First-principle study of structural, electronic and optical properties of Cu₂FeSnS₄ semiconductor

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A B S T R A C T

The Cu_2FeSnS_4 semiconductor with its stannite structure represents one of the most promising candidates for the photovoltaic devices. For this purpose, we address this work to study their structural, electronic and optical properties using the Density Functional Theory. The generalized gradient approximation showed that this material exhibits a half-metallic behavior, with an optimal band gap value obtained by the generalized gradient approximation with the modified Becke-Johnson correction GGA-mBJ. The optical properties showed a good optical absorption and conductivity in the visible range. Thus, a good optical band gap is obtained, confirming its applicability as an absorber layer in photovoltaic solar cells.

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1. Introduction

Photovoltaic technology has been known as a considerable source of green energy. A solar cell consists of several layers where the absorber represents the most important one. Solar cell based on silicon material is the most used in the commercial solar cells with high energetic efficiency [1]. While, the high cost of manufacturing brings down the interest towards this generation of photovoltaic panels.

Photovoltaic solar cells industry is mostly based on crystalline and polycrystalline silicon [1] wafer technologies. However, the inconvenient with this absorber cells are mainly due to the indirect band gap of silicon, thereby requiring a ticker layer for absorbing, which could be problematic if the mobility of the compound are low. There is also the inconvenient of the high cost processing of these silicon crystals. As an alternative for these photovoltaic cells, researches went looking for another generation of solar cells (thin film solar cells), which are based on a direct band gap and a thinner layer such as CIS, CIGS and CdTe [2,3]. However, these materials are containing toxic elements such as Cd and Se and also rare elements that could limit their production. As another alternative, attention was paid for new compounds CZTS and CFTS [4–9] because of the direct band gap the thin layer and also the non-toxicity and abundance of its elements.

In order to explore a friendly environmentally material for the absorber layer in the solar cell with low-cost and high efficiency, studies have been focused on the Cu based chalcogenide semiconductors such as Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ which have a direct band gap around 1.5eV, a high absorption coefficient ($>10^4\,cm^{-1}$) and a high-power conversion efficiency of 8.4% and 11.1% respectively [4–9]. Related to Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$, the Cu_2FeSnS_4 (CFTS) is based on the abundant element of iron that is considered as a competitor photovoltaic material due to its band gap between 1.2 and 1.5 eV and its large absorption coefficient of $10^4\,cm^{-1}$ [10,11] comparable to other absorber compounds such as silicon and $CH_3NH_3PbI_3$ [12], the CFTS compound has been experimentally confirmed to crystallize in both kesterite and stannite structures even a disordered structure has been reported by Schorr [13]. Some theoretical works have studied this material on its kesterite structure as was reported by Palaz et al. [14]. The Cu_2FeSnS_4 (CFTS) have the advantage over corresponding $CuIn(Ga)Se_2$ absorber as reported by Jackson et al. [15] to involve abundant, nontoxic, and less expensive chemical elements. In addition to its interesting properties for photovoltaic application, theoretical study based on density functional theory has predicted that CFTS compound exhibits a half-metallic ferromagnetic character which makes it a suitable material for spintronic application [16].

Herein, we studied firstly the structural stability of this material between the two configurations. The most stable structure was found to be the stannite one, that's what this work was based on,

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same as what was done by Dhruba and al experimentally [17].

For this purpose, we are interested in studying the structural, electronic, optical and electric properties of Cu_2FeSnS_4 compound, with its stannite structure, using both PBE-GGA and GGA-mBJ approximations provided by the density functional theory (DFT) as implemented in the WIEN2K package [18] and also Boltztrap code for electric calculations [19]. Our paper is organized as follow: Starting with a first section dedicated to the study of the crystal structure and computational details used for incoming calculations, followed by the study of electronic, optical and electric properties, and a conclusion is presented in the last section.

2. crystal structure and computational details

First principle calculations were carried out on the structural, electronic and optical properties of tetragonal CFTS. To get loyal results, a Full Potential Linearized Augmented Plane Wave (FP-LAPW) method is used, as implemented in the WIEN2k package based on Density Functional Theory (DFT) [18] [20]. The exchange correlation effect is discussed using the modified Becke-Johnson with Generalized Gradient Approximation (mBJ-GGA) [21] and Perdew-Burke-Ernzerhof with Generalized Gradient Approximation (PBE-GGA) [22].

To obtain the energy convergence of the eigenvalues, the basic functions, charge density, and potential is expanded inside the muffin-tin spheres in combination with spherical harmonic function with a cut-off $I_{max} = 10$. $R_{MT}*K_{max} = 7$ parameter was used, which determines the matrix size (convergence), where K_{max} is the plane wave cut-off and R_{MT} is the smallest of all atomic sphere radii. For Cu_2FeSnS_4 compound, the muffin−tin radii, R_{MT} were chosen equal to 2.39, 2.44, 2.5 and 1.95 a. u for Cu, Fe, Sn, and S respectively. 500 k-points were used in the irreducible wedge of the Brillion zone for optimization. The iteration process is repeated until the calculated total energy of the crystal converges to less than 10^{-4} Ry and force converged below 1 mRy/a. u.

Cu_2FeSnS_4 has been found to crystallize into the tetragonal structure with the I-42 m space group (N° 121) and lattice parameters a = b = 5.43 Å, c = 10.671 Å. The structural stability shows that the stannite structure exhibits the minimum energy compared to the kesterite structure as seen in Table 1. Fig. 1 shows the structures of CFTS, CFTS stannite structure will be referred as CFTS_SS.

An optimization of the total energy as a function of the volume is done with respect to the Murnaghan equation of state given by:

$$E(V) = E_0 + \frac{B_0 V}{B'_0} \left[\frac{\left(V_0/V \right) B'_0}{B'_0 - 1} + 1 \right] - \frac{B_0 V}{B'_0 - 1} \tag{1}$$

Where, E_0 is the total energy at T = 0, V_0 is the equilibrium volume, B_0 is the bulk modulus at pressure P = 0, and B'_0 is the first derivative of the bulk modulus with respect to pressure. The structural properties could be determined at equilibrium and is governed by the minimization of the energy given in equation (1). The optimized lattice parameters (a,c), equilibrium volume V_0 and bulk modulus B_0 are represented in Table 2, the obtained values are in good agreement with experimental and theoretical results.

Table 1
Equilibrium energy (Ry) of Cu_2FeSnS_4 compound by PBE-GGA.

Type of structure	Stannite	Kesterite
Energy (Ry)	−24717.74988288	−24717.73943214

3. Results and discussion

3.1. Electronic properties

The importance of the electronic properties of a material lies in the fact that, they allow us to analyze and understand the nature of the bonds formed between the different elements and it also permits to evaluate the spectral distribution of the absorption, mobility and others. The electronic properties of CFTS_SS are explained employing the band structure, total and partial density of states (TDOS) calculated within optimized values. Spin polarized calculations were done using both mBJ-GGA and PBE-GGA approximations. The calculated band structure path along the higher symmetry points is Γ-X-P-Γ-N zone and it was performed using PBE-GGA and mBJ-GGA as shown in Fig. 2. The valence band maximum (VBM) and the conduction band minimum (CBM) are located at the Γpoint. For PBE-GGA approximation it can be clearly seen that from up to down behavior changes. For spin up, we found a semi-conducting behavior. While for the spin down, the band structure is metallic. The band gap energy for spin up is equal to 0.41 eV. In mBJ-GGA approximation, the band gap in spin up and down opened more. For spin down the behavior changed from metallic to a semi-conductor with an indirect band gap of 0.96 eV, while for spin up we found a direct band gap of 0.97 eV higher than the one obtained by PBE-GGA.

However, Figs. 3 and 4 presents the total and partial densities of states of both PBE-GGA and mBJ-GGA approximation. As seen from Fig. 3, the compound CFTS_SS acts as a half-metal. The spin up density of states has a semi-conductor behavior, and the metallic comportment is seen in spin down. From Fig. 4, the same behavior was noticed for spin up but we can see that the spin down is no longer metallic and it is due to the fact that the Fe band gap opened up with mBJ correction.

The partial DOS show fragments energies from the valence band −7 eV to Fermi level originated from more localized Cu-d orbital, and delocalized S-p and d orbital and Sn-p orbital. The structure from conduction band presents an admixture of Cu (s, p), Sn (p, d), Fe (s, p) and S (p) states. One can see a strong hybridization between Cu-p, Fe-d and Sn-d states, as can be seen from the two figures below including PBE-GGA and mBJ-GGA approximations.

An electronic transition between the mixed state of Cu(d), S(p) and Fe(d) at the valence band to Fe(d) state at the conduction band can be seen from spin-down density of states below, and it is responsible of the band gap transition. For spin-up, the transition is seen between Cu(d), S (p-), Fe(d) from the maximum of the valence band to Sn(p) and S(p) in the minimum of the conduction band which is related to the band gap transition.

3.2. Optical and electric properties

Optical properties have an important role in understating the nature of material. As well as knowing the photon and electron interaction with each other. In materials, it can be described in terms of time-dependent perturbations of the ground-state electronic states. The electric fields of the photon produce the transitions between occupied and unoccupied states. The spectra getting from these excitations can be described as a joint density of states between the valence and conduction bands.

The response of electrons in a solid can be described macroscopically by the complex dielectric function $\varepsilon\,(\omega)$, which connects the electric field vector $\vec{E}$ to the electric induction in solid $\vec{D}$. This feature has important consequences on the physical properties of solids. The relationship between the real and imaginary part of the dielectric constant are called Kramers-Kronig relations. The complex dielectric constant is given by this relation [25,26]: