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Mechanical Properties Calculation of II-VI Semiconductors: $Cd_{1-y}Zn_yTe(0\leq y\leq 1)$

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Abstract

Mechanical properties of semiconductors: CdTe, ZnTe and CdTe alloyed with 2% and 5 at% of Zn have been calculated, using the computer code WIEN2k. The program uses the Density Functional Theory. The results show that increasing the amount of Zn, results in greater values of mechanical properties and contraction of the lattice parameter since replacement of Cd by Zn establish lower Zn-Te distance compared with Cd-Te. The behavior is different for the C_{12} constant of $Cd_{0.90}Zn_{0.10}Te$, the shear and Young modulus of CdTe. While Poisson's ratio is constant. The calculated values for CdTe and ZnTe differ from the experimental values between 8% and 21%. The calculated values differ from others authors between 2% and 21%. There are no experimental data of the alloyed CdTe. Values of CdTe alloyed whit Zn are between the CdTe and ZnTe closest to the CdTe. Differences with data calculated by other authors are noticeable.

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Keywords: semiconductors II-VI; DFT; CZT detectors; WIEN2K; X-ray and gamma detectors.

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1. Introduction

Properties of II-VI semiconductors are calculated [$Cd_{1-y}Zn_yTe$ ($0 \leq y \leq 1$) (CZT)], among them: CdTe, ZnTe, $Cd_{0.96}Zn_{0.04}Te$ and $Cd_{0.9}Zn_{0.10}Te$, using WIEN2k code by Blaha et al. (2001). This code analyses different physical and chemical properties of crystalline structures applying solid state theories, based on density functional theory (DFT) by Kohn and Sham (1965) and Hohenberg and Kohn (1964). This theory allows an approximate resolution of the equations of quantum mechanics that govern the behaviour of electrons, to determine how atoms move and simulate the physical and chemical processes at atomic level, without any experimental data, it is an ab-initio method.

A model describing the matter structure establishes the arrangement of atoms, representing their relative positions and their distribution in each material. For the atom structure, it is considered a nucleus and electrons around it, each different type of atom has Z characteristic electrons. Each one of the electrons is in a characteristic state and has a unique energy that corresponds to the required energy to remove it from the atom. The values of these energies can be represented by a model with electrons in clearly separate layers and only a certain number of electrons in each layer. The physical changes and chemical reactions are only related to the most external electrons. It might be said in good approximation, that the core of the atom, the nucleus plus the internal electrons, are immutable.

Properties such as temperature, pressure, composition, electronic structure, disorder are those that determine the materials properties. Quantum mechanics is used to describe the electronic structure that is responsible for the properties such as chemical stability, relaxation of the atoms, phase transitions, magnetic, optical, mechanical, electrical behaviour, etc. Ab-initio calculations can be performed not only at 0 K but taking into account the variation with temperature.

Materials properties have become accessible to computational calculation including a broad range of studies as the structure of solids, defects, surfaces, interfaces, thermo chemistry, mechanical properties, electronic excitations and magnetic behaviour. This capacity for analysis and study is of utmost importance for the experimental researchers and today forms part of industrial research and material engineering. Ab-initio methods, provide an approach that gives us a unique and deep view within materials and has a huge predictive capacity in new systems

Nowadays literature presents very limited experimental physical-chemistry properties for CZT, so there is in general a serious lack of information when ternary alloys are considered. In this paper properties are simulated using first principles quantum mechanics methods. Computer calculations allow obtaining properties values that would be impossible to measure experimentally (at high temperatures and high pressures such as those in the depth of the mantle) or dangerous (with radioactive materials). There are also factors of cost and time that make the computer calculations to be chosen. This is why today the design by computers today is an indispensable tool in the research for the materials industry.

The main goal is to carry out the properties modelling for CdTe, ZnTe, $Cd_{0.96}Zn_{0.04}Te$, and $Cd_{0.90}Zn_{0.10}Te$, such as the optimum lattice parameters and mechanical properties such as elastic constants, bulk module, shear module, Young's modulus and Poisson ratio. Detectors based on CZT present technological interest since they can be used at room temperature. This material is used to manufacture x-ray and gamma detectors, and also as a substrate for epitaxial film growth of HgCdTe sensitive to IR radiation. Alloyed CdTe, since several years ago, has been preferred to binary CdTe as a substrate in the epitaxial growth of MCT, because Zn gives greater hardness to CdTe lattice and produces a lower dislocations density in the interface substrate-epitaxy as can be seen in Nöllmann et al. (1991), Di Stefano et al. (2004) and Walukiewicz (1989) during the growth stage.

The ZnTe emit at wavelengths of 540 nm, with a promising use in diode lasers and emitters of high intensity light as was presented in Tribugó et al (2010). CZT detector applications occur in a wide range of areas: medicine (associated with imaging techniques such as x-ray or gamma ray tomography, x-ray fluorescence, x-ray simultaneous dual-energy), space technology (high energy focus telescope-HEFT) and security (monitoring of radioactive materials in nuclear plants) and others such as the use of CZT detector for the non-destructive examination of art objects in museums and archaeological sites, by Schlesinger et al. (2001), Diéguez (2011), McGregor (1997) and Schlesinger et al. (1995). These materials are grown in UNIDEF-MINDEF, Martínez (2012).

2. Metodology

The calculations were performed with WIEN2k program, developed in Vienna in 1990, by Blaha and collaborators (2001). Socket functions base method of linearized augmented plane waves plus orbital locations

(LAPW+lo). It is proven that the method LAPW+lo is one of the most precise study for solids electronic structure within the DFT approximation. LAPW method solves the Kohn-Sham (1965) equation of density of states for the fundamental states, the total energy and the band energy using functions specially adapted for the problem.

This code is used to study the properties of the cells of CdTe and ZnTe and CdTe alloyed with 2% and 5% at. Zn (Fig 1). The ZnTe and CdTe belong to space group 216 (F-4 3 m) and Zn-doped cells belong to the space group 215 (P - 43m).

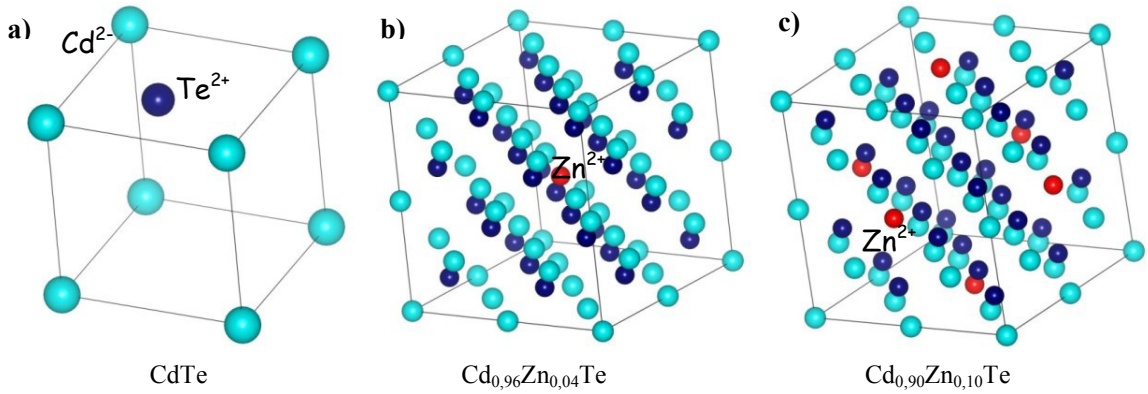

Fig. 1. Models for different compositions cells (a) CdTe (original cell) and ZnTe (Zn replaces the Cd), (b) $Cd_{0.96}Zn_{0.04}Te$ and (c) $Cd_{0.90}Zn_{0.10}Te$.

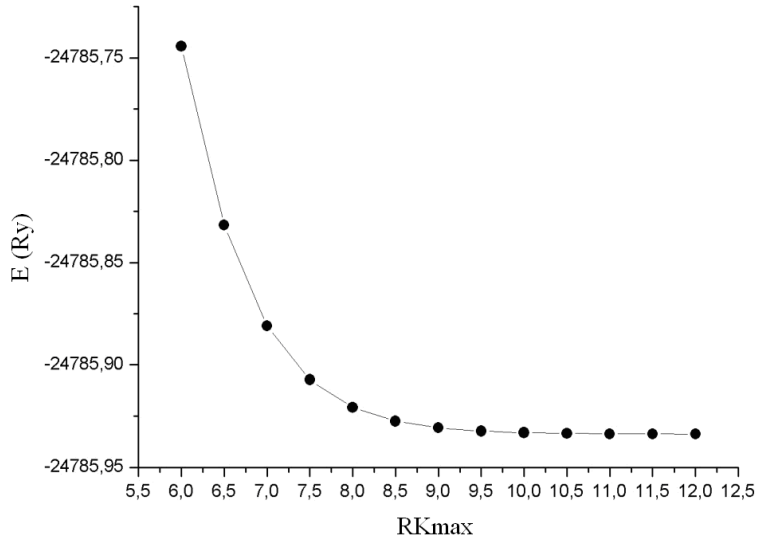

Fig. 2. RKmax parameter optimization for CdTe.

Correlation and exchange potentials were used, in particular those based on parameterization PBE-GGA by Perdew, Burke and Ernzerhof (1996)- the generalized gradient approximation. The convergence of the base is regulated through the parameter RKmax which results from the product between the smaller radius of the "muffin tin" (RMT) and the largest expansion of reciprocal vector module (Kmax), a selected value of RKmax = 9 for pure CdTe and RKmax = 7.2 and 6.8 for CdTe cells alloyed with 2% and 5% at. Zn was respectively used (see Fig. 2 for the CdTe optimization). Also a lattice parameter optimization was performed (see Fig. 3 for the CdTe optimization); and the total necessary number of k-points (see Fig. 4 for the CdTe optimization) to sample the reciprocal space and

ensure the convergence of the total energy. The first Brillouin zone is sampled with a total of 2000 k-points for CdTe and 250 k-points for the supercell. In the previous mentioned cases the optimal values are presented in Table 1.

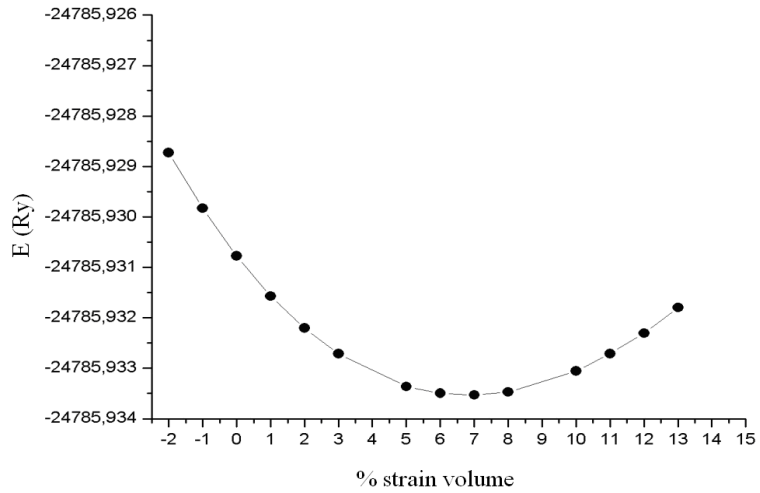

Fig. 3. Lattice parameter optimization for CdTe.

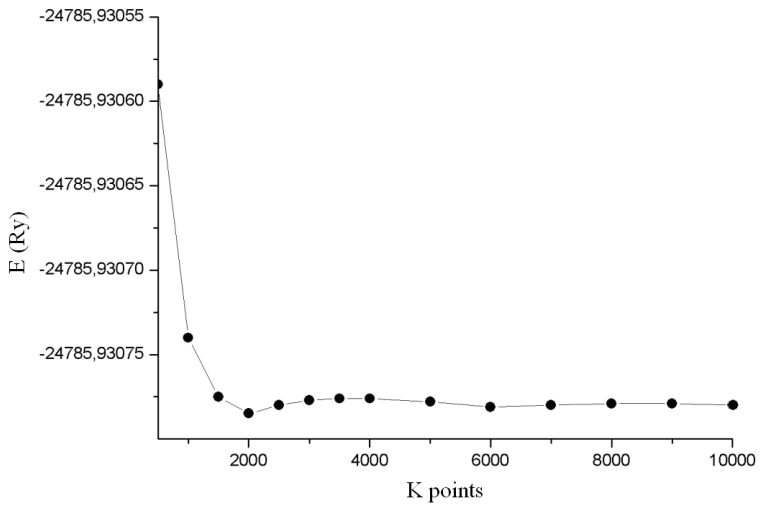

Fig. 4. Optimization of the total number of k-points for CdTe.

Table 1. Optimized data entry for Wien2k calculation.

Semiconductors	CdTe	ZnTe	$Cd_{0.96}Zn_{0.04}Te$	$Cd_{0.90}Zn_{0.10}Te$
Optimized Lattice parameter (Å)	6.615	6.193	13.1920 (6.596)	13.1660 (6.583)
Spatial group	216 (F-4 3 m)	216 (F-4 3 m)	215 (P-43m)	215 (P-43m)
Atom positions	Cd: $(0,0,0)$ Te: $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$	Zn: $(0,0,0)$ Te: $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$	Zn: $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	Zn: $(\frac{1}{2},\frac{1}{2},0)$ Zn: $(\frac{1}{2},0,\frac{1}{2})$ Zn: $(0,\frac{1}{2},\frac{1}{2})$
Muffin tin radius (a. u.)	RMT (Cd) = 2.35; RMT (Te) = 2.55	RMT (Zn) = 2.35; RMT (Te) = 2.55	R_{MT} (Cd) = 2.35 R_{MT} (Te) = 2.55 R_{MT} (Zn) = 2.35	R_{MT} (Cd) = 2.35 R_{MT} (Te) = 2.55 R_{MT} (Zn) = 2.35
Number of k-points	2000	2000	250	250
RKmax	9	9	7.2	6.8

3. Results and discussion

The variation of the energy as a function of the lattice parameter (Figures 5, 6 and 7) was calculated through the WIEN2k to get the mechanical properties of the CZT semiconductor at 0 K. It was used the GGA exchange and correlation potential. The mechanical properties, using the method developed by Thomas Charpin and Morteza Jamal by Reshak and Jamal (2012), which is integrated in the calculations of the program WIEN2k package, were calculated from these data. The potential GGA was also used to obtain the optimum lattice parameters that minimize the energy of the cell.

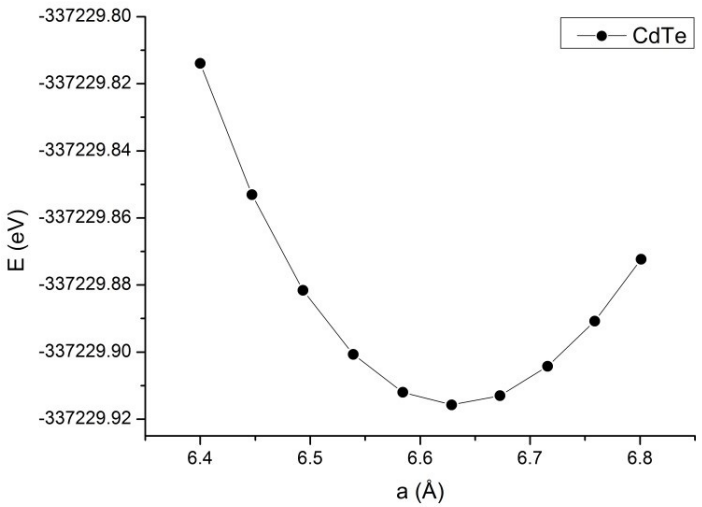

Fig. 5. Energy variation with the CdTe lattice parameter.

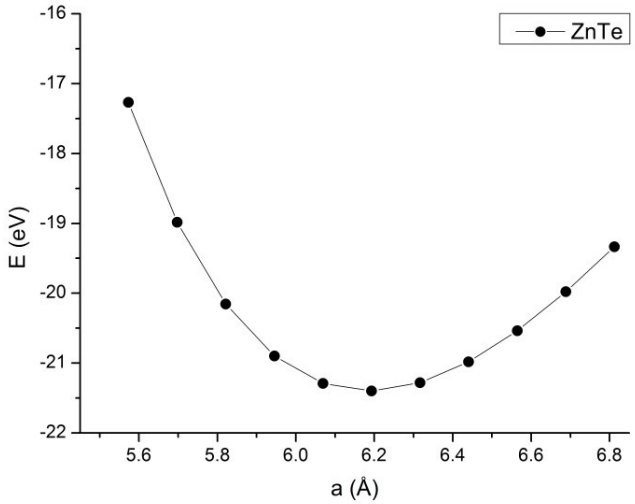

Fig. 6. Energy variation with ZnTe lattice parameter.

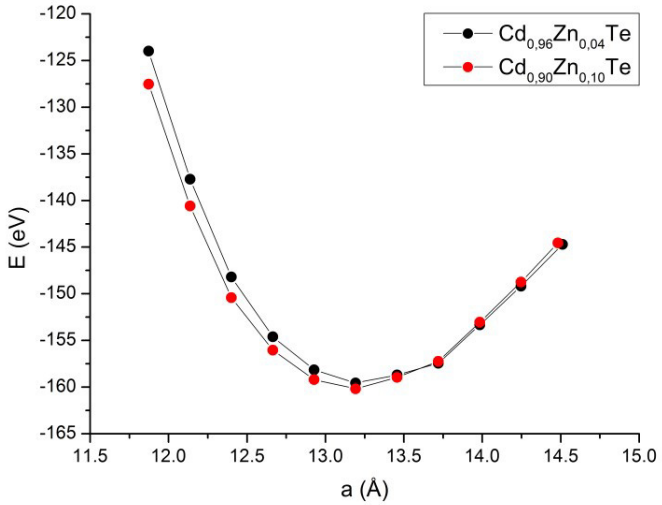

Fig. 7. Energy variation with the lattice parameter of CdTe alloyed with 2 and 5 % atomic Zn.

In Table 1 the results for the calculation of mechanical properties and lattice optimum parameters are presented for pure CdTe, ZnTe and CdTe alloyed with 2% and 5% at. Zn. Calculated mechanical properties were: the elastic constants, shear modulus, bulk modulus, Young's modulus and Poisson coefficient, while in Table 2 bibliographic citations of experimental works were collected and in Table 3 are other values reported in the literature.

Table 2. Wien2k calculations in this work.

	CdTe	$Cd_{0,96}Zn_{0,04}Te$	$Cd_{0,90}Zn_{0,10}Te$	ZnTe
Lattice Parameter (Å) (supercell)	-	13.192	13.166	-
Lattice Parameter (Å) (crystallographic)	6.615	6.596	6.583	6.193
Elastic Constant C_{11} (GPa)	44.38	45.48	45.88	59.41
Elastic Constant C_{12} (GPa)	29.32	30.47	30.02	32.20
Elastic Constant C_{44} (GPa)	17.67	19.61	19.64	28.68
Bulk Modulus, B (GPa)	34.34	35.47	35.31	41.27
Shear Modulus μ (GPa)	7.53	7.51	7.93	13.60
Young Modulus Y (GPa)	21.05	21.04	22.14	36.77
Poisson Coeficient ν	0.40	0.40	0.40	0.35

Table 3. Experimental data.

	CdTe	Cd0,96Zn0,04Te	Cd0,90Zn0,10Te	ZnTe
C_{11} (GPa)	53.5 [a,b]	-	-	71.7[c]
C_{12} (GPa)	36.5[a] ; 36.81[b]	-	-	40.7[c]
C_{44} (GPa)	19.9[a,b]	-	-	31.2[c]
Bulk modulus B (GPa)	39[d] ; 44.5[d,e]	-	-	52.8; 50.9[c,e,f]
Experimental lattice cell parameter (Å)	6.48[g]; 6.4827[d]	a = 6.4819-0,401.x, with $0 \leq x \leq 1$ [h], for x = 0.04: a = 6.46586 and for x = 0.10: a = 6.4418		6.06[f]; 6.1[e]

[a]Agrawal and Agrawal (1992), [b]McSkimm and Thomas (1962),
[c]Lee (1970), [d]Hellwege and Madelung, Vol. 17[a] (1982),
[e]Hellwege and Madelung Vol 22[a] (1982), [f]Becerril et al. (2004),
[g]Korozlu et al. (2009), [h]Capper (1997).

Table 2 shows that Cd replacement by Zn in CdTe results in a contraction of the lattice parameters, Zn-Te bonds are shorter compared to Cd-Te bonds and this lattice has greater hardness.

The Zn increment in CdTe alloys (Table 2) determines mechanical properties increment simultaneously to lattice parameter contraction of the same compounds, with a few exceptions, such as C_{12} that is constant for $Cd_{0.90}Zn_{0.10}Te$ and shear and bulk module are constant for CdTe, meanwhile Poisson coefficient is virtually constant for all of them.

Ternary compounds are in the range between CdTe and ZnTe closer to CdTe values because the percentage of Zn is low.

Mechanical properties comparison between calculated (WIEN2k) and experimental data in Table 3 (no data for the cut-off module, the module of deformation and coefficient of Poisson were found) differences within the range 8% to 21% can be seen. Comparison with values calculated by other authors (Table 4), there are differences within 2% - 21%. The comparison of the optimum lattice parameter calculated with correlation and GGA exchange potential, with the experimental values in Table 3, there are good fitting, 102.08% for CdTe, 101.52% for ZnTe, 102.01% for $Cd_{0.96}Zn_{0.04}Te$ and 102.19% for $Cd_{0.90}Zn_{0,.10}Te$.

As there are no experimental data for CdTe alloyed with 2% and 5% at. Zn, mechanical properties were then calculated with the WIEN2k and compared with some data calculated by other authors (Table 4). There are appreciable differences of approximately up to 64% for the values of shear modules. The smallest difference (7.1%) is for the C_{12} constant for CdTe alloyed 5% at. Zn. Other mechanical properties differences are within the range from 22.8% to 39.3%.

Table 4. Theoretical bibliography values.

	CdTe	$Cd_{1-y}Zn_yTe$ ($0 \le y \le 1$)	ZnTe
C_{11} (GPa)	57.3 [g]	$7.34+2.14x+0.49x^2$ (10^{10} Nm^{-2}) $0 \le x \le 1$ [l], for x = 0.04: C_{11} = 74.26384 GPa and, for x = 0.10: C_{11} = 75.589 GPa	75.17 [g]
C_{12} (GPa)	39.63 [g]	$3.14+0.9x+0.22x^2$ (10^{10} Nm^{-2}) $0 \le x \le 1$ [l], for x = 0.04: C_{12} = 31.76352 GPa and, for x = 0.10: C_{12} = 32.322 GPa	42.94 [g]
C_{44} (GPa)	19.04 [g]	$2.97+0.86x+0.20x^2$ (10^{10} Nm^{-2}) $0 \le x \le 1$ [l], for = 0.04: C_{44} = 30.0472 GPa and, for x = 0.10: C_{44} = 30.58 GPa	38.86 [g]
Bulk Modulus B (GPa)	33.79 and 46.68 [i]; 46.179 [j]	$4.54+1.30x+0.32x^2$ (10^{10} Nm^{-2}) $0 \le x \le 1$ [l] for x = 0.04: B = 45.92512 GPa and, for x = 0.10: B = 46.732 GPa	55.672 [i]
Shear Modulus μ (GPa)	13.68 [g]	$2.09+0.6x+0.14x^2$ (10^{10} Nm^{-2}) $0 \le x \le 1$ [l], for x = 0.04: **μ** = 21.14224 GPa and, for x = 0.10: **μ** = 21.514 GPa	27.29 [g]
Young Modulus Y (GPa)	24.88 [g]; 49.55 [k]	-	43.94 [g]
Poisson Coefficient ν	0.40 [g]; 0.33 [j]	-	0.36 [d]

[i] Merad et al. (2005),
[j] Lalitha et al. (2007),
[k] Deligoz et al. (2006),
[l] Mnasri et al. (2009).

4. Conclusions

The lattice parameters are well described by the computational code WIEN2k, through the correlation and exchange potentials based on PBE-GGA parameterization, developed by Perdew, Burke and Ernzerhof - giving close to the experimental values.

Mechanical properties calculation for semiconductor CdTe and ZnTe, such as: the elastic constants: C_{11}, C_{12} and C_{44}, compression modulus, shear modulus, Young's modulus and Poisson coefficient, give acceptable results, close to the experimental values. Mechanical properties of CdTe alloyed with 2% and 5% at. Zn, have values between CdTe and ZnTe, closest to the CdTe, and they present significant differences compared to other authors. The general trend is that the Zn amount increase in CdTe alloys determines the increased values of mechanical properties meanwhile there is a contraction of the lattice parameter. The Zn addition gives greater hardness to the CdTe lattice, since Cd replacement by Zn in CdTe establishes shorter Zn-Te bonds compared to the Cd-Te ones.

It is possible to simulate the properties of II-VI semiconductor materials: CdTe, $Cd_{0.96}Zn_{0.04}Te$, $Cd_{0.90}Zn_{0.10}Te$ and ZnTe, using ab-initio methods, without need to adjust to any experimental data.

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