Microscopic Optical Absorption, Analysis and Applications of Famatinite Cu_3SbS_4

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Abstract

Cu-Sb-S semiconductors are a large group of materials promising for a variety of applications, especially as thin-film solar cell absorbers. We present first-principles calculations of the optical and electronic properties of Cu_3SbS_4 in the famatinite structure. The effect of the microscopic properties on macroscopic optical and photovoltaic parameters is analyzed. By splitting the optical properties, we identified microscopically the origin of the high absorption coefficients. It is because an elevated contribution from S-S and Sb-Sb transitions. In addition, we estimate the macroscopic potential of these compounds for photovoltaic applications obtaining solar cell efficiencies using different spectra. The results indicate the great potential of these materials for photovoltaics.

Keywords: optical absorption, photovoltaics, electronic structure, semiconductors.

1. Introduction

Ternary copper antimony sulfide $\text{Cu}_x\text{Sb}_y\text{S}_z$ semiconductors are p-type semiconductors with an energy band gap which varies between ~ 0.46 and 1.9 eV depending on the crystalline structure. They usually have a high absorption coefficient and abundant, cheap, readily available, and comparatively abundant elements. These

properties make it attractive for semiconductor-based device applications and a particularly attractive candidate for photovoltaic solar cells.

Copper antimony sulphide has four common crystal phases: famatinite (Cu_3SbS_4), tetrahedrite ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$), skinnerite (Cu_3SbS_3), and chalcostibite (CuSbS_2). The famatinite- Cu_3SbS_4 and other compounds have also shown promising optical properties because of the high absorption coefficients^{1,2}.

Previous research into antimony sulfide semiconductors focused mainly on outlining the synthetic method necessary to produce it. In general, there are several phases in the Cu-Sb-S experimental samples, albeit in different proportions. Occasionally famatinite (Cu_3SbS_4) is produced as a subproduct of the tetrahedrite $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ syntheses. They can be easily separated manually because tetrahedrite is shiny black, whereas famatinite has a characteristic bronze sheen¹. Furthermore, the annealing of tetrahedrite films in sulfur vapor can generate pure famatinite films². It opens up the possibility of tuning the crystalline structure of these ternary copper antimony sulfide films. Therefore, famatinite- Cu_3SbS_4 is relatively simple to synthesize.

The experimental energy band gap of famatinite- Cu_3SbS_4 is between 0.46 eV³ and 1.0 eV², and the absorption coefficient is high, greater than 10^4 cm^{-1} over the visible region^{2,4}. These properties indicate that this compound could be suitable as a solar radiation absorber in solar cells.

However, despite intensive experimental research activities, a microscopic knowledge of the influence of the electronic and optical properties on the absorption coefficients is needed in order to analyze the potentiality for photovoltaic solar cells. Understanding the fundamental factors responsible for the high absorption in these materials will provide new insight, refinement and focusing design pathways for the discovery of improved materials. To achieve the aforementioned objectives, we present

a study of these properties and of the fundamental factors affecting the absorption using first-principles. In addition, we will analyze the potentiality for photovoltaics obtaining the maximum efficiencies when these materials are used as a light absorbent in solar cell devices.

2. Methodology

The electronic properties were obtained using first principles within the density functional (DFT) formalism^{5,6}. Standard functionals used in the local density approximation (LDA) and in the generalized gradient approximation (GGA) underestimate the band gap of a wide range of semiconducting materials. Therefore, a further extension beyond the standard DFT was carried out using the DFT+U method⁷⁻¹¹ including an orbital-dependent one electron potential to account explicitly for the important Coulomb repulsions not dealt with adequately in the standard approaches. The value of U depends on the choice of the orbital subspace on which the correction is applied, on the orbital occupations numbers, and the implementation chosen⁸⁻¹¹. In this work we applied the orbital-dependent one-electron potential using the DFT+U formalism described in references^{8,9}. For the exchange-correlation potential, we used the GGA from Perdew, Burke and Ernzerhof¹². The standard Troullier–Martins¹³ pseudopotentials are adopted and expressed in the Kleinman–Bylander¹⁴ factorized form⁶. The valence wave functions are expanded into a numerically localized pseudoatomic orbital basis set¹⁵. In all of the results presented in this work periodic boundary conditions, 128 special k points (symmetry reduced 8x8x4 k-grid) in the irreducible Brillouin zone, and a double-zeta with polarization localized basis set have been used.

In order to obtain the optical properties we have calculated the momentum matrix elements $p_{\mu\lambda}$ between the μ and λ bands at $\vec{k}$ points in the Brillouin zone, where

$\mathbf{p} = i(m / \hbar)[H, \mathbf{r}]$. Both, the local and non-local parts of the pseudopotentials have been considered in the calculation of the momentum matrix elements. With the energies $E_{\mu, \vec{k}}$, occupations $f_{\mu, \vec{k}}$ and momentum matrix elements at $\vec{k}$ points we have obtained the complex dielectric function:

$$\epsilon_2(E) \sim \frac{1}{E^2} \sum_{\lambda > \mu} \int d\vec{k} |p_{\mu\lambda}|^2 [f_{\mu, \vec{k}} - f_{\lambda, \vec{k}}] \delta(E_{\lambda, \vec{k}} - E_{\mu, \vec{k}} - E)$$

other optical properties have been obtained by using the Kramers-Kronig relationships.

The optical properties depend on the square of the momentum operator matrix elements $p_{\mu\lambda}$. These matrix elements can be split as $p_{\mu\lambda} = \sum_A \sum_B p_{\mu\lambda}^{AB}$, where $p_{\mu\lambda}^{AA}$ is the intra-specie component that couples the localized basis set functions on the same specie atom A, and $p_{\mu\lambda}^{AB}$ is the inter-specie component that couples basis set functions on different specie atoms A and B. Similarly, the absorption coefficients and other optical properties can be split: $\alpha = \sum_A \alpha^{AA} + \sum_A \sum_{B \neq A} \alpha^{AB} +$ (terms involving three and four different species).

We have additionally split $p_{\mu\lambda}^{AB}$ into angular momentum contributions as $p_{\mu\lambda}^{AB} = \sum_{l_A} \sum_{l_B} (p_{\mu\lambda}^{AB})_{l_A l_B}$, where $(p_{\mu\lambda}^{AB})_{l_A l_B}$ is the contribution of the transition between the l_A shell-states (in A) and the l_B shell-states (in B). As usual we use the notation s, p, d , etc for $l=0, 1, 2$, etc. Therefore, the absorption coefficients can also be split: $\alpha = \sum_{A, l_A} \sum_{B, l_B} \alpha_{l_A l_B}^{AB} +$ (terms involving three and four different species and l -shells).

A useful magnitude for evaluating the contribution of the momentum operator matrix elements to the A-B optical transitions is the mean-value of the $\langle p_{AB}^2 \rangle$, defined

$$\text{as } \langle p_{AB}^2 \rangle = \sum_{\mu < \lambda} \int d\vec{k} \cdot |(p_{\mu\lambda}^{AB})|^2 [f_{\mu, \vec{k}} - f_{\lambda, \vec{k}}] .$$

In order to compare the absorption coefficient of the famatinite-Cu₃SbS₄ with similar materials we have included in this study the chalcostibite-CuSbS₂. The chalcostibite compound crystallize into orthorhombic structure *Pnma* (space group 62). In this structure there are two non-equivalent S atoms (S₁ and S₂). The Sb form trigonal pyramids linked to three S atoms (S₁+2S₂) and the Cu have a tetrahedral environment surrounded by 2S₁+2S₂. For this calculation we have used the experimental lattice parameters¹⁶ (*a*, *b*, *c*) = (6.0160, 3.7968, 14.4990) Å and $\alpha = \beta = \gamma = 90^\circ$. The energy band gap obtained with $U_a=5$ eV is 1.19 eV, within the range of experimental values (1.1 eV¹⁷-1.44 eV⁴), and lower than other theoretical results in the literature (1.56 eV⁴-1.60 eV¹⁷).

3. Results and Discussion

3.1. Structure and electronic properties

Cu₃SbS₄ in the famatinite structure (space group *I*-42*m*, n° 121) has experimental lattice parameters *a*=5.285 Å and *c*=10.748Å¹⁸. Other lattice data parameters in the literature are between *a*=5.285-5.391 Å and *c*=10.748-10.764 Å^{3,18-21}: (*a*,*c*) Å =(5.285, 10.748)¹⁸, (5.385, 10.754)³, (5.385, 10.754)¹⁹, (5.383, 10.772)²⁰, (5.391, 10.764)²¹, (5.384, 10.762)²². Figure 1 shows the details of the crystalline structure. In this structure there are two non-equivalent Cu atoms, labeled Cu₁ and Cu₂. The distribution of the first shells of the neighbors around Cu₁, Cu₂ and Sb are four S atoms at 2.31 Å, 2.26 Å and 2.37 Å respectively. In the structure there are double the number of Cu₂ atoms than Cu₁ atoms, i.e. the chemical equation is (Cu₁)(Cu₂)₂SbS₄.

The Cu₃SbS₄ experimental gaps reported in the literature are between 0.46-1.2 eV: 0.46 eV³, 0.74 eV²³, 0.88 eV⁴, 0.9-1.0 eV^{2,22}, and 1.2 eV¹⁷. Theoretically this compound has been researched as candidate for 3D topological insulator, and the energy band gap obtained using GGA is between 0.042 eV²⁴ and 0.10 eV²⁵. With more

sophisticated methods the energy band gap obtained is 0.88 eV (HSE²⁶), 0.9 eV (HSE06²⁷) 0.98 eV (HSE06+GW⁴), 1.0 eV, and 2.5 eV (HSE06¹⁷). These theoretical results find that Cu₃SbS₄ in the famatinite structure has a direct band gap^{4,22,24-27}, except in reference¹⁷.

We have used several GGA+U schemes in order to apply the orbital-dependent one-electron potential: U=3 and 5 eV for the d(Cu) states and U=3 and 5 eV for all d(Cu), p(S) and p(Sb) states. The latter schemes in which U is applied to d(Cu), p(S) and p(Sb) states will be labeled as U_a=3 and U_a=5 eV respectively. The main difference between the different schemes is the energy band-gap value. The energy band gap obtained using the experimental lattice parameters with U=0, U=3 eV, U=5 eV, U_a=3 eV and U_a=5 eV are 0.31, 0.43, 0.49, 0.64 and 0.86 eV respectively. When the electronic structure calculations were carried out by relaxing the cell atoms positions (forces on the atoms fall below 0.004 eV.Å⁻¹) the values of the energy band gap obtained with U=0, U_a=3 eV and U_a=5 eV are 0.07, 0.62 and 1.18 eV respectively. After geometry optimization, the calculated lattice constants are (a,c) Å=(5.45, 10.89), (5.41, 10.82) and (5.39, 10.74) for U=0, U_a=3 eV and U_a=5 eV respectively. The calculated energy band-gap E_g and the lattice parameters with U=0 are in good agreement with the available theoretical results with GGA in the literature: (a,c) Å=(5.41, 10.84)²⁵ and E_g between 0.042 eV²⁴ and 0.10 eV²⁵. The gap and lattice parameters results obtained with U_a=5 eV are in good agreement with the available experimental results: a=5.285-5.391 Å, c=10.748-10.764 Å, and E_g between 0.46-1.2 eV. We found that the U_a=5 eV scheme gave the most accurate reproduction of experimental band-gap values, whereas the other U schemes tend towards an energy band-gap underestimation. The energy-band diagram using GGA+U with U_a=5 eV along high symmetry lines in the Brillouin zone is shown in Figure 2.

3.2. Projected electronic properties

According to the ionic model, the Cu-V-VI compounds are usually classified as high-valence (Cu-V⁵⁺-VI) and low-valence (Cu-V³⁺-VI) according to the oxidation state of the V-group atom. Cu₃SbS₄ is included in the high-valence group. Other CuVS₂ compounds and tetrahedrites would be included in the low-valence group. One of the main differences between the high-valence and low-valence Cu-V-VI compounds is that the orbital contribution of group V atoms in the high-valence compounds is larger in CB states than that in VB states for the s(V) orbitals^{4,28}, while in low-valence compounds it is larger for the p(V) orbitals^{4,26}.

In order to contrast our results with previous results in the literature we have obtained the atomic and orbital composition of the VB and the CB edges by calculating the projected density of states (PDOS) as a function of energy. A detailed analysis of the PDOS per non-equivalent atom (Figure 3a) reveals that the states of the VB edge are derived mainly from d(Cu₁) and d(Cu₂) states, and with a lower contribution of the p(S) states. The CB edge states are derived mainly from s(Sb) and p(S) states. These results compare well with Cu₃-V-VI₄ ternary compound results in the literature^{4,26}. Note that the d(Cu₁) contribution per Cu₁ atom is larger than the contribution of the d(Cu₂) per Cu₂ atom. Nevertheless, as the chemical equation of famatinite-Cu₃SbS₄ is (Cu₁)(Cu₂)₂SbS₄ if all non-equivalent atoms are considered, the total d(Cu₂) contribution is twice the d(Cu₂) contribution per Cu₂ atom (Figure 3b). Similarly the total p(S) contribution is six times the p(S) contribution per S atom.

3.3. Absorption coefficients

The energy band gap of famatinite Cu₃SbS₄ indicates that this compound could be suitable as a solar radiation absorber in solar cells. Nevertheless, a good candidate for photovoltaic applications must also have a high optical absorption. In order to confirm

their application in photovoltaics we have obtained the optical absorption coefficients, which are shown in Figure 4. Our results indicate that famatinite has high absorption coefficients, greater than 10^4 cm^{-1} over the visible region and reaching 10^5 cm^{-1} at energies greater than $\sim 1 \text{ eV}$ above the energy band gap. Such high absorption coefficients make famatinite an attractive candidate for use as light absorber in solar photovoltaic devices. In Figure 4 our results are compared with other experimental^{2,4} and theoretical⁴ results in the literature.

The comparison with experimental data in Figure 4 shows that our results are closer to the experimental results E2² for $E-E_g < 0.8 \text{ eV}$ and closer to the experimental results E1⁴ for $0.9 \text{ eV} < E-E_g < 1.4 \text{ eV}$.

The difference between the experimental results E1 and E2 might be due to the different experimental geometries (nanocrystal² /thin-film⁴). The difference between theoretical and experimental results near E_g might be due to excitonic effects and phonon-assisted transitions not considered theoretically although experimentally measured. On the other hand, the absorption measured experimentally may also contain the contribution from defects or surfaces which are not considered in the theoretical calculations.

Our results show a peak around $E-E_g=0.3-0.5 \text{ eV}$ above of the energy band gap ($1.2-1.5 \text{ eV}$ without using the gap as a reference). This peak appear in Figure 4, 5 and 6. It corresponds to intra-atomic transitions between the S atoms (Figure 5), and more specifically to transitions s-p between S atoms (Figure 6). This peak is also present in the theoretical results T1⁴ in Figure 4. The theoretical results T2¹⁷ do not show the peak previously mentioned, and the absorption is lower than the T1 and our results. In fact among $1.2-1.5 \text{ eV}$ there is not absorption because the theoretical gap of T2 is 2.5 eV .

This larger gap leads to a lower absorption in the visible region. Other peak around $E_g \sim 1.0$ eV is shown for all theoretical results: Ua=5, T1, and T2.

3.4. Projected absorption coefficients

In order to analyze microscopically the cause of the high absorption we have split the absorption coefficients into intra-species contributions according with the methodology section. The splitting of the Cu_3SbS_4 absorption coefficient on intra- and inter-species components is shown in Figure 5. The largest contribution to the absorption coefficient corresponds to the $\text{S} \rightarrow \text{S}$ transitions. The $\text{Sb} \rightarrow \text{Sb}$, $\text{S} \rightarrow \text{Sb}$, and $\text{Cu}_i \rightarrow \text{S}$ contributions are also significant. Finally, the $\text{Cu}_i \rightarrow \text{Sb}$ and $\text{Cu}_i \rightarrow \text{Cu}_i$ transitions ($i=1,2$) make a very low contribution. This characteristic is similar in tetrahedrites²⁸.

According to the total PDOS in Figure 3b, the largest contribution to the VB and CB edges are from $d(\text{Cu}_1)+d(\text{Cu}_2)+p(\text{S})$ and from $p(\text{S})+s(\text{Sb})$ states respectively. Therefore, from an analysis based only on the joint DOS (JDOS) the high absorption should arise mainly from $d(\text{Cu}_i) \rightarrow s(\text{Sb})$, $d(\text{Cu}_i) \rightarrow p(\text{S})$, $p(\text{S}) \rightarrow s(\text{Sb})$, and $p(\text{S}) \rightarrow p(\text{S})$. It is because of high $[p(\text{S})+s(\text{Sb})]_{\text{CB}}-[d(\text{Cu}_1)+d(\text{Cu}_2)+p(\text{S})]_{\text{VB}}$ JDOS for energies near of the semiconductor gap.

Apparently, the analysis based on the JDOS does not exactly match the largest intra- and inter-species contribution to the absorption coefficients in Figure 5. It is because the transition probabilities (via momentum operator matrix elements) are not taken into account in the simplified JDOS analyses. In order to deepen into this matter we have additionally split the absorption coefficient into angular momentum contributions according with the methodology section. The more important $\alpha_{l_A l_B}^{AB}$ contributions to the absorption coefficient are represented in Figure 6: α_{ps}^{SS} , α_{ps}^{SbSb} and α_{ps}^{SbS} . It corresponds to the intra-species $p(\text{S})-s(\text{S})$, $p(\text{Sb})-s(\text{Sb})$, and inter-species $p(\text{Sb})-p(\text{S})$ transitions.

It is interesting stress that the intra-species transitions indicate all transitions between states of the atoms of the same specie (identical and symmetrically equivalent atoms). It includes intra-atomic and inter-atomic transitions involving mono-centric and bi-centric matrix elements respectively. Therefore, although for atoms the (intra-atomic) transitions between states with equal angular momentum l are forbidden, the inter-atomic transitions between atoms located at different sites can be allowed. It is because of that the translation of a regular lm -solid harmonic gives a finite expansion of regular $\lambda\mu$ -solid harmonics with λ from 0 to l and with μ from $-\lambda$ to λ ²⁹. As a consequence, the transition selection rules are determined by the system (atomic, molecular, solid) symmetry³⁰. Therefore, depending on the symmetry, the intra-specie transitions between states with equal angular momentum may be allowed, unlike what happens in atoms. The same applies to the inter-species transitions.

From previous analyses is clear that the differences between the simplified JDOS and, the α^{AB} and the $\alpha_{l_A l_B}^{AB}$ came from the momentum operator matrix elements not considered in the oversimplified JDOS. For instance, when an atom or a group of atoms makes a larger contribution to the band edge states, it does not necessarily mean that they contribute significantly to the optical properties. The contribution depends on both, the JDOS and the momentum operator matrix elements. If one is large but not the other, the contribution will be very small. For this reason a splitting of the absorption coefficients into inter- and intra-species contributions α^{AB} and into angular momentum contributions $\alpha_{l_A l_B}^{AB}$ should always be considered.

Since the momentum operator matrix elements is the key factor, in Figure 7 the mean-value of the $\langle p_{AB}^2 \rangle$ (see methodology section) for all A-B transitions is shown. From this figure it can be elucidated that the main contributions to the absorption coefficients, using as criteria the momentum operator matrix elements, are the

transitions between states of the S atoms. Otherwise, the $\text{Cu}_i - \text{Sb}$ and $\text{Cu}_i - \text{Cu}_i$ transitions ($i=1,2$) contribute in a very low way.

All our previous quantitatively analyses on the absorption coefficient, on the absorption coefficients split into inter- and intra-species contributions α^{AB} , and into angular momentum contributions $\alpha_{l_A l_B}^{AB}$ are based on the space group of the crystal without any approximation of symmetry. Nevertheless, a simple qualitative description can be made considering the environment of the atoms. Note that this qualitative description is an oversimplification with respect the quantitative description. The purpose is to illustrate in a simple manner the possible transitions among atomic states. The geometry around of the B ($=\text{Cu}_1, \text{Cu}_2$ and Sb) sites is approximately tetrahedral. The degenerated d -states are split by the crystalline field at the B sites into $d_e(\text{B})$ (d_{z^2} and $d_{x^2-y^2}$) and $d_t(\text{B})$ (d_{xy} , d_{xz} , and d_{yz}) states, whereas the s and p atomic states have a and t tetrahedral symmetry respectively, i.e. $s_a(\text{B})$ and $p_t(\text{B})$. For tetrahedral symmetry the a - a , a - t , e - t , and t - t transitions are allowed, i.e. $s_a \leftrightarrow (s_a, p_t, d_e, d_t)$ and $(p_t, d_e, d_t) \leftrightarrow (p_t, d_e, d_t)$. This qualitative analysis is in agreement with the previous projected absorption coefficients into angular momentum species contributions quantitative analysis (the largest contribution to the absorption coefficient corresponds to the intra-species $p(\text{S})$ - $s(\text{S})$, $p(\text{Sb})$ - $s(\text{Sb})$, and inter-species $p(\text{Sb})$ - $p(\text{S})$ transitions).

In order to compare with related materials included in the low-valence group, the absorption coefficient split into angular momentum contributions of the chalcostibite- CuSbS_2 is shown in Figure 6b. Similarly to the Cu_3SbS_4 , the results of the CuSbS_2 absorption coefficient show a peak around $E - E_g = 0.4 - 0.5$ eV above of the energy band gap. This peak is also present in experimental⁴ and theoretical⁴ results of the CuSbS_2 . Unlike what happens with famatinite- Cu_3SbS_4 where the peak is mainly because the $s(\text{S})$ - $p(\text{S})$ transitions, the chalcostibite- CuSbS_2 peak corresponds to intra-atomic

transitions between the S atoms and the Sb atoms. More specifically it correspond to transitions $s(S)-p(S)$ and $s(Sb)-p(Sb)$. As it has been mentioned previously, the contribution to the optical properties depends on both, the JDOS and the momentum operator matrix elements. The $p(Sb)$ orbital contributions in the low-valence compound is higher than in the high-valence compound near both VB and CB edges⁴. Therefore, qualitatively the absorption coefficient for the low-valence $CuSbS_2$ is larger than for the high-valence Cu_3SbS_4 mainly because the $s(Sb)-p(Sb)$ JDOS is larger for the low-valence $CuSbS_2$.

3.5. Solar cell Efficiencies

The semiconductor band gaps are often used as an evaluation criterion of the potential for solar cell applications. However, a more important feature, the functional form with respect to the photon energy of the absorption coefficients, has not been paid much attention so far. In part it is due to assuming that the solar cell absorbs all incident photons above the band gap. It implies that the absorption coefficient is a step function. This assumption is common when the maximum efficiencies of a solar cell are calculated. Other usual assumptions are: the cell operates at 300 K, any non-radiative recombination is suppressed, carrier mobilities are infinite (no ohmic losses), and illumination comes from an isotropic gas of photons. Of course, these standard assumptions³¹⁻³⁴ represent an idealized case to determine limiting device performance. When non-ideal conditions are considered the real efficiencies are lower than the maximum efficiencies. For example the non-radiative recombination reduces the lifetime of the carriers, the quantum efficiency is usually lower than 1, etc. In addition to the properties of the absorbent material, the real efficiency depends on the architecture of the solar cell, the contacts, etc. Nevertheless, the maximum efficiency is

a criterion to evaluate the potentiality as a solar cell: if it is small the material is not a good candidate for absorbing solar radiation.

The amount of light absorbed depends on the optical path length and the absorption coefficient. Therefore, unlike that which is usually done when maximum efficiency is obtained, we have used the absorption coefficients obtained from first-principles. As a consequence, the efficiencies depend in the thickness w of the device. Additionally, the amount of light absorbed depends on the incident spectrum on the solar cell, and on the concentration. The spectral intensity can be modified by the f_c factor, where $f_c = 1$ suns ($1 \text{ sun} = 1 \text{ kW/m}^2$) corresponds to the spectra without concentration and $f_c \sim 46200$ suns to maximum light concentration.

There are several types of spectra ³⁵ usually used: the spectrum of a 5760 K black body reduced by the factor 46200 (BB), the extraterrestrial radiation (solar spectrum at the top of the atmosphere) at mean Earth-Sun distance (AM0), the spectral radiation from solar disk plus sky diffuse and diffuse reflected from ground on south-facing surface tilted 37 deg from horizontal (AM1.5), Direct + Circumsolar spectrum (AM1.5D), etc. The BB spectrum is extensively used because it has a simple analytic equation whereas the other spectra are tabulated ³⁵. Of course, there are some unsuitable spectra-concentration combinations. Nevertheless, it is used in the literature and in this study with a comparison objective.

Using the absorption coefficients obtained from first-principles, we have determined the maximum efficiency for maximum solar concentration using several spectra (Figure 8). From the results in the figure, solar cell devices with a few microns thick based on Cu_3SbS_4 materials could reach efficiencies close to the maximum overall efficiency ($\sim 41\%$). Therefore, these materials are very interesting for photovoltaics when used as an absorbent in solar cell devices.

4. Conclusions

Using GGA+U first-principles density-functional theory with several U schemes, we have studied the structural, electronic, and optical properties of Cu_3SbS_4 ternary semiconductor in the famatinite structure. From the analyses of atomic and orbital contributions to the band edges, the states with larger contribution are $d(\text{Cu}_1)$ and $d(\text{Cu}_2)$ to the VB, and $s(\text{Sb})$ to the CB. Furthermore, the $p(\text{S})$ states make a high contribution to both the VB and CB edges.

The absorption coefficients have been split into inter- and intra-species contributions in order to understand microscopically the cause of the high absorption. From the results, high absorption in these materials arises from an elevated contribution from $\text{S} \rightarrow \text{S}$, $\text{Sb} \rightarrow \text{Sb}$ and $\text{Sb} \rightarrow \text{S}$ transitions to the absorption coefficient.

Using the first-principles results we have estimated the maximum efficiency of this photovoltaic absorber material as a function of sunlight concentration using several spectra. The efficiency of this compound is near the maximum efficiency for single-gap solar cells even using small-width devices

Notes: The authors declare no competing financial interest.

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List of Figures

Figure 1: The crystalline structure of the Cu_3SbS_4 compound in the famatinitite structure.

Figure 2: Energy-band diagram with GGA+U ($U_a=5$ eV) for Cu_3SbS_4 along high symmetry lines in the BZ. The VB edge has been chosen as the origin of the energy.

Figure 3: Projected DOS on species states with more contribution to the VB and CB edges: (a) per atom, (b) total. The VB edge has been chosen as the origin of the energy.

Figure 4: Absorption coefficients $\alpha(E)$ for the $U_a=5$ eV scheme, and experimental ($E1^4$ and $E2^2$ labels) and theoretical ($T1^4$ label and $T2^{22}$ label) data. The region between the $E1$ and $E2$ experimental data has been shaded in the figure. The band gap energies E_g have been chosen as the energy origin.

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Figure 7: Mean-value of the p_{AB}^2 for all $A \rightarrow B$ transitions scaled by the maximum value.

Figure 8: Efficiency η (%) versus cell thickness w using several standard spectra for maximum concentration ($f_c \sim 46200$ suns, sun units=1 Kw/m²).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

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