Journal of Alloys and Compounds 592 (2014) 150–156

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Microscopic partition of pressure and elastic constants in CdTe polymorphs

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A R T I C L E I N F O

Article history:
Received 10 October 2013
Received in revised form 15 December 2013
Accepted 16 December 2013
Available online 24 December 2013

Keywords:
Atomic scale structure
High-pressure
Computer simulations
Semiconductors
Phase transitions

A B S T R A C T

Within the framework of density functional theory, first principles calculations were carried out to determine pressure stability ranges of zinc-blende (B3), cinnabar (Cinn), rock-salt (B1), orthorhombic (*Cmcm*), and cesium chloride (B2) phases of CdTe. In agreement with experimental observations, we found a B3 → Cinn → B1 → *Cmcm* pressure-induced sequence, and predict the B2 phase as a potential high pressure polymorph. The equations of state of all these polymorphs and the components of the elasticity tensor of the B3 phase at zero pressure were determined and microscopically analyzed in terms of atomic contributions. The concept of local pressure allows for quantifying differences in the role played by Cd and Te as regards the compressibility of CdTe phases, and suggests the existence of a general behavior under pressure for binary II–VI semiconductors.

1. Introduction

CdTe is a II–VI semiconductor compound belonging to the cadmium chalcogenide crystal family. This is a group of important materials for the development of solid state devices (e.g. solar cells) and other modern technologies [1]. In particular, CdTe has an ideal direct band gap energy of 1.45 eV and a high absorption coefficient, which makes a very thin layer of this material sufficient for a high energy conversion efficiency [2]. Along with the electronic properties, the mechanical behavior of CdTe has also been the subject of many experimental studies, including pressure effects using Raman spectroscopy [3] and transport measurements [4]. Special attention has been paid to the structural changes of this compound in connection with the reconstructive phase transition sequence exhibited by other binary chalcogenides at high pressure [3–6].

Using angle-dispersive techniques and image–plate detectors, Nelmes et al. [6] rather unexpectedly found that CdTe undergoes a rich polymorphism under applied high pressure. They found the transition sequence zinc-blende (B3) → cinnabar (Cinn) → rock-salt (B1) → *Cmcm* with transition pressures of 3.5 GPa (B3-Cinn), 3.8 GPa (Cinn-B1), and 10 GPa (B1-*Cmcm*), respectively. According to this work, the cinnabar phase of CdTe only exists in a narrow pressure range around 3.5 GPa, which explained why it had not been found in previous experiments. This polymorphic sequence is now well established and clarifies controversy regarding the existence of the cinnabar phase for CdTe (see for example Ref. [7]). From the theoretical side, only a few works have accurately simulated the correct sequence of pressure-induced phase transitions for CdTe [8–10]. Moreover, there is still a lack of fundamental understanding of several aspects regarding the role played by the atomic constituents of these binary semiconductors in their compressibility and in the corresponding transition pressures.

Though it is clear according to previous works (see for example Ref. [11]), that macroscopic compressibility is one of the key parameters linked to polymorphic sequences, phase stability is ultimately determined by the crystalline bonding network, and hence by the valence electrons of the particular atomic constituents of the solid. To understand the complex factors connecting stability and equation of state (EOS) parameters of compounds, one appealing route is to decompose macroscopic observable properties in terms of local contributions, and more specifically, of meaningful chemical entities as the atomic constituents of the materials. This is also of critical importance in materials design and earth studies where a decomposition of compressibility as a sum of atomic-like contributions allows one to rationalize trends and to guide materials synthesis [12,13]. A formalism that is best suited along this line relies on the rigorous quantum-mechanical analysis of the topology of the crystalline electron density provided by the *Atoms in Molecules* theory (AIM) [14]. With this formalism,

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http://dx.doi.org/10.1016/j.jallcom.2013.12.153

we have shown in previous works how the partition of static thermodynamic properties like the bulk modulus can be used, for example, to explain the uniform behavior of a number of cubic oxide spinels under pressure [12,13]. Greater fractional occupation of the oxide anion sublattice and the greater compressibility of these anions (around 200 GPa) are the parameters that control the response to hydrostatic pressure of all of these oxide spinels. More recently, Otero-de-la-Roza and Luaña also proposed a feasible method for partitioning the non-isotropic elastic components into atomic contributions by means of the AIM formalism [15].

Further insight into the behavior of solids under pressure can be given using a new definition of local pressure: the resistance exerted by an atom against volume reduction when pressure is applied [16]. The way several ZnX (X: S, Se, Te) polymorphs nicely follow a common trend when these atomic-like (Zn and X) pressures are considered has been recently illustrated [16]. An extension of our previous calculations to other polymorphs with a different cation is desirable to test the performance of this new concept in the binary II–VI semiconductor family.

In this contribution, our main goal is to clearly identify the role played by Cd and Te in the rich polymorphic sequence exhibited by CdTe under hydrostatic pressure. To this end, we analyse the partition of the unit cell volume of all observed CdTe polymorphs (plus the hypothetical B2 phase) into well-defined, disjoint, and space-filling regions (basins) associated with these atomic constituents, applying the AIM formalism to the crystalline wave functions obtained after extensive first principles computations. Quantitative data of the pressure effects on the calculated atomic-like basins is obtained through careful equation of state fittings. This information is used to evaluate local pressures, compressibilities, and elastic constants for Cd and Te. A comparison with our previous results in other binary chalcogenides is also performed to check if our findings are general for this crystal family.

The rest of the paper is organized as follows. In Section 2, the computational modeling is presented, giving details on the electronic structure calculations, EOS fitting procedure, the scheme for the evaluation of the components of the elasticity tensor, and a brief presentation of the topological partition formalism applied to the crystalline electron density. Results and discussion in Section 3 are split into two subsections. The first one presents bulk properties: EOS parameters, the phase transition diagram and elastic constants. Comparison with available experimental data and results from other theoretical calculations is included. The second one deals with the microscopic partitioning of macroscopic properties focusing on the common trend of atomic pressures for all polymorphs of the binary II–VI compounds studied so far. A brief summary and the main conclusions are gathered in Section 4.

2. Computational modeling

Unlike simple theoretical calculations for cubic unit cell structures, some of the phases belonging to the pressure-induced polymorphic sequence of CdTe involve several structural parameters to optimize, and not only total energy, but also atomic forces and stress tensor components have to be computed. We have calculated the crystalline energy (E) at different volumes of the unit cell (V) for the following polymorphs: wurtzite (B4), zinc blende (B3), cinnabar (Cinn), rock-salt (B1), orthorhombic ($Cmcm$), and cesium chloride (B2); E and V always refer to one CdTe formula unit. B3 ($F\bar{4}3m$), B1 ($Fm3m$), and B2 ($Pm\bar{3}m$) are cubic structures and only the lattice parameter a has to be determined. B4 ($P6_3mc$) and cinnabar ($P3_121$) are hexagonal phases and both a and c lattice parameters are needed to determine the unit cell size. In addition, the z coordinate of Te (usually referred to as u) for the B4 structure, and the x coordinate of Cd and Te non-equivalent atoms (usually referred to as u and v, respectively) for the cinnabar structure need to be evaluated. Finally, the orthorhombic ($Cmcm$) unit cell is completely defined with the unit cell parameters a, b, and c, and the y coordinate of Cd and Te non-equivalent atoms.

First-principles total-energy calculations at selected volumes of the corresponding primitive unit-cells of all the polymorphs structures were performed under the formalism of the density functional theory with the `ABINIT` code [17]. We used the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional [18] and norm-conserving Troullier–Martins pseudopotentials [19] with 12 and 6 valence electrons for Cd an Te, respectively. Due to the existence of energetically competitive structures, we ensured that the absolute total energies converged to 10^{-6} hartree/atom. To this end, we used $8 \times 8 \times 8$, $6 \times 6 \times 8$, and $4 \times 8 \times 6$ Monkhorst–Pack meshes [20] for the cubic, tetragonal and hexagonal, and orthorhombic lattices, respectively and the plane-wave cutoff energy was set to 60 hartrees. Optimization of the unit cell geometry and atomic positions at each volume was performed via a Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization (see Ref. [17]) of the total energy using the Hellmann-Feynman forces on the atoms and the stresses on the unit cell. During the calculations, relaxations of both the internal structural parameters and the cell shape were included. The structural relaxation was performed until the residual forces and stresses were less than 5×10^{-5} hartree/bohr and 5×10^{-7} hartree/bohr^3, respectively. The chosen computational parameters (cutoff energy, k-point meshes, force tolerance, etc.) guarantee an accurate determination of the polymorphic sequence and the corresponding structural and energetical properties.

For each polymorph, the equilibrium volume V_0, the bulk modulus B_0, and its first pressure derivative B_0' (the 0 subscript meaning that all these quantities were evaluated at zero pressure) are then obtained by introducing the corresponding energy-volume (per unit formula) (E, V) points as input to the GIBBS code [21]. This is a well-tested computational code that implements a combined statistical numerical analysis with well-known analytical EOS such as those of Vinet, Birch, Murnaghan, etc. (see Ref. [21] and references therein). The standard strategy for the evaluation of the relative stability of high-pressure phases at static conditions (zero temperature and zero point vibrational contributions neglected) is based upon the examination of enthalpy ($H = E + pV$) as a function of pressure (p) for different phases. This task is also performed with the GIBBS code.

Dynamical stability of high pressure cubic phases was also analyzed after the determination of the phonon dispersion curves for the B1 and B2 phases. We computed the interatomic force constants by Fourier transformation of the dynamical matrices computed on $4 \times 4 \times 4$ regular q-point grids. Due to the metallic character of the high pressure phases of CdTe, the calculations of the initial wave functions were performed on $16 \times 16 \times 16$ k-point meshes and including a cold smearing of 0.01 hartree. Whereas this parameter is relevant to the evaluation of the phonon dispersion curves, we have checked that it does not affect the energy-volume curves.

First-principles calculation of the components of the elasticity tensor of crystalline solids can be approached with different methodologies as discussed in Ref. [22]. One elegant scheme, involving first derivatives of the stress and not second derivatives of the energy, has been proposed by Le-Page and Saxe [23], and illustrated by Hector *et al.* and others including pressure effects (see for example [24–27]). For the evaluation of these components just at zero pressure and in the cubic structure of the B3 phase of CdTe, we can carry out a simple procedure described in Ref. [15] and detailed as follows. Within the elastic domain of the crystal (*i.e.* infinitesimal deformations with respect to the equilibrium configuration), stress (τ) and strain (ϵ) are related by linear transformations:

$$\tau_{ij} = \sum_{kl} c_{ij,kl}\epsilon_{kl} \quad \text{and} \quad \epsilon_{ij} = \sum_{kl} s_{ij,kl}\tau_{kl}, \qquad (1)$$

where the indexes run over the three (x, y, z) cartesian coordinates and $c_{ij,kl}$ and $s_{ij,kl}$ are the elastic constant and the elastic compliance components, respectively. The bidimensional τ and ϵ tensors can be transformed into one index of vectors using the Voigt [28] notation:

$$[\tau_{11}, \tau_{22}, \tau_{33}, \tau_{23}, \tau_{31}, \tau_{12}] \Rightarrow [\tau_1, \tau_2, \tau_3, \tau_4, \tau_5, \tau_6] \qquad (2)$$

and

$$[\epsilon_{11}, \epsilon_{22}, \epsilon_{33}, \epsilon_{23}, \epsilon_{31}, \epsilon_{12}] \Rightarrow [\epsilon_1, \epsilon_2, \epsilon_3, \epsilon_4, \epsilon_5, \epsilon_6]. \qquad (3)$$

Under the Voigt notation, and in the limit of infinitesimal deformations, $c_{ij,kl}$ and $s_{ij,kl}$ can be expressed with just two indexes as follows:

$$c_{ij} = \left(\frac{\partial \tau_i}{\partial \epsilon_j}\right)_{\epsilon',\mathbf{0}} \quad \text{and} \quad s_{ij} = \left(\frac{\partial \epsilon_i}{\partial \tau_j}\right)_{\tau',\mathbf{0}}, \qquad (4)$$

where primes and the zero subscripts indicate, respectively, that all other strains (stresses) are null and the derivatives are evaluated at the equilibrium geometry.

Alternatively, in terms of the total volume, Eq. (4) becomes:

$$c_{ij} = \left(\frac{\partial \tau_i}{\partial \varepsilon_j}\right)_{\varepsilon',0} = \left(\frac{\partial \tau_i}{\partial V}\frac{\partial V}{\partial \varepsilon_j}\right)_{\varepsilon',0}. \qquad (5)$$

These equations will be further exploited below. Now, for the practical calculation of the elastic constants, we recall the following expression for the elastic energy of the crystal (see Ref. [15]):

$$\phi = \frac{E - E_0}{V_0} = \frac{1}{2}\sum_{ij,kl} c_{ijkl}\epsilon_{ij}\epsilon_{kl}, \qquad (6)$$

where V_0 and E_0 are the equilibrium cell volume and energy, respectively.