. PL1, PL2, PL3 and PL4 correspond to refs. [8], [4], [9] and [10], respectively.
Table 1 summarizes the theoretical and experimental results of the bowing parameter \( (b \text{ in eV units}) \) for the two studied II-VI common-cation ternary alloys versus lattice mismatch \( (\Delta a/a_0) \), the valence-band offset (VBO) and the electro-negativity \( (\chi \text{ in units of Pauling}) \) of the elements. It gives a clear evidence that the bowing parameter is proportional to the following quantities: the lattice mismatch, VBO, anion electro-negativity and cation electro-positivity.

Table 1: Bowing parameter \( (b \text{ in eV}) \) versus VBO, lattice mismatch, and electronegativity \( (\chi \text{ in Pauling units}) \) for the II-VI compound-semiconductor common-anion ternary alloys

| alloy     | \( a_0 (\Delta a_0 / a_0 \%) \) | VBO (eV) | \( b \text{ (eV)} \) | \( \chi_{\text{anion}} \text{ (Pauling)} \) | \( \chi_{\text{cation}} \text{ (Pauling)} \) |
|-----------|---------------------------------|----------|----------------------|-----------------------------------------------|-----------------------------------------------|
| ZnSeTe    | 5.88 (7.3%)                     | 0.73^A   | 1.41^B, 1.239^C      | 2.325^E                                       | 1.69^E                                       |
| CdSeTe    | 6.28 (6.8%)                     | 0.57^A   | 0.904^D, 0.916^E     | 2.325^E                                       | 1.65^E                                       |

^AReference [11]; ^BReference [4]; ^CReference [12]; ^DPresent work; ^EReference [8]; ^FReference [13]

4. Conclusions
Within the VCA framework, we have used both the sp\(^3\)s*-TB method, with inclusion of spin-orbit interactions, and the FP-LAPW technique to investigate the existence and origins of the bandgap bowing character. The results are summarized as follows:

(i) The common-cation \( (\text{CdSe}_x\text{Te}_{1-x} \text{ and ZnSe}_x\text{Te}_{1-x}) \) ternary alloys possess the bowing character as a result of a competition between the anions in trapping/losing the charge provided by the cation;

(ii) The common-anion \( (\text{Cd}_{1-x}\text{Zn}_x\text{Se} \text{ and Cd}_{1-x}\text{Zn}_x\text{Te}) \) ternary alloys possess rather a linear behaviour of bandgap versus composition. The bowing is absent because of the complete lack of competition between constituents to trapping/losing the charge;

(iii) Furthermore, in the case of the common-cation, the bowing is found to be proportional to the lattice mismatch, VBO, anion electro-negativity and cation electro-positivity;

(iv) The excellent agreement between our theoretical results and the PL data has corroborated our claims.

Acknowledgements
The authors are indebted to thank Dr. N. Jisrawi for fruitful discussions. This work was partially supported by the Research Affairs at the UAE University under Grant Number 08-02-2-11/09.

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