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First principles study of structural, optoelectronic and thermoelectric properties of Cu_2CdSnX_4 (X = S, Se, Te) chalcogenides

Sajjad Hussain[a], G. Murtaza[b,*], Shah Haidar Khan[a], Afzal Khan[a], Malak Azmat Ali[a], M. Faizan[a], Asif Mahmood[c], R. Khenata[d,*]

[a] Department of Physics, University of Peshawar, Peshawar, Pakistan
[b] Materials Modeling Lab, Department of Physics, Islamia College Peshawar, KPK, Pakistan
[c] College of Engineering, Chemical Engineering Department, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia
[d] LPQ3M Laboratory, Faculty of Science and Technology, University of Mascara, Algeria

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ABSTRACT

In this work, structural, electronic, optical and thermoelectric properties of Cu_2CdSnX_4 (X = S, Se, Te) have been studied through the full potential linearized augmented plane wave method. Calculated ground state lattice parameters are in good agreement with the experimental results. Lattice constant and bulk moduli vary inversely by replacing the anion X from S to Te in Cu_2CdSnX_4. The WC-GGA shows that the materials are metallic in nature. The EV-GGA predicts better band gaps compared to WC-GGA. The calculated bandgap values are 1.8, 1.06 and 0.8042 for Cu_2CdSnX_4, Cu_2CdSnX_4, Cu_2CdSnX_4 respectively. Cd-d, Sn-s and X-p states contribute significantly in the density of states of the compounds. Absorption peaks and optical conductivity is high in the visible and ultraviolet energy regions. All the semiconductors have figure of merit above 0.70. The optical and thermoelectric properties clearly show that Cu_2CdSnX_4 are potential candidates in the fields of solar cell and thermoelectric technology.

1. Introduction

Quaternary chalcopyrite semiconductors have received considerable interest in the recent past due to their applications in the fields of solar cell technology [1], magneto-ferric and magneto-optics [2]. These materials have high optical absorption coefficient ($\sim 10^5\ cm^{-1}$), direct band gap ($E_g \sim 1.5$ eV), low cost and abundant availability [3–6].

Quaternary chalcogenides are generally represented by I_2–II–IV–VI_4 (I = Cu, Ag; II = Cd, Zn; IV = Sn, VI = Se, S, Te). These compounds can be derived from binary II–VI semiconductors under a systematic combination [7] but their structure is more complicated than that of the binary and ternary semiconductors [8]. For example the Cu_2ZnSnS_4 is obtained from the ZnS. The ZnS has zinc-blend structure but if four Zn^{2+} cations are replaced by two Ga^{3+} and two Cu^{+} cations, the ternary semiconductor $CuGaS_2$ is formed. Further, replacing two Ga^{3+} cations by one Sn^{4+} cation and one Zn^{2+} cation without violation of the octet rule, the quaternary semiconductor Cu_2ZnSnS_4 is formed as shown in Fig. 1 [9].

The Cu_2CdSnX_4 (X = S, Se, Te) compounds are important candidates among the quaternary chalcopyrite semiconductors of type I_2–II–IV–VI_4. These compounds crystallize in the kesterite or stannite structure with tetragonal symmetry [10], having space groups I-4 and *I*-42*m*, respectively [11]. The electronic structure of Cu_2CdSnX_4 compounds is like that of binary II–VI semiconductors but their physical properties are much more different [12].

The Cu_2CdSnX_4 (X = S, Se, Te) compounds have been the subject of many experimental and theoretical works. Guan et al. [3] prepared thin films of Cu_2CdSnS_4 using simple solution method. They calculated the optical band gap of Cu_2CdSnS_4 as 1.45 eV. The nanoparticles of Cu_2CdSnS_4 were synthesized by Shi et al. [13] using microwave irradiation method. According to their finding, the band gap of this compound is 1.26 eV. Fan et al. [14] have prepared experimentally mono-dispersed nanocrystals of $Cu_2CdSnSe_4$ using solution-based method and studied the thermoelectric properties of these compounds. They have generated copper dopant and selenium vacancies in it during chemical synthesis and observed effective enhancement in the power factor of $Cu_2CdSnSe_4$. A figure factor (ZT) up to a peak value of 0.65 at 723 K was achieved. Dong et al. [15] have synthesized $Cu_2CdSnTe_4$ by direct reaction of the corresponding elements. According to their theoretical calculation, the calculated lattice parameters are a = 6.2889 Å, c = 12.5159 Å and a = 6.3099 Å, c = 12.5812 Å using the

* Corresponding author.
E-mail addresses: murtaza@icp.edu.pk (G. Murtaza), khenata_rabah@yahoo.fr (R. Khenata).

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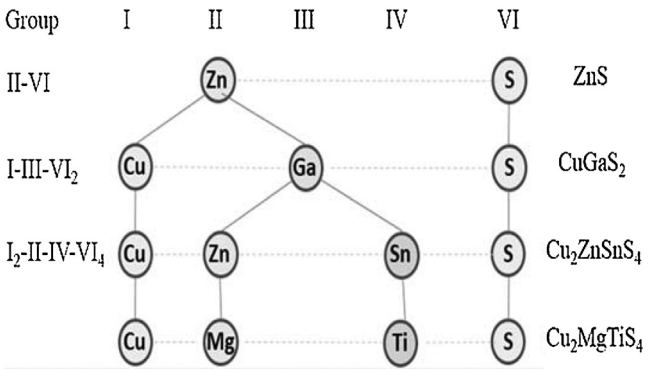

Fig. 1. Scheme of formation of I_2–II–IV–VI_4 semiconductor from binary II–VI compounds.

generalized gradient approximation (GGA) and generalized gradient approximation with spin orbit coupling (GGA + SOC) respectvely.

A lot of experimental work has been done to study compounds of the type Cu_2CdSnX_4, but according to the best of our knowledge, relatively less attention has been given to the theoretical aspect of this important family of compounds. It is, therefore, important to thoroughly investigate the structural, electronic, optical and thermo-electric properties of Cu_2CdSnX_4 compounds using Density Functional Theory (DFT).

2. Calculation methodology

To study the physical properties of the quaternary Cu_2CdSnS_4, $Cu_2CdSnSe_4$ and $Cu_2CdSnTe_4$ compounds, the full-potential linearized augmented plane wave (FP-LAPW) method implemented in the Wien2K code [16] has been used. This is one of the most successful computational techniques based on DFT for the study of the ground state properties of materials. The exchange-correlation potential is treated with GGA [17] and Engel-Vosko GGA (EV-GGA) [18]. A mesh of 1000 k-points in the full Brillouin zone (BZ), and suitable muffin-tin radii (R_{MT}) for Cu, Cd, Sn, S, Se, and Te are selected. The wave function inside the sphere is expanded in spherical harmonics up to $l_{max} = 10.0$, and the charge density is Fourier expanded up to $G_{max} = 12.0$. The value of $R_{MT}.K_{Max}$ was taken as 7.0. The self-consistent calculations are considered to be converged when the total energy is less than 10^{-3} Ry.

3. Results and discussions

3.1. Structural properties

The compounds Cu_2CdSnX_4 are crystallized in the kesterite structure (space group I–4), the stannite structure (space group *I*-42*m*) and the primitive mixed CA structure (space group P-42) in tetragonal phase [19]. Compare to the other structures, the

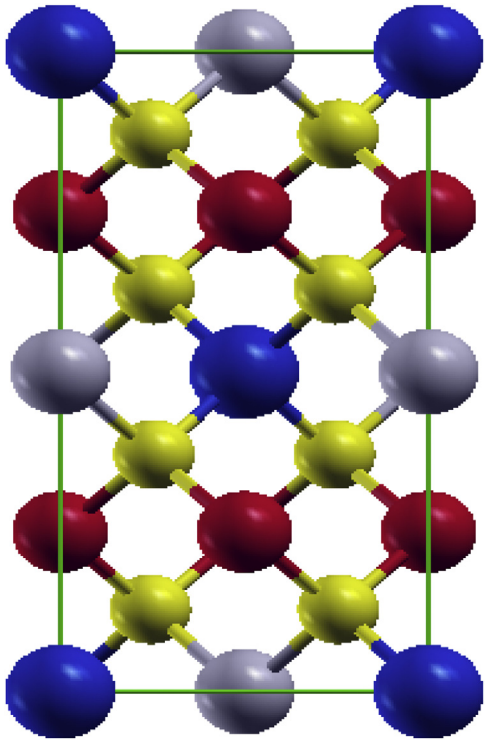

Fig. 2. Crystal-structure representation of stannite Cu_2CdSnX_4 (X = S, Se, Te). Blue, red, silver and yellow balls show the Cd, Cu, Sn and X atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).