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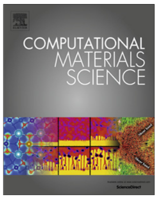

Ab initio investigation into structural, mechanical and electronic properties of low pressure, high pressure and high pressure-high temperature phases of Indium Selenide

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ABSTRACT

All-electron self-consistent full potential augmented plane waves+local orbital method (FP-APW+lo) within generalized gradient density approximation (GGA) is used to study crystalline Indium Selenide (InSe) compound at low pressure (hexagonal), high pressure (cubic) and high pressure – high temperature (monoclinic) phases. Bulk properties such as equilibrium lattice constants, bulk modulus and its pressure derivative of these phases are determined and compared to available experimental and theoretical data. Our calculations show that InSe exhibits a slight preference to crystallize at zero pressure in $\beta\left(D_{3h}^{1}\right)$ phase rather than in $\varepsilon\left(D_{6h}^{4}\right)$ polytype, and under appropriate pressures, phase transitions occur toward B1 (rock-salt) phase. Stiffness constants are calculated and other elastic properties such as sound velocity, Debye temperature and elastic anisotropy are then determined for all the studied structures and compared with available literature results. Our results show that monoclinic InSe phases are both lamellar structures and present strong elastic anisotropies compared to the other phases. Moreover, we predict a possible phase transition under pressure from $P2/m$ to $C2/m$ phase. Our electronic investigation, with and without neglecting spin-orbit effect and using both modified Becke-Johnson (mBJ) and Engel-Vosko (EV) corrections, shows that a substantial improvement of the band gap value has been achieved for hexagonal InSe over previous theoretical results in literature, besides the indirect gap value of monoclinic InSe is reported for the first time.

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1. Introduction

Indium selenide is a layered semiconductor compound which has attracted great interest in the last decay due to its interesting electronic and optical properties [1–4]. Indeed, it is evoked in many applications such as photosensitive heterojunctions [5], fast optical detector in the visual and near-IR ranges [6], nonlinear optic [7,8], coherent near-infrared emitter [9], solar cells [10–12] and current supply [13–16]. It is noteworthy that this III—VI compound crystallizes in different polytypes due to the arrangement of its complex layers; each formed by four atomic sublayers in a sequence of Se—In—In—Se. The four atomic sheets are bounded together by covalent bonds with some ionic character, whereas the complex layers are bounded by weak Van der Waals (vdW) interactions [17]. The most encountered polytypes in literature are $\beta\left(P6_3mmc, D_{6h}^{4}\right)$, $\varepsilon\left(P\bar{6}2m, D_{3h}^{1}\right)$ and $\gamma\left(R3m, C_{3v}^{5}\right)$ [17,18] (see Fig. 1(a)–(c)). From an experimental point of view, InSe growth may be reach from numerous deposition techniques [20–26] but. The most used one is the Bridgman-Stockbarger technique [27]. Many authors reported that the latter leads to γ and/or ε-polytype(s) [5,4,28–30] while the chemical vapor deposition (CVD) method [25] generates a β structure [3,31,32]. The InSe polytypism was addressed in detail on melt grown crystals [33–35].

Our investigation, however, also reveals that β and γ polytypes may be reached from Bridgman-Stockbarger and CVD methods respectively [36–39]. Furthermore, numerous theoretical works were done on γ-polytype [19,40–46] since many of the obtained experimental results were for γ InSe. In order to reduce the computational load, some scientists preferred to use the β structure in their calculations [47–51]. In contrast to the above InSe structures, the ε-polytype was rarely addressed in theoretical studies [52,53]. Moreover, few works employed two polytypes, i.e. γ and β or ε and β to study the electronic and optical properties of InSe

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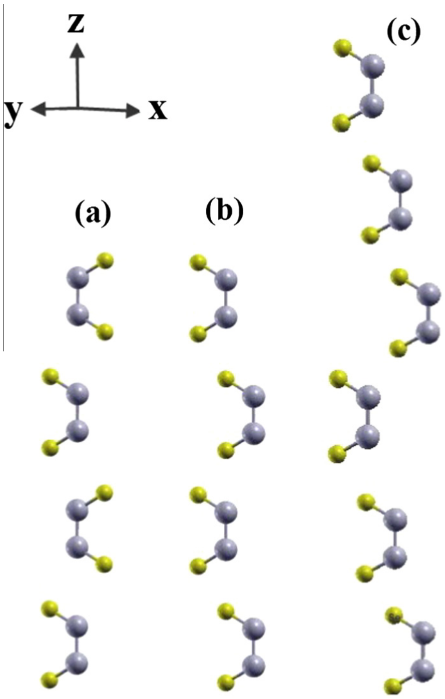

Fig. 1. Unit cell of InSe compound (extended over two layers) in: (a) hexagonal β phase $\left(D_{6h}^{4}\right)$, (b) hexagonal ε phase $\left(D_{3h}^{1}\right)$, (c) rhombohedral γ phase $\left(C_{3v}^{5}\right)$. Note the rotation induced between two adjacent layers in β InSe stacking scheme. Big grey and small yellow balls represent In and Se atoms respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

[17,18,54,55]. The use of either ε or γ polytype is justified by their energy bands similarity [18]. InSe high pressure - high temperature (HP-HT) phase opens another debate. Vezzoli [56] reported for the first time the phase transformation of β-InSe under HP and moderate temperature, but without establishing the crystal structure of the resulting phase. Iwasaki et al. [57] and Watanabe et al. [58] stated that γ-InSe transforms at HP-HT into a monoclinic non-lamellar structure $P2/m(C_{2h}^{1}$, #10). Cenzual et al. [59] proposed thereafter the $C2/m(C_{2h}^{3}$, #12) structure as the InSe HP-HT phase. Errandonea et al. [41] asserted that $P2/m$ InSe is lamellar and semiconductor, besides, it becomes more symmetric upon compression and transforms into a non-layered tetragonal structure at 19.4 GPa. The InSe HP phase was reported to have a metallic like character [40,41,46]. To the best of our knowledge, the lonely electronic study on InSe HP-HT phase was done on a non-fully optimized monoclinic structure [40], using a pseudopotential approach.

That being said, the aim of our study is to enrich the literature more by shedding light on the structural, mechanical and electronic properties of InSe HP and HP-HT fully optimized cells, using an all-electrons full potential method within DFT [60]. This will further revitalize the debate on the theoretical ground state structure of the InSe compound. Hence, this paper is organized as follows: in Section 2 we describe our technical calculations and give its details. In Section 3, we present and discuss our results with reference to other existing ones in literature. We end with conclusions in Section 4.

2. Computational details

Theoretical studies of structural, mechanical stability and electronic properties of materials, even under pressure, are now routinely performed by means of ab initio calculations. Herein, in the frame of the DFT [60], an all-electron self-consistent full potential augmented plane waves plus local orbitals (FP-APW+lo) method is used [61] as implemented in the WIEN2K code [62]. The generalized gradient approximation (GGA), based on Perdew et al. [63,64], was chosen to describe the exchange-correlation contribution. All atomic orbitals bellow −7.0 Ry are considered as core states. Thus, in our calculations, the 3*d*, 4*s* and 4*p* electrons of Se atom and the 4*p*, 4*d*, 5*s* and 5*p* electrons of In atom were treated as valence electrons. The valence wave functions inside muffin-tin spheres are expanded in terms of spherical harmonics up to *lmax* = 10, whereas plane waves (*PWs*) describe electron wave functions in the interstitial region with a wave vector cut off *Kmax* = 8.5/*Rmt*, where *Rmt* is the less muffin-tin radii. The convergence of our calculations was checked in terms of the plane wave basis set size and the k-points sampling within the irreducible part of the Brillouin Zone (BZ). The *k*-integration over the BZ is performed using the mesh of Monkhorst-Pack [65]. Due to its accuracy for semiconductor and insulator compounds, the modified Becke-Johnson (mBJ) correction [66] within GGA was applied for bands structure investigation of all studied structures. The spin-orbit effect has been taken into account in our calculations, though their effects are reported to be small for III–VI compounds [47,50]. For comparison purpose, we conducted also band structure calculations with GGA and Engel-Vosko [67] correction (GGA + EV). Additional parameterisations are listed in Table 1. To reach the equilibrium energy (E_0) and its relative equilibrium volume (V_0) in the B1 (NaCl) structure, we optimized the InSe unit cell volume by minimising its total energy keeping the ratio of the lattice constants *a*:*b*:*c* fixed. Convergence was assumed when the total energy difference between the self-consistent cycles was less than 0.1 mRy. For hexagonal structures, namely $\beta\left(D_{6h}^{4}\right)$ and $\varepsilon\left(D_{3h}^{1}\right)$, we followed the procedure listed in Ref. [68] except for determining free atom positions, we chose to simultaneously optimize the charge density and forces during the scf-cycle leading to more accuracy [69]. Here also, a complete convergence was assumed when simultaneously the atomic forces convergence was smaller than 1.0 mRy/a.u. and the charge convergence was less than 10^{-4} *e*. Monoclinic InSe structures were firstly full optimized using the 4D optimization procedure as implemented in the WIEN2K code [69]. Hence, 256 structures for each phase were generated and optimized with respect to three criteria: total energy convergence $\leqslant$0.1 mRy, charge convergence for each atom $\leqslant 10^{-4}$ *e* and magnitude of force convergence $\leqslant$1.0 mRy/a.u. The optimum structure was then subject to the volume optimization by minimising the total energy of the unit cell. Atom positions in the optimized structure were determined following the same procedure adopted in hexagonal cases.

3. Results and discussion

3.1. Structural properties

Calculated total energies versus volumes of InSe compound in $\beta\left(D_{6h}^{4}\right)$, $\varepsilon\left(D_{3h}^{1}\right)$, B1$\left(O_{h}^{5}\right)$, $P2/m\left(C_{2h}^{1}\right)$ and $C2/m\left(C_{2h}^{3}\right)$ structures are plotted in Fig. 2. When they are fitted to the Birch-Murnaghan equation of state [70], equilibrium volumes, bulk modulus and their derivatives can be obtained (see Table 2). As noticed from E (V) curves in Fig. 2, the ground state phase of InSe compound is β-polytype followed by ε-polytype. These results are in well concordance with those reported in literature [71,72], approving previous theoretical works choosing the $\beta\left(D_{6h}^{4}\right)$ structure to study InSe semiconductor compound [47–49]. Our calculated $\varepsilon\left(D_{3h}^{1}\right)$ and $\beta\left(D_{6h}^{4}\right)$ phases exhibit a total energy difference of about

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