

# AB INITIO STUDY OF PHASE SEPARATION AND ORDERING IN II-IV-BASED TERNARY ALLOYS

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Received: 31 July 2007; accepted: 26 Aug 2007

First-principles calculations of the ground-state properties and the stability of  $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$  solid solutions are presented using the full-potential linearized augmented plane wave (FP-LAPW) method in combination with the local density approximation (LDA). It is found that the structural parameters, i.e. lattice constants and bulk moduli follow a linear function of the composition  $x$ . The stability of the alloys is viewed as an energetic balance between pure structural constraints and quantum chemical effect. Our calculations yield to the prediction of an ordering tendency for low Zn content, occurrence of an intermediate disordered phase at 50-50 % of composition and phase separation for the Zn-rich range. These results agree well with the recent experimental work by Arbaoui et al. *Sol. Ene. Mater. Sol.-Cells*. 2006. 90. P. 1364.

**Keywords:** materials for solar-hydrogen energy, photovoltaic effect in semiconductor structures



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## Introduction

The mixed crystals of II-VI compounds semiconductors have attracted much attention in recent years because of the relevance of their optical properties. These materials permit many applications as infrared detectors, solar cells and other optoelectronic devices [1]. The  $\text{CdZnTe}$  (CZT) alloy is one of the most promising II-IV-based alloys that have been the subject of many interesting experimental studies. CZT was successfully grown both in bulk and in thin film forms by different techniques such as two-stage process [2], molecular beam epitaxy [3], chemical vapour deposition [4, 5] and electrodeposition technique [6].

Very recently, Arbaoui et al. [7] reported on the growth of CZT by the RF magnetron sputtering technique. They showed that the formation of the polycrystalline ternary alloy is favoured for a small concentration of Zn. In

contrast, for samples with higher Zn content, the XRD spectra showed no formation of  $\text{CdZnTe}$ . The measured lattice constants are found to vary linearly with Zn composition as expected from the Vegard's law.

The main goal of the present work is to investigate theoretically the possibility to form the CZT ternary alloys with varying Zn composition. Since ordering phenomena can influence directly both electronic and optical properties of a material, it motivates us to investigate the stability of  $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$  ordered structures by using the Full-Potential Linearized Augmented Plane Wave (FP-LAPW) method [8]. This method is one of the most accurate schemes to calculate structural, electronic and thermodynamic properties of materials. We considered that the ternary alloys are cubic pseudo-binary semiconductors with one of the two fcc sublattices occupied by Te atoms and the other by Cd

and Zn. Furthermore, we introduce the disordering effect and predict that the alloys prefer ordering for low Zn content and clustering elsewhere.

The paper is organized as follows. In section 2, we briefly describe the calculation procedure. Results and discussions are presented in section 3 and the paper is summarized in section 4.

### Method of calculation

Our calculations have been made using FP-LAPW approach within the framework of the Density Functional Theory (DFT) [9, 10] as implemented in WIEN2K [11] code. The exchange-correlation contribution to the total energy is described within the Local Density approximation (LDA) [12].

Kohn-Sham wave functions were expanded in terms of spherical harmonic functions inside the non-overlapping muffin-tin spheres surrounding the atomic sites (MT spheres) and in Fourier series in the interstitial regions. Inside the MT spheres of radius  $R_{MT}$ , the  $l$ -expansion of the wave function were carried out up to  $l_{max} = 10$  while the charge density was Fourier expanded up to  $G_{max} = 14$  (Ryd) $^{1/2}$ . In order to achieve energy eigenvalues convergence, the wave functions in the interstitial region were expanded in plane waves with a cut-off parameter of  $K_{max} = 8/R_{MT}$  for both binary and ternary alloys.  $R_{MT}$  values were assumed to be 2,2 a.u. for Zn, 2,6 a.u. for Cd and 2,4 a.u. for Te atoms, respectively for all structures. A mesh of 30 special  $k$ -points for both binary and ternary compounds was taken in the irreducible wedge of the Brillouin zone. Both the MT radius and the number of  $k$ -points were varied to ensure total energy convergence. The core states that are completely confined inside the corresponding MT spheres were treated fully relativistic, while for the valence states we used the scalar relativistic approach that includes the mass velocity and Darwin  $s$ -shift, but omits spin-orbit coupling.

### Results and discussions

#### Structural parameters

First, we calculated the structural properties of the binary compounds CdTe and ZnTe in the zinc blend structure. Then, the ordered ternary alloys  $Cd_{1-x}Zn_xTe$  were simulated at the compositions  $x = 0,25, 0,5$  and  $0,75$ . For each composition, we carried out a structural optimization by minimizing the total energy with respect to the cell volume and also the atomic positions. A simple cubic structure (luzonite) of eight atoms is used to model compositions of  $x = 0,25$  and  $x = 0,75$ . For  $x = 0,5$  the smallest ordered structure is a four-atom tetragonal cell, which corresponds to the (001) superlattice.

The calculated lattice constants and bulk moduli were obtained by fitting the total energy versus unit cell volume to the Murnaghan's equation of state [13]. In Fig. 1 and Fig. 2 we depicted, respectively the lattice constants and the bulk moduli as a function of the composition  $x$ . From Fig. 1, one can see that the calculated lattice parameters

are close to those obtained by considering an ideal mixing between CdTe and ZnTe, the differences between them are less than 0.4 %. The calculated lattice constants follow a decreasing linear function of composition  $x$  as expected by the Vegard's law, this concords well with the results reported in Refs. [7, 14-16]. A fitting of both the experimental data reported in Ref. [7] and the calculated ones leads to the following linear equations:

$$a_{exp}(x) = 6.479 - 0.432x, \quad (1)$$

$$a_{th}(x) = 6.421 - 0.411x. \quad (2)$$

Considering the general trend that the LDA usually underestimates the lattice parameters, our LDA results are in reasonable agreement with experiment and the other theoretical values. In Fig. 2, the composition dependence of the bulk moduli is compared with the results predicted by the linear concentration dependence (LCD). The bulk moduli exhibit a small deviation from the LCD and are in reasonable agreement with those obtained by Wei et al. [17].

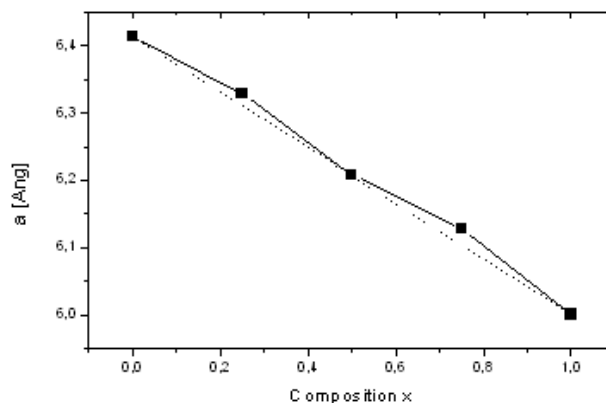


Fig. 1. The calculated lattice constants (solid squares) and lattice constants of ideal mixing solid solutions (dotted line) for the five ordered structures  $(Cd)_{1-n}(Zn)_nTe$  ( $n = 0, 1, 2, 3, 4$ )

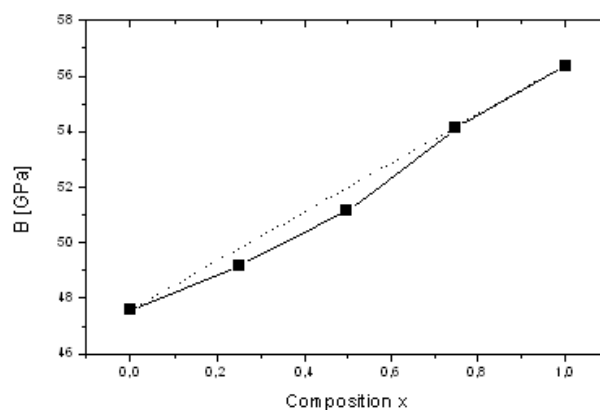


Fig. 2. Calculated bulk moduli (solid squares) and those of ideal mixing (dotted line) as a function of composition

#### Stability of the ordered phase

In order to study the stability of CdZnTe in the ordered form, we calculated the formation energies of the five ( $n = 0, 1, 2, 3, 4$ ) structures using the following relation

$$E_{form}(n) = E_{(Cd)_{1-n}(Zn)_nTe} - \frac{n}{4} E_{ZnTe} - \left(1 - \frac{n}{4}\right) E_{CdTe}, \quad (3)$$

where  $E_{(Cd)_{1-n}(Zn)_nTe}$  is the total energy of the  $n$ th ordered alloy,  $E_{ZnTe}$  and  $E_{CdTe}$  are total energies of ZnTe and CdTe binaries, respectively. The results are viewed in Fig. 3 (solid squares) together with those for disordered alloys (solid line).

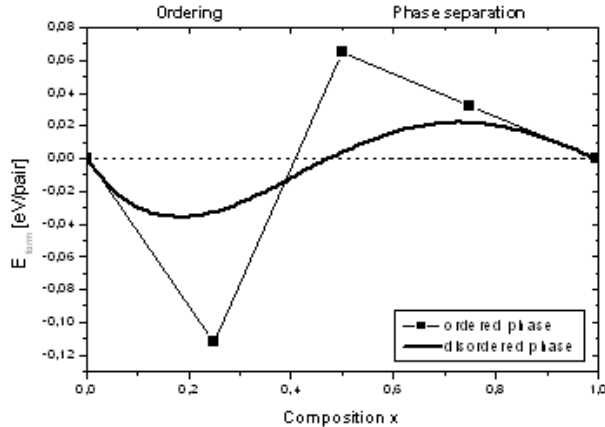


Fig. 3. The calculated formation energies for ordered structures and disordered alloys

The formation energy can give a measure of the stability of a material. For low Zn compositions we notice that it is negative below  $x = 0.41$  and positive elsewhere. This trend indicates an ordering tendency that occurs for low Zn content and a phase separation for Zn-rich range. Thus, our results are consistent with the experimental ones from Ref. [7].

In order to clarify the physical origin of this behaviour, we decompose  $E_{form}$  into three physically recognizable contributions [18-20] as follows:

$$E_{form} = E_{VD} + E_{CE} + E_{ER}, \quad (4)$$

where  $E_{VD}$  is the hydrostatic “volume deformation” contribution due to the dilatation of ZnTe and compression of CdTe from their equilibrium lattice constants (6.00 Å and 6.414 Å, respectively) to the common (Vegard-like) lattice constant of the alloy;  $E_{CE}$  is the “charge exchange” energy that releases when ZnTe and CdTe, taken at common lattice constant, combine to give  $Cd_{1-x}Zn_xTe$  ordered alloy. The internal relaxation effects are not included in this energy;  $E_{ER}$  is the “structural relaxation” term due to the full relaxation of cell-internal degrees of freedom. From the equation (2), one can derive two different energetic terms  $E_{struct}$  and  $E_{elec}$  that have different physical meanings:

$$E_{form} = E_{chem} + E_{struct}, \quad (5)$$

where  $E_{chem}$  means a chemical contribution associated to an electronic mismatch between cations and  $E_{struct}$  means a structural contribution (positional relaxation + volume deformation) induced by both lattice and atom-size mismatches.

Fig. 4 shows the splitting of the formation energies of the ternary alloys into the three physical contributions; we can deduce the following important remarks:

- The large lattice mismatch ( $\approx 6\%$ ) between the binary constituents leads to a large and positive  $E_{VD}$  that tends to decrease the stability of CdZnTe alloys over the whole range of composition. Because of the atom-size mismatch, including one Zn atom in a CdTe host leads to a less strained structure than including one Cd atom in a ZnTe host. This behaviour can be deduced from the fact that  $E_{VD}(x = 0.25) < E_{VD}(x = 0.75)$ .

- In contrast to  $E_{VD}$ , internal relaxations tend to increase the stability of the alloys by taking a negative  $E_{SR}$  values. However, the sum  $E_{VD} + E_{SR}$  remains positive and increases with increasing the concentration.

- The electronic contribution  $E_{CE}$  to the formation energies appears to be a relevant term.

For  $x = 0.25$ , the energy  $E_{CE}$  is negative and overwhelms the  $E_{VD} + E_{SR}$  term. This let us to conclude that the expected stability of CdZnTe alloys for low Zn content have a chemical nature.

- At 50-50 % content, both structural and chemical parts are positive, leading to a phase separation. We notice that the chemical part contributes significantly to the formation energy. For the highest Zn composition (i.e.  $x = 0.75$ ), the alloy instability takes a structural nature and the structural energy contribution overwhelms the chemical one.

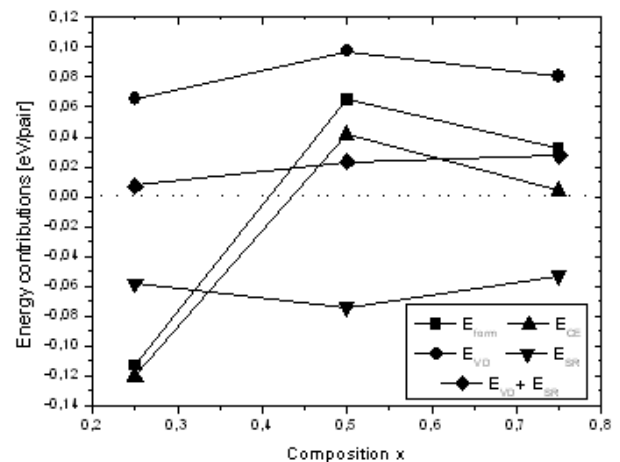


Fig. 4. Energy contributions to the formation energies of ordered alloys

#### Stability of the disordered phase

In this section, the energetics of the disordered alloys are calculated using a cluster expansion. Following the idea of Connolly and Williams [21], the energy of formation of the disordered solid solutions can be written as

$$E_{form}^{dis}(x) = \sum_{n=0}^4 P_n(x) E_{form}^n(x); \quad (6)$$

$$P_n(x) = \binom{4}{n} x^n (1-x)^{4-n}, \quad (7)$$

where  $E_{form}^{dis}(x)$  is the energy of formation of each of the five ordered structures.  $P_n(x)$  is a statistical weight representing the probability that the  $n$ th short-range ordered structure occurs in the alloy. From Fig. 3 (solid line), it is observed that a maximum of alloy stability is attained at  $x = 0.22$  and that a negative curvature appears. Calculating inflexion points of the curve corresponding to  $\partial^2 G(x)/\partial x^2 = 0$  where  $G(x)$  is the Gibbs free energy of mixing, leads to the concentrations  $(c_1, c_2) = (0.409, 0.997)$  that delimit a spinodal decomposition domain.

Comparing both ordered and disordered phases for the whole range of  $x$  leads to the evidence that ordered phase remains more stable than the disordered one for compositions less than  $x = 0.38$ . From the later concentration to  $x = 0.41$ , the coexistence of the two phases is predicted. Then, the disordered phase becomes more stable than the ordered phase until  $x = 0.48$ , in this range the ordered phase is unstable. Finally, both phases become unstable for higher Zn content and a miscibility gap is expected.

Then, our explanations on the stability trends of the alloys may be suggested as follows. First, the ordering at low composition of Zn needs the intermixing of Cd and Zn elements and rearrangements of atoms. This is induced by the long time and the high temperature of the annealing of the samples [7]. Also, as explained before, the charge exchange between Cd, Zn and Te atoms acts like a driving force that tends to stabilize the alloy. All these factors cause the interdiffusion of Cd and Zn, which results in a grain nucleation and growth leading to a polycrystalline material. By increasing Zn content, the electronic contribution to the formation energy increases rapidly and tends to separate the alloy into regions with short-range periods consisting of the mixed clusters ( $Cd_3ZnTe_4$ ,  $Cd_2Zn_2Te_4$  and  $CdZn_3Te_4$ ). After that, the system exhibits an excess of the "pure" ( $Cd_4Te_4$  and  $Zn_4Te_4$ ) clusters and a deficiency in the mixed ones.

### Conclusion

In summary, we performed accurate FP-LAPW calculations to investigate the structure and the stability of  $Cd_{1-x}Zn_xTe$  solid solutions in the ordered and disordered forms. It was shown that the lattice constants are a decreasing linear function of composition, in agreement with available experimental works. The calculated formation energy of the ordered structures is resulting from a competition between three different physical contributions, i.e. the volume deformation, the internal relaxation and the charge exchange. The ordering tendency for low Zn content is explained to have a chemical nature.

The experimental threshold reported in Ref. [7] at which a phase separation occurs ( $x < 0.4$ ) is well predicted by our calculations.

### References

1. Gunshor R.L., Nurmiko A.V. II-VI blue/green light emitters: devices physics and epitaxial growth //

Semiconductors and Semimetals. 1997. Vol. 44. Academic press, New York.

2. Basol B.M., Kapur V.K., Ferris M.L. Low cost technique for preparing CdZnTe films and solar cells // J. Appl. Phys. 1989. 66. P. 1816.

3. Ringel S.A., Sudharsanam R., Rohatgi A. et al. A study of polycrystalline Cd(Zn, Mn)Te/CdS films and interfaces // J. Electron. Mater. 1990. 19. P. 259.

4. Chu T.L., Chu S.S., Ferekids C. et al. Films and junctions of cadmium zinc telluride // J. Appl. Phys. 1992. 71. P. 5635.

5. Cohen K., Stolyarova S., Amir N. et al. MOCVD growth of ordered  $Cd_{1-x}Zn_xTe$  epilayers // J. Cristal Growth. 1999. 198. P. 1174.

6. Bansal A., Rajaram P. Electrochemical growth of CdZnTe thin films // Mater. Lett. 2005. 59. P. 3666.

7. Arbaoui A., Outzourhit A., Achargui N. et al. Effect of the zinc composition on the formation of ternary alloy  $Cd_{1-x}Zn_xTe$  thin films // Sol. Ene. Mater. Sol.-Cells. 2006. 90. P. 1364.

8. Andersen O.K. Linear methods in band theory // Phys. Rev. B 1975. 42. P. 3060.

9. Hohenberg P., Kohn W. Inhomogeneous electron gas // Phys. Rev. 1964. 136. P. B864.

10. Kohn W., Sham L.S. One-particle properties of an inhomogeneous interacting electron gas // Phys. Rev. 1965. 140. P. A1133.

11. Blaha P., Schwarz K., Madsen G.K.H. Electronic structure calculations of solids using the WIEN2k package for material sciences // Comput. Phys. Commun. 2002. 147. P. 71.

12. Ceperley D.M., Alder B.J. Ground state of the electron gas by a stochastic method // Phys. Rev. Lett. 1980. 45. P. 566.

13. Murnaghan F.D. The compressibility of media under extreme pressures // Proc. Natl. Acad. Sci. USA. 1944. 30. P. 244.

14. Ammar A.H. Studies on some structural and optical properties of  $Zn_xCd_{1-x}Te$  thin films // App. Surf. Sci. 2002. 201. P. 9.

15. Soliman H.S., Allam F.M., El-Shazily A.A. Structural and optical properties of  $Cd_{1-x}Zn_xTe$  thin films // J. Mater. Sci. Mater. Elect. 1996. 7. P. 233.

16. Schenk M., Hähnert I., Duong L.T.H. et al. Validity of the lattice-parameter Vegard-rule in  $Cd_{1-x}Zn_xTe$  solid solutions // Crys. Res. Tech. 1996. 31. P. 665.

17. Wei S.H., Ferreira L.G., Zunger A. First-principles calculation of temperature-composition phase diagrams of semiconductor alloys // Phys. Rev. B 1990. 41. P. 8240.

18. Satani M., Hart G.L.W., Zunger A. Ordering tendencies in octahedral MgO-ZnO alloys // Phys. Rev. B 2003. 68. P. 155210.

19. Bernard J.E., Zunger A. Electronic structure of ZnS, ZnSe, ZnTe, and their pseudobinary alloys // Phys. Rev. B 1987. 36. P. 3199.

20. Zunger A., Wei S.-H., Ferreira L.G. et al. Special quasirandom structures // Phys. Rev. Lett. 1990. 65. P. 353.

21. Connolly J.W.D., Williams A.R. Density-functional theory applied to phase transformations in transition-metal alloys // Phys. Rev. B 1983. 27. P. 5169.

