Computational and Theoretical Chemistry 1010 (2013) 67–72

Contents lists available at SciVerse ScienceDirect

Computational and Theoretical Chemistry

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

A study of the electronic structures and optical properties of $CuXTe_2$ (X = Al, Ga, In) ternary semiconductors

Zhang Xian-Zhou [a], Shen Ke-Sheng [a], Jiao Zhao-Yong [a,*], Huang Xiao-Fen [b]

[a] College of Physics and Information Engineering, Henan Normal University, Xinxiang, Henan 453007, China
[b] College of Physics and Electronic Engineering, Sichuan Normal University, Chengdu, Sichuan 610068, China

ARTICLE INFO

Article history:
Received 10 January 2013
Received in revised form 1 February 2013
Accepted 5 February 2013
Available online 14 February 2013

Keywords:
Ternary semiconductors
Electronic structure
Optical properties
First-principle calculations

ABSTRACT

Using first-principle calculations, the electronic and optical properties of chalcopyrite crystals $CuXTe_2$ (X = Al, Ga, In) are analyzed in detail. It is found that the prominent peaks of the dielectric functions and the refractive index significantly shift towards lower energies in the order of Al → Ga → In, and these compounds are characterized by similar optical spectra with some anisotropy effects. Present findings predict that $CuGaTe_2$ and $CuInTe_2$ are promising for photovoltaics due to their high absorption of solar radiations and photoconductivity in the visible range.

1. Introduction

The ternary semiconductors with the general formula I–III–VI_2 have attracted considerable attention due to their widely applications in nonlinear optical (NLO) devices, detectors, solar cells etc. [1–4]. I–III–VI_2 chalcogenides are the most extensively used materials for photovoltaic applications, and there are numerous studies on these semiconductors, especially $CuInSe_2$, due to its high conversion efficiency and low cost used for high-efficient solar cells. Jaffe and Zunger [5] have studied the chemical trends on a series of Cu-based ternary chalcopyrite semiconductors using the potential variation mixed basic (PVMB) approach. Laksari et al. [6] calculated the structural, electronic and optical properties of $CuGaS_2$ and $AgGaS_2$ using the full potential linear augmented plane wave (FP-LAPW) method and Reshak and Auluck [7] reported related electronic properties of the chalcopyrite compounds $CuAlX_2$(X = S, Se, Te) using the same method. The optical properties of $CuGaS_2$ have been studied by Ahuja et al. [8] using the full-potential linear muffin-tin orbital (FPLMTO) method. Recently, Brik [9] and Zhou et al. [10] discussed the electronic and optical properties for series of $CuXS_2$ (X = Al, Ga, In) and $CuAlX_2$(X = S, Se, Te) semiconductors.

Despite considerable efforts made by the previous studies, there are still no theoretical studies focusing on the I–III–VI_2 ternary semiconductors of $CuXTe_2$ (X = Al, Ga, In) up to now. In this work, we first analyze the electronic properties of the I–III–VI_2 ternary semiconductors of $CuXTe_2$ (X = Al, Ga, In) compounds, based on first-principle calculations. Then, the optical properties of these compounds are discussed in more details and we found that they are characterized by similar optical spectra with some anisotropy effects.

2. Details of calculation

All calculations are performed using the ultrasoft pseudopotential method based on the density functional theory (DFT) [11] packaged in Cambridge Serial Total Energy Package (CASTEP) [12]. The exchange–correlation effects are treated by the Perdew–Berke–Ernzerhof (PBE) [13] functional within the generalized gradient approximation (GGA) [14]. The Brillouin-zone is sampled with the Monkhorst–Pack scheme ($8 \times 8 \times 4$ k-mesh) [15]. The optimization of the lattice constants is made by minimization of the total energy. We choose a cutoff energy of 800 eV which gives energy convergence less than 5.0×10^{-7} eV/atom. The maximum force tolerance, the maximum stress, and the maximum displacement tolerance are selected as 0.03 eV/nm, 0.05 GPa, 10^{-4} nm, respectively. The electronic configurations are taken as Al:$3s^2 3p^1$, Ga:$3d^{10} 4s^2 4p^1$, In:$4d^{10} 5s^2 5p^1$, Cu:$3d^{10} 4s^1$, Te:$5s^2 5p^4$ in the calculations.

3. Results and discussion

3.1. Structural and electronic properties

Fig. 1 presents considered semiconductors of $CuXTe_2$ (X = Al, Ga, In) crystallized in the chalcopyrite structure, space group I-42d

* Corresponding author. Tel./fax: +86 373 3326151.
E-mail address: zhy_jiao@htu.cn (Z.-Y. Jiao).

2210-271X/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.comptc.2013.02.002

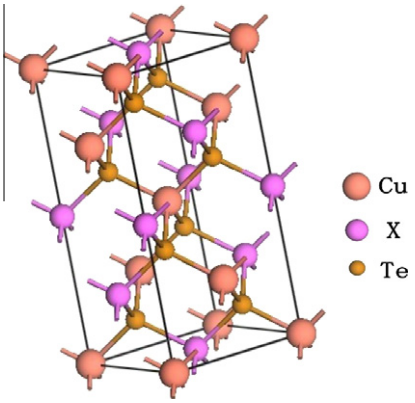

Fig. 1. A unit cell of $CuXTe_2$ (X = Al, Ga, In) crystals with the chalcopyrite structure.

Table 1
Crystal lattice constants a and c, as well as the volume (V) of $CuXTe_2$ (X = Al, Ga, In).

	$CuAlTe_2$			$CuGaTe_2$		$CuInTe_2$	
	This work	Exp.[a]	Cal.[b]	This work	Exp.[a]	This work	Exp.[a]
a(Å)	6.10	5.964	6.022	6.109	5.994	6.315	6.167
c(Å)	12.14	11.78	12.309	12.18	11.91	12.616	12.34
V(Å^3)	452	419	446	454	428	503	469

[a] Ref. [18].
[b] Ref. [17].

(No. 122), with four formula units in a unit cell. Each atom in this structure is fourfold coordinated, like in the zinc-blend or diamond crystal structures [16]. Calculated lattice parameters at ambient conditions are summarized in Table 1, and present results agree well with the available experimental data and other theoretical calculations listed in Table 1, considering the overestimation of GGA for the lattice constants. From Table 1, one can see that calculated lattice constants increase with increasing atomic number of the trivalent metal ion Al → Ga → In for the $CuXTe_2$ series.

Based on optimized structures, the band structures of $CuXTe_2$ (X = Al, Ga, In) and the density of states (DOSs) for $CuAlTe_2$ are presented in Figs. 2 and 3, respectively. The band structures in Fig. 2a show that the highest energy of valence bands and the lowest energy of conduction bands are both located at gamma point, giving a direct band gap of 0.94 eV for $CuAlTe_2$. This is in accordance with

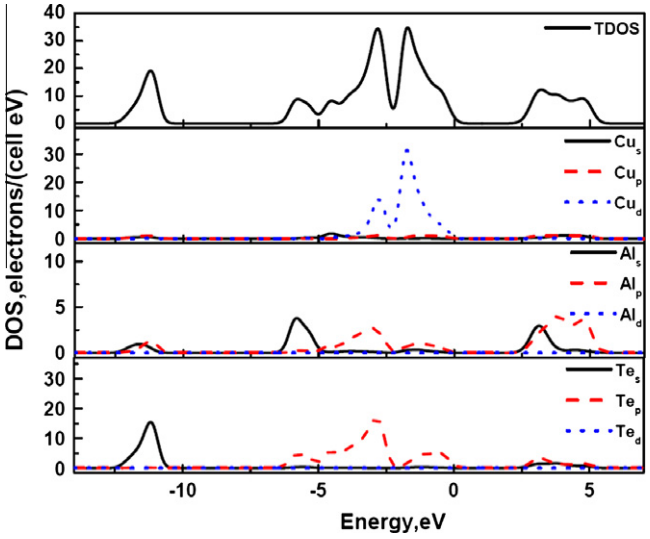

Fig. 3. Total and atom-projected density of states (DOSs) for $CuAlTe_2$.

previous theoretical values of 1.066 eV [10] and 1.032 eV [17] (using the virtual-crystal approximation) and is underestimated in comparison with the experimental data of 2.06 eV [18]. To overcome the discrepancy between experimental and theoretical results, the so called scissor operator corrections [19] was applied for the compounds considered in the calculations. The experimental value of the band gap for $CuGaTe_2$ is about 1.23 eV, whereas our present calculations gave a value as about 0.088 eV, smaller than the value of 0.43 eV given in Ref. [20] (using the LDA), such a result may be attributed to different calculation methods. So a scissor operator of 1.142 eV was applied. At last, the experimental value of the band gap for $CuInTe_2$ is 1.06 eV while our calculations performed gave practically a zero value, which is smaller than 0.18 eV [20], but is similar to $CuInS_2$ (the theoretical value of the band gap is also zero) [9], so the scissor operator was used with a value of 1.06 eV to overcome such a discrepancy. The band gaps discussed above are summarized in Table 2, including the experimental, theoretical band gaps and the scissor operator values. It is obvious the band gaps of $CuXTe_2$ decrease in the Al → Ga → In series.

Fig. 3 plots the total and atom-projected density of states (DOSs), and it shows that the conduction band between about 2.0 and 6.0 eV are mainly composed of *s* and *p* states of Al atoms,

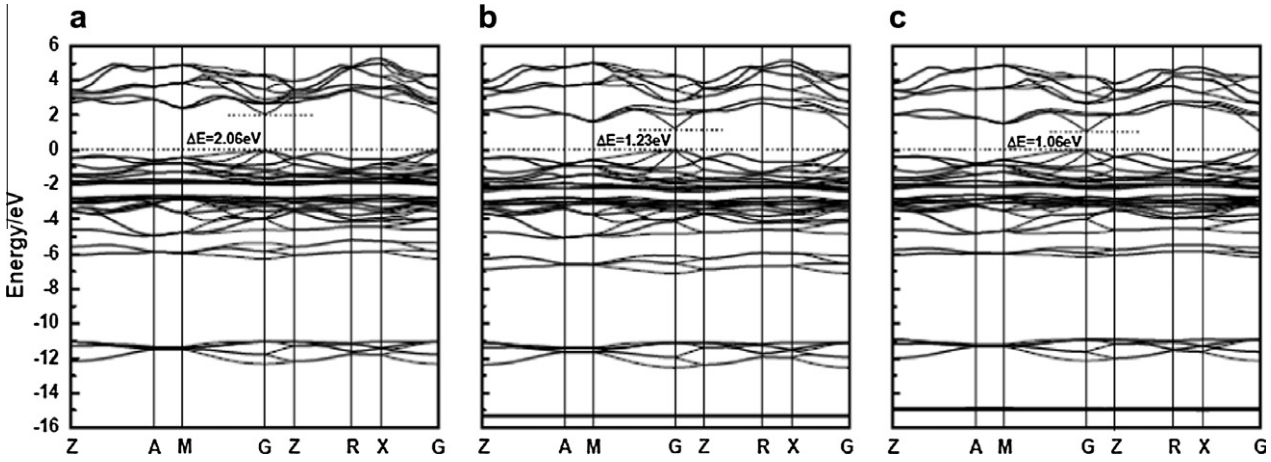

Fig. 2. Band structures of $CuAlTe_2$ (a), $CuGaTe_2$ (b) and $CuInTe_2$ (c) along the high symmetry directions.