Photovoltaic applications of Cu(Sb,Bi)SM (M = Ag, Pb, Pt)

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A B S T R A C T

Ternary Cu-(Sb,Bi)-S compounds are great absorbers of the solar radiation with a variety of applications including optoelectronic and photovoltaic applications. The analyses of several quaternary semiconductors derived from Cu-(Sb,Bi)-S materials is carried out using first-principles density-functional theory with orbital-dependent one-electron potentials. These analyses focus on the optoelectronic properties and the potential for solar cells. The optical properties are obtained from first-principles calculations, and split into inter- and intra-shell-species contributions in order to quantify the optical transitions responsible for the absorption. The absorption coefficients are then used as criteria to evaluate the efficiencies of these materials under several sunlight concentrations. The results indicate high energy photovoltaic conversion efficiency because of the large intra shell s-p absorption of the S and Sb or Bi atomic species.

Keywords:
Optical properties
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Efficiency

1. Introduction

A lot of the effort to find new materials has focused on the synthesis and characterization of binary and ternary semiconductors. Part of this effort has recently extended to exploring more complex ternary and quaternary structures. Ternary I-III-VI₂ chalcogenides, in particular CuInSe₂, are among the strongest absorbers known. However, while the overall absorption is strong, it is necessary to use rather thick films because of weak onset absorption near the band gap. Among the ternary materials Cu-(Sb,Bi)-S-type derived semiconductors (famatinite-Cu₃SbS₄, chalcobite-CuSbS₂, skinnerite/wittichenite-Cu₃SbS₃ and tetrahedrite-Cu₁₂Sb₄S₁₃) also have a high absorption coefficient of above 10⁴–10⁵ cm⁻¹ throughout a wide range of the visible region [1–4]. These properties make them attractive for semiconductor-based device applications and a particularly attractive candidate for photovoltaic solar cells.

Some quaternary compounds derived from the ternary Cu-(Sb,Bi)-S system could be suitable as solar radiation absorbers in solar cells. Among them are semiconductors such as BiCuPbS₃, CuPbBi₃S₆, CuPtBiS₃, and (Ag,Cu)SbS₂. These compounds [5–8] can be found as the minerals Aikinite, Krupkaite, Lisiguangite, and Miargyrite respectively. They present new opportunities in thin-film photovoltaics through the identification and design of new absorbent materials.

The main processes involved in photovoltaic generation are: (1) photon absorption, (2) charge separation and transport of electrons and holes from the point of generation to their respective contacts and (3) collection at the contacts. The first process only depends of the material that absorbs photons. The absorber thickness w determines the absorption of the solar spectrum. It is determined mainly by the absorption coefficient of the material that absorbs photons. The other two processes usually dictate the basic device structure (pn, pin, etc). This device architecture determines the width l of the space charge region and the transport properties. With low (high) l/w the transport is controlled mainly by diffusion (drift). During the transport to and collection at the contacts there is unwanted recombination. This recombination may depend on impurities, defects, dislocations, grain boundaries, and the type and material of the contacts. Note that the semiconductors considered in this work are not doped ternary semiconductors but quaternary semiconductors without impurities.

The global efficiency η_G of the device will be the product of the efficiencies of the three processes: absorption efficiency η_A , charge separation and transport efficiency η_T , and efficiency of the collection at the contacts η_C : $\eta_G = \eta_A \eta_T \eta_C$. In this work we will evaluate η_A that does not depend on the device structure. It depends on the absorption spectrum and thickness of the absorber, and this allows different efficiencies for materials having the same gap. With this initial filter, if η_A is small, then η_G will be small and these semiconductors are not good candidates for solar cell devices. The other factors, dependent on the device structure and on the

imperfections (defects, doping, metal contacts, fabrication-induced effects, etc), should be evaluated at a later stage.

The classic approach to obtain the absorption efficiency $\eta \approx \eta_A$ selects good photovoltaic absorbers exclusively on the basis of their bandgap. Under this criterion, the optimal solar cell efficiency for single-gap solar cells (~41% [9–11]) is achieved when the bandgap is $E_g \sim 1.1$ eV. This criterion based on the bandgap is due partially to the difficulty in obtaining absorption coefficients (theoretically or experimentally) with respect to obtaining energy bandgaps. However this criterion alone is insufficient. It does not consider the transition probabilities. In fact, some materials with the bandgap closer to the optimum might have low transition probabilities, or even be a forbidden transition in the energy range close to the energy bandgap.

The photon absorption efficiency mainly depends on photon absorptivity. The classic bandgap selection criteria assumes a step function absorptivity (i.e., $a(E) = 1$ for $E \geq E_g$ and $a(E) = 0$ for $E < E_g$). However, the absorptivity depends on the absorption coefficient and the thickness w of the absorbent. A strong absorption coefficient enables the use of a small amount of material (i.e., thin films). Therefore, we use the criterion based on the sunlight absorbed and on the thickness of the solar cell, i.e. on the absorption coefficient and the absorptivity.

First principles are an important and powerful complementary tool which allows basic properties that may be less accessible or more expensive by experiments to be obtained and quantified. For this reason we present a study using first-principles of the electronic and optical properties, splitting the different contributions. We focus this study on the quaternary materials derived from the ternary Cu-(Sb,Bi)-S compounds: Aikinite-BiCuPbS₃, Krupkaite-CuPbBiS₃, Lisiguangite-CuPtBiS₃, and Miargyrite-(Ag,Cu)SbS₂. In addition, with the absorption coefficients theoretically obtained, we will evaluate the potentiality for photovoltaics obtaining the maximum efficiencies when these materials are used to absorb the sunlight in solar cell devices.

2. Methodology

The electronic and optical properties have been analyzed using first principles within the Density Functional Formalism [12,13]. With the traditional exchange-correlation functionals the interactions are treated in a mean field. These approximations lead to band-gap underestimation, band-width overestimation, binding energy overestimation, etc. This problem may be avoided using many-body methods. However, they are very expensive computationally and present delicate convergence issues. At an intermediate level, methods such as DFT + U and hybrid DFT studies incorporate a U parameter or a fraction of the exact exchange in order to avoid partially these problems. Therefore, a further extension beyond the standard DFT was carried out using the DFT + U method [14–19]. The value of U depends on the choice of the orbitals on which the correction is applied, on the way the orbital occupations are computed, and on the DFT + U implementation chosen [16–19]. In this work we applied the orbital-dependent one-electron potential using the GGA + U formalism described in Refs. [16,17]. For the exchange-correlation potential, we use the generalized gradient approximation (GGA) from Perdew, Burke and Ernzerhof [20]. The standard Troullier–Martins [21] pseudopotentials are adopted and expressed in the Kleinman–Bylander [22,23] factorized form. The valence wave functions are expanded into a numerically localized pseudoatomic orbital basis set [24].

In all of the results presented in this work we use periodic boundary conditions and the crystal structures detailed in Table 1. The Miargyrite-(Ag,Cu)SbS₂ crystal structure has a static

positional disorder. This positional disorder is typically manifested by site occupancy factors different from unity. The simplest approach for dealing with disorder in first-principles calculations is the Virtual crystal approximation (VCA) [25] with a similar computation cost as calculations for ordered structures. There is a virtual atom at each disordered site, which reflects the behavior of the positional disorder components. Of course, this approach does not reproduce the finer details of the disordered structures very accurately.

In order to obtain the optical properties, we have also calculated the momentum ($\mathbf{p} = i(m/\hbar)[H, \mathbf{r}]$) matrix elements $p_{\mu\lambda}$. With these matrix elements and the single-particle energies $E_{\mu, \vec{k}}$ and occupations $f_{\mu, \vec{k}}$ of the μ bands at $\vec{k}$ points in the Brillouin zone we have obtained the complex dielectric ϵ_2 function in accordance with:

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

The other optical properties are obtained using the Kramers-Kronig relations. Both, the local and non-local parts of the pseudopotentials have been considered in the calculation of the momentum matrix elements.

In addition, the optical properties have been split taking into account the dependence on the matrix elements $p_{\mu\lambda}$. These matrix elements can be split into atomic species contributions $p_{\mu\lambda} = \sum_A \sum_B p_{\mu\lambda}^{AB}$, and into angular momentum contributions as $p_{\mu\lambda}^{AB} = \sum_{l_A \in A} \sum_{l_B \in B} (p_{l_A l_B}^{AB})_{\mu\lambda}$. Here $p_{\mu\lambda}^{AB}$ is the inter-specie component that couples the basis set functions on different species atoms A and B and $(p_{l_A l_B}^{AB})_{\mu\lambda}$ is the contribution of the transition between the l_A shell-states of the specie atom A and the l_B shell-states of the specie atom B. As usual we use the notation s, p, d , etc. for $l = 0, 1, 2$, etc. As the complex dielectric function depends on the square of the momentum operator matrix elements $p_{\mu\lambda}$, the absorption coefficients and other optical properties can also be split as $\alpha = \alpha_S + \alpha_{34}$, where $\alpha_S = \sum_A \sum_{l_A} \sum_B \sum_{l_B} \alpha_{l_A l_B}^{AB}$ and α_{34} are the terms involving three and four different species and l -shells. In general the absorption coefficient can be approximated by α_S ($\alpha \approx \alpha_S$) because $\alpha_S \gg \alpha_{34}$. In these equations the intra-species contributions $\alpha_{l_A l_A}^{AA}$ indicate the contribution of all transitions between states with angular momentum l_A and l'_A of the atoms of the same specie. It includes intra-atomic and inter-atomic transitions involving mono-centric and bi-centric matrix elements respectively.

3. Results and discussion

3.1. Structure and electronic properties

The crystal structure and lattice parameters of the Aikinite-BiCuPbS₃, Krupkaite-CuPbBiS₃, Lisiguangite-CuPtBiS₃, and Miargyrite-(Ag,Cu)SbS₂ are shown in Table 1. Fig. 1 shows the details of the crystalline structure of these compounds.

As a result of the well-known DFT bandgap underestimation tendency, we have applied the orbital-dependent one-electron potential using the DFT + U formalism in accordance with the calculation section to obtain the optoelectronic properties. In this work we use the same values as those used for some ternary Cu-(Sb,Bi)-S compounds [4,26,27] ($U_A = 5$ eV). The results obtained with these values agree well with the theoretical and experimental data available in the literature. The gaps obtained are summarized in Table 1. The energy band gaps of these quaternary

Table 1Lattice parameters (a , b , c , α , β and γ), space group and energy band gaps for several quaternary compounds analyzed.

Compound	$a/b/c$ (Å)	$\alpha/\beta/\gamma$ (°)	Space group	E_g (eV) ($U = 5$ eV)
Aikinite-BiCuPbS ₃	11.638/4.039/11.319	90/90/90	$Pnma$ (n° 62)	1.22
Krupkaite-CuPbBi ₃ S ₆	4.013/11.208/11.560	90/90/90	$Pmc2_1$ (n° 26)	1.10
Lisiguangite-CuPtBiS ₃	7.715/12.838/4.925	90/90/90	$P2_12_12_1$ (n° 19)	0.83
Miargyrite-(Ag,Cu)SbS ₂	12.862/4.411/13.220	90/98.63/90	Cc (n° 9)	1.55

Fig. 1. The crystalline structure of the (a) Aikinite-BiCuPbS₃, (b) Krupkaite-CuPbBi₃S₆, (c) Lisiguangite-CuPtBiS₃, and (d) Miargyrite-(Ag,Cu)SbS₂ where the symmetrically non-equivalent chemical species are shown.

semiconductors vary between ~ 0.83 and 1.55 eV. Therefore, in a first approximation, using only the band gap criterion, these semiconductors could be attractive for solar cells because their energy band-gaps are closer to the optimum for single-gap solar cells ($E_g \sim 1.1$ eV with a solar efficiency of $\sim 41\%$ [9–11]).

The analysis of the projected density of states (PDOS) on atomshells (Fig. 2) reveals that the states of the valence band (VB) edge are derived mainly from the $p(S)+d(Cu)$ states ($d(AgCu)$ for the Miargyrite-(Ag,Cu)SbS₂), whereas the conduction band (CB) edge states are derived mainly from the $p(Sb,Bi)+p(S)$ states ($+p(Pb)$ states for the Aikinite-BiCuPbS₃). These states, or part of them, will be involved in the optical properties.

3.2. Optical properties

As described in the methodology section, the optical properties involve optical transitions between states and depend on the transition probabilities via the momentum operator matrix elements. In a simplified analysis, the momentum operator matrix elements can be considered constant. Then the optical properties are proportional to square of the momentum operator matrix elements and the joint DOS (JDOS). In almost all analyses of the different contributions to the optical properties only the JDOS is considered.

According to the PDOS, the VB and CB edge states are derived mainly from the $p(S)+d(M)$ states ($M = Cu$ or $(AgCu)$ for the

Fig. 2. PDOS on species states with more contribution to the VB and CB edges: (a) Aikinite-BiCuPbS₃, (b) Krupkaite-CuPbBi₃S₆, (c) Lisiguangite-CuPtBiS₃, and (d) Miargyrite-(Ag,Cu)SbS₂. The VB edge has been chosen as the origin of the energy.

Fig. 3. JDOS split into angular momentum species contributions with more contribution to the VB and CB edges: (a) Aikinite-BiCuPbS₃, (b) Krupkaite-CuPbBi₃S₆, (c) Lisiguangite-CuPtBiS₃, and (d) Miargyrite-(Ag,Cu)SbS₂. The band gap energies E_g have been chosen as the energy origin.

Fig. 4. Same legend as that in Fig. 2, but for the absorption coefficients split into angular momentum species contributions $\alpha_{l_h l_g}^{AB}$.

Fig. 5. Efficiency η (%) as a function of the cell thickness w for the BB spectrum and several sun-light concentrations (from $f_c = 1$ sun to maximum concentration $f_c = \text{max} \sim 46200$) for (a) Aikinite-BiCuPbS₃, (b) Krupkaite-CuPbBi₃S₆, (c) Lisiguangite-CuPtBiS₃, and (d) Miargyrite-(Ag,Cu)SbS₂. The marks indicate the calculated values. Lines between the marks have been added for visual effect.

Fig. 6. Same legend as that in Fig. 5, but for the AM1.5G spectra.

Miargirite-(Ag,Cu)SbS₂) and the p(B)+p(S) states (B=Bi or Sb). Therefore it is reasonable to think that the larger contribution to the JDOS (and to the optical properties if this simplified model is used) correspond to the combinations of [p(S)+d(M)] and [p(B)+p(S)], i.e. p(S)-p(B), p(S)-p(S), d(M)-p(B), d(M)-p(S) transitions. The main contributions to the JDOS are shown in Fig. 3. Of course, these results are what one would expect from the PDOS.

Nevertheless, it is an oversimplification. Even with the previous approximate model the optical properties depend on both the JDOS and the transition probabilities via the momentum operator matrix elements. If one is large but not the other, the contribution will be very small. As well as the matrix elements of the momentum operator are subjected to selection rules which depend on the symmetry while the JDOS are not.

Therefore we have obtained the optical properties, and the absorption coefficients have been split, in accordance with the calculation section, into contributions $\alpha_{l_A l_B}^{AB}$ between pairs of atom-shells $l_A l_B$ ($l_A \in A$ and $l_B \in B$). The results are shown in Fig. 4. They indicate that these compounds have high absorption coefficients, greater than 10^5 cm^{-1} at energies greater than $\sim 1 \text{ eV}$ above the energy band gap. Such high absorption coefficients make these semiconductors attractive candidates for use as a light absorber in solar photovoltaic devices. Later we verify this fact quantitatively obtaining the maximum efficiencies from the theoretical absorption coefficients.

Another significant result from Fig. 4 is that the largest contributions to the absorption coefficients are from α_{sp}^{AA} ($A = S$, and Bi or Sb), i.e. to s(A)-p(A) intra-specie transitions. The contributions of the other intra- and inter-shell transitions $\alpha_{l_A l_B}^{AB}$ are lower than that

those shown in Figure. This behavior is similar to that observed in the ternary Cu-(Sb,Bi)-S phase compounds [4,26,27].

3.3. Solar cell efficiencies

In order to obtain maximum efficiencies, the habitual conventions have been assumed [9–11]: the cell operates at 300 K, any non-radiative recombination is suppressed, carrier mobilities are infinite (no ohmic losses), etc. For illumination we have used two spectrums: the AM1.5G [28] and the Black-body (BB): spectrum of a 5760 K black body reduced by the factor 46200. With these assumptions the current flowing out of the device J is equal to the difference between the current generate by the photons absorbed (J_a) and emitted due to radiative recombination (J_e), i.e. $J = J_a - J_e$, where $J_\mu = q \int a(E, w) g_\mu(E) dE$ ($\mu = a, e$). In this expression $a(E, w)$ is the absorptivity ($a(E, w) \approx 1 - e^{-\alpha(E)2w}$), α is the absorption coefficient, w is the device thickness, q is the electron charge, and g_a and g_e are the absorbed and emitted photon flux densities. If the sun-light is concentrated with a light concentration factor f_c ($1 \leq f_c \leq f_c^{(\max)} = 46200$), then g_a will be multiplied by this factor. The efficiency $\eta = P_{out}/P_{abs}$, with $P_{out} = VJ$, depend on the absorption coefficient, on the device thickness, on the current flow J , and on the applied bias V .

The common bandgap selection criteria assumes a step function absorption coefficient (i.e., $\alpha(E) = 0$ for $E < E_g$ and $\alpha \rightarrow \infty$ for $E \geq E_g$). However, we have used the absorption coefficients obtained from first-principles in order to obtain the maximum efficiencies for several solar concentrations f_c (Figs. 5 and 6). With this criterion

based on the absorption coefficient the efficiencies depend in the thickness w of the device. Of course, the real efficiency is lower when some of these ideal assumptions are eliminated or when the architecture of the solar cell, the contacts, the defects, the carrier transport properties, etc. are taken into account. Nevertheless, the maximum efficiency is a criterion based on the absorbent properties for evaluating the potentiality as a solar cell: if it is small, then the material is not a good candidate for absorbing solar radiation.

The results in Figs. 5 and 6 indicate that solar cell devices just a few microns thick could reach efficiencies close to the maximum overall efficiency ($\sim 31\%$ and 41% for $f_c = 1$ and $f_c \sim 46200$ respectively [9–11]). In particular with the Krupkaite-CuPbBi₃S₆ and the Lisiguangite-CuPtBiS₃ compounds. Therefore, these materials could have a great potential for photovoltaics when used as an absorbent in solar cell devices.

A screening [1] of several Cu-V-VI materials using the standard AM1.5G spectrum with a film thickness of 0.2 μm shows that CuSbS₂, CuSbSe₂, Cu₃SbS₄, Cu₃PSe₄, Cu₃AsSe₄, Cu₆As₄S₉, and CuBiS₂ have efficiencies (23, 27, 26, 24.5, 25.5, 21, and 21% respectively) comparable or higher ($>20\%$) than CuInSe₂. The modeled film thickness is thinner than that commonly found in CuInSe₂ solar cells. From our results of Fig. 6, with $f_c = 1$ sun and using the standard AM1.5G spectrum, the efficiencies for Aikinite-BiCuPbS₃, Krupkaite-CuPbBi₃S₆, Lisiguangite-CuPtBiS₃, and Miargyrite-(Ag,Cu)SbS₂ are 27, 28, 28, and 21% respectively. These results indicate high energy photovoltaic conversion efficiency compared with other absorbent materials.

4. Conclusions

We have used GGA + U first-principles in order to study the electronic and optical properties of several quaternary semiconductors (Aikinite-BiCuPbS₃, Krupkaite-CuPbBi₃S₆, Lisiguangite-CuPtBiS₃, and Miargyrite-(Ag,Cu)SbS₂) derived from the ternary Cu-(Sb,Bi)-S system.

The absorption coefficients have been obtained and split into inter- and intra-shell species contributions. The results indicate that these compounds have a high absorption coefficient of above 10^4 – 10^5 cm^{-1} in a wide range of the visible region. This large absorption is due mainly to the $s(S)$ - $p(S)$ and $s(A)$ - $p(A)$ intra-specie transitions ($A = \text{Bi}$ or Sb).

To conclude, using the theoretical absorption coefficients, the potentiality as a single-gap solar cell has been evaluated. Solar cells just a few microns thick of these semiconductors could reach efficiencies close to the maximum.

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