The investigation of transition metal doped CuGaS₂ for promising intermediate band materials

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Here, we have systematically investigated the electronic structure and optical properties of transition metal (M) doped CuGaS₂ (M = Fe, Co, and Ni) systems, using a density functional theory by considering a non-local interaction. Isolated intermediate bands (IBs), with the potential of achieving the efficiency of photovoltaic materials, are introduced in the main band gap of the host CuGaS₂ by doping Fe or Ni with a favorable position and width. Therefore, extra absorption peaks appear in the optical spectrum of the Fe and Ni doped CuGaS₂ compounds, accompanied with a greatly enhanced light absorption intensity and a largely broadened light absorption energy range. Whereas for Co doped CuGaS₂, the material turns into a half-metal. Consequently, Fe and Ni doped CuGaS₂ could be potential materials for future applications in the photovoltaic area.

1 Introduction

The concept of an intermediate band solar cell (IBSC) was first put forward in an attempt to increase the efficiency of solar cells by making full use of solar energy in 1997. Traditionally, the absorption layer of a solar cell is a single band gap semiconductor, where electrons are directly promoted from the valence band (VB) to the conduction band (CB) by absorbing photons, while a three-photon absorption process happens when a partially filled intermediate band (IB) is inserted into the forbidden band gap. As shown in Fig. 1, electrons can be excited not only from the VB to the CB but also from the IB to the CB and from the VB to the IB. As the IB is isolated, the IBSC will have a higher photocurrent benefited from the sub-band gap absorption without photo-voltage degradation, which promises a high conversion efficiency. The upper limit efficiency of the IBSC was predicted to be about 63.1% from the detailed balance limit theory calculation,1 which largely exceeds the efficiency of the Shockley–Queisser single-junction solar cell (40.7%). By further increasing the number of IBs, the efficiency will be extended to nearly 80%. Theoretical and experimental reports have verified that IB materials could effectively increase the optical absorption.4–6

Since the IB concept was proposed, large efforts have been made to implement IB solar cells. In practice, an IB can be created through quantum dots or the insertion of appropriate impurities into the bulk host semiconductor, in which the bulk IB material is easier to fabricate than quantum dots and has a stronger absorption because of the higher density of the IB states.7 The candidate bulk IB host materials contain III–V,8,9 II–VI,10 spinel compounds11 and chalcopyrite materials. In particular, it has been reported that the optimum band gap of Cu-based chalcopyrite solar cells for photovoltaic energy conversion is 2.41 eV with the IB located at 0.92 eV from the CB or VB.12 CuGaS₂13 has a relatively wide band gap of 2.43 eV, thus being an ideal IB host material14 though not suitable to act as a light absorption layer in a single-junction solar cell. Up to now, many first-principle calculations, based on the density functional theory (DFT),14–15 have been made to design and understand the bulk CuGaS₂ IB materials. Elements of the 3d transition metals and group IVA have been identified as interesting candidates to act as substitutes in the cation sites of the CuGaS₂ chalcopyrite hosts.15–17 It is worth noting that Ti,18 Sn19 and Fe doped CuGaS₂ IB semiconductors have been successfully synthesized and that sub-gap transitions are detected in photovoltaic devices based on Fe doped CuGaS₂.20 There are many studies in the literature about Ti, V,
Cr, Mn and group IVA doped CuGaS_{2} too.\textsuperscript{15-19,21-23} Nevertheless, a seldom systematic theoretical study of Fe, Co and Ni doped CuGaS_{2} has never been made. The key factor in an IBSC is that the IB must be isolated. Whereas for the issue of isolated IB, no consistent conclusion has been drawn from theoretical calculations by using GGA and GGA + U. Taking Ti doped CuGaS_{2} for example, the GGA calculation results\textsuperscript{14} show that the partially filled IB overlaps only a little with the CB, while the GGA + U\textsuperscript{14} shows that the IB is filled. The contradiction is inherent of the DFT, because it is well known that DFT underestimates the band gaps of materials and that the position and width of the IB is not reliable, which is severely harmful to predicting the optical properties of IB materials. Therefore, an advanced theoretical method should be used to provide a more accurate description of the electronic and optical properties of IB semiconductors. Attractively, the range-separated hybrid functional of Heyd–Scuseria–Ernzerhof [HSE06] makes the exact exchange mixing with exchange from a semilocal Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA) functional, thereby overcoming the problems in GGA and LDA that d and f electrons are handled improperly due to insufficient electron correlations and relativistic effects. The investigations have indicated that hybrid functionals can describe the band gap of such chalcopyrite systems very well.\textsuperscript{19,21}

In this work, we employ a screened-exchange hybrid density functional HSE06 to calculate the electronic structure and optical properties of M (M = Fe, Co, and Ni) doped CuGaS_{2}. We calculated the band gap of CuGaS_{2} to be 2.01 eV, which is in good agreement with the experimental value of 2.43 eV.\textsuperscript{26} Our results show that the M doped CuGaS_{2} systems exhibit a good IB concept with IB states appearing in the band gap. Consequently, two additional absorption peaks appear in the absorption spectrum around 1.0 eV and 1.7 eV when CuGaS_{2} is doped with Fe, arising from the sub-gap absorptions, which is consistent with the experimental results.\textsuperscript{26,27} Additionally, the Ni dopant induces isolated IB states slightly above the valence band. For both Fe and Ni doping, the optical absorptions are greatly enhanced compared to that of the host CuGaS_{2}. Conversely, the IBs induced by the Co dopant overlap with the conduction band, with the doped material developing into a half-metal. Our results explicitly indicate that the CuGa_{1-x}M_{x}S_{2} system, with M = Fe or Ni, is a potential candidate for an IB photovoltaic material.

2 Model and method

2.1 Theoretical model

The ternary semiconductor, CuGaS_{2}, is a chalcopyrite structure with a space group of I42d. Each atom in this structure is fourfold coordinated. Namely, each sulfur ion is coordinated with two gallium and two copper ions, and each cation is coordinated with four sulfur ions. A supercell approach is used to construct the compound by replacing one Ga atom with a M (M = Fe, Co, and Ni) dopant in a 16-atom cell [see Fig. 2], which corresponds to a 25% dopant concentration. In this case, the concentration of the M dopant equals 3.3 \times 10^{21} \text{cm}^{-3}, which is in the optimal range of 10^{21} \text{cm}^{-3}, so that the Shockley–Read–Hall (SRH) recombination might be suppressed.\textsuperscript{28}

2.2 Computational method

The whole investigation is performed within the framework of the density functional theory (DFT) implemented in the Vienna \textit{ab initio} simulation package (VASP).\textsuperscript{29} Previous studies indicate that hybrid functionals can describe such chalcopyrite systems very well.\textsuperscript{24,25} However, relaxation and electronic structure calculations, using Heyd–Scuseria–Ernzerhof [HSE06], are very time consuming. We test the geometry optimization for the Fe doped case within HSE06 and Perdew–Burke–Ernzerhof [PBE].\textsuperscript{30} The results show that the PBE relaxed structure can capture the main properties of the electronic structure. Therefore, for the exchange correlation functional, the PBE version of the generalized gradient approximation (GGA) is used for full structure relaxation, while the hybrid nonlocal exchange-correlation functional of HSE06 is used to calculate the electronic structure and optical properties. The projector augmented wave (PAW)\textsuperscript{31} method has been used to describe the inert core electrons. In the HSE06 \textsuperscript{32,33} functional, 25% of the screened Hartree–Fock (HF) exchange is mixed with the PBE exchange functional and the screening parameter is set to 0.2 Å\textsuperscript{-1}. The relaxation is performed until the total energy changed within 0.0001 eV per atom and the Hellmann–Feynman force on each atomic site is less than 0.01 eV Å\textsuperscript{-1}. The cutoff energy for the plane-wave basis is set to 400 eV. We apply a 6 \times 6 \times 3 \textit{Γ}-centered Monkhorst–Pack\textsuperscript{24} \textit{k}-point mesh in both PBE and HSE calculations. Spin polarization is studied due to the existence of a magnetic M (Fe, Co, and Ni) atom.

To get a better prediction in both the intensities and the peak positions in the optical absorption spectrum, a complex dielectric function is performed using HSE06 with the consideration of interband and direct transitions, but not the local-field effects. The optical calculations count the contribution from 300 electronic bands.
3 Results and discussion

3.1 Structural and electronic properties

The optimized structure of the host CuGaS$_2$ compound presents an average bond length of Ga–S of 2.32 Å, which is consistent with previous theoretical and experimental values.

The doping of M into the host CuGaS$_2$ leads to decreased M–S bond lengths, as shown in Table 1. The bond lengths decrease to 2.29 Å, 2.24 Å and 2.23 Å for Fe–S, Co–S and Ni–S in M doped CuGaS$_2$, respectively. The magnitude of the bond length is determined by the size mismatch between the Fe/Co/Ni and Ga ions. The decreased bond lengths of Ga–S and Cu–S in M doped CuGaS$_2$ are much smaller compared to that of M–S, which is about 0.01 Å. The characteristics of the structure change in M doped CuGaS$_2$ indicate that the M dopant mainly alters the local structure around the M ions.

The structure changes for M doped CuGaS$_2$ are accompanied with electronic structure changes, as shown in Fig. 3. The band structure of host CuGaS$_2$ shows a direct band gap at the $\Gamma$ point of 2.01 eV, which is larger than the previous DFT computational results within the LDA/GGA scheme (0.68 eV to 1.25 eV) and close to the experimental value of about 2.43 eV. The spin polarized band structures are plotted for M doped CuGaS$_2$ in Fig. 3 based on the magnetic nature of the M ions. The most obvious change of the band structures with the doping of M ions is the appearance of additional IBs in the band gap. The IBs are contributed by the down spin states with 5, 3, and 3 bands for the Fe, Co and Ni doped CuGaS$_2$ systems, respectively. Regarding the up spin, it can be seen from Fig. 3 that the Fe and Ni dopants do not change the host band structure much but the Co dopant greatly changes the band structure of the host material with an up shift of the valence band. This shifting makes Co doped CuGaS$_2$ a half-metal. The IB induced by Fe and Ni divides the main band gap into two sub-bands and therefore may benefit the solar cell performance. The main gaps for Fe and Ni doped CuGaS$_2$ are 2.14 and 2.17 eV, with a little broadening, as presented in Table 1, which can be explained by the energy level repulsion between the IBs and the conduction band maximum (CBM). In order to have a better understanding of the origin of the IB, we show the density of states (DOS) and projected density of states (PDOS) in Fig. 4.

The IB is mainly contributed from the M-3d states, as seen from the PDOS of the M doped CuGaS$_2$ in Fig. 4(b). Whereas, the IB states also contain a small amount of the 3p states of the neighboring S atoms and the 3d states of the Cu atoms because of the weak hybridization among the M, Cu and S ions. The IBs for the Fe doped CuGaS$_2$ locate at the energy region from 1.05 eV to 1.76 eV, with a width of 0.71 eV. We also perform one case for Fe at a concentration of 12.5% and 6.25% to get the effect of the dopant concentration. The results suggest that the use of larger supercells only slightly changes the positions of the IBs but the IBs are still isolated, which does not change our main conclusions. Therefore, the use of a 16-atom supercell is reasonable. The IBs induced by the Co dopant up shift and overlap with the CBM. This is a little different from the reported LSDA results stating that an isolated IB appears in the band gap, which may be caused by either the real nature of the material or the computational method deviation. The IBs induced by Ni are slightly lower than those by Fe, ranging from 0.23 eV to 1.16 eV, with a width of 0.93 eV. The M induced IBs are stronger for Fe than those for Co and Ni. Moreover, the up-spin states for Fe, Co and Ni are almost fully occupied, while the down-spin states are empty for Fe, and partially occupied for Co.

Table 1 Lattice parameter $a$, bond length $d$ (in Å) and band gap $E_g$ (in eV) of host CuGaS$_2$ and M doped CuGaS$_2$ after relaxation

<table>
<thead>
<tr>
<th></th>
<th>$a$</th>
<th>$d_{Ga-S}$</th>
<th>$d_{Cu-S}$</th>
<th>$d_{M-S}$</th>
<th>$E_g$</th>
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<tr>
<td>CuGaS$_2$</td>
<td>5.36</td>
<td>2.32</td>
<td>2.31</td>
<td>—</td>
<td>2.01</td>
</tr>
<tr>
<td>Cu$_4$Ga$_3$FeS$_8$</td>
<td>5.34</td>
<td>2.31</td>
<td>2.30</td>
<td>2.29</td>
<td>2.14</td>
</tr>
<tr>
<td>Cu$_4$Ga$_3$CoS$_8$</td>
<td>5.32</td>
<td>2.31</td>
<td>2.30</td>
<td>2.24</td>
<td>2.19</td>
</tr>
<tr>
<td>Cu$_4$Ga$_3$NiS$_8$</td>
<td>5.31</td>
<td>2.31</td>
<td>2.30</td>
<td>2.23</td>
<td>2.27</td>
</tr>
</tbody>
</table>

Fig. 3 Spin polarized band structures of (a) host CuGaS$_2$ and (b) Fe, (c) Co, (d) and Ni doped CuGaS$_2$. The solid (blue)/dashed (red) lines denote spin up/down, respectively. The horizontal dashed line denotes the Fermi level.
and Ni. The differences in PDOS for the M doped CuGaS$_2$ can be understood from the atomic environment and the 3d electron configurations of the M ions, as discussed below.

In chalcopyrite CuGaS$_2$, the four nearest neighboring S atoms around the Ga atom form a tetrahedral crystal field. The M ions substitute the Ga atom in CuGaS$_2$ and therefore are located in a tetrahedral crystal field environment. Based on the crystal field theory, the fivefold degenerated 3d orbital of M will split into two main manifolds: lower twofold degenerate $e_g$ states ($d_{z^2}$ and $d_{x^2-y^2}$) and upper threefold degenerate $t_{2g}$ states ($d_{xz}$, $d_{yz}$, and $d_{x^2}$). In addition, it is usual to take CuGaS$_2$ as an ionic compound for convenience where the Ga atom has the formal charge of Ga$^{3+}$. The substitution of Ga with M leads to a M$^{3+}$ oxidation state, with the number of d electrons being Fe$^{3+}(d^5)$, Co$^{3+}(d^6)$, and Ni$^{3+}(d^7)$. The orbital splitting in the tetrahedral crystal field combined with the PDOS of M-3d leads to Fe$^{3+}$ 3d$^5$ $e_g^{11}$ $t_{2g}^3$, Co$^{3+}$ 3d$^6$ $e_g^{11}$ $t_{2g}^3$, and Ni$^{3+}$ 3d$^7$ $e_g^{11}$ $t_{2g}^3$ orbital occupations, as schematically shown in Fig. 5. These orbital occupations indicate that the crystal field splitting of $e_g$ and $t_{2g}$ is small and therefore the orbital occupation of the d electrons obey the Hund’s rule. The corresponding magnetic moments of these configurations should be 5 $\mu_B$, 4 $\mu_B$, and 3 $\mu_B$ for the Fe, Co, and Ni atoms, respectively. However, the calculated magnetic moments are much smaller, with about 3.83 $\mu_B$, 2.40 $\mu_B$, and 1.55 $\mu_B$ for the Fe, Co and Ni atoms, respectively. This obviously arose from the hybridization of the S-3p and Cu-3d states with the M ions, resulting in that the magnetic moment spreads over the neighboring S and Cu atoms, as shown in Table 2. The Co ions induce negative moments on the S atoms and Cu atoms with 0.20 $\mu_B$ and 0.35 $\mu_B$, respectively. While, the S atoms and Cu atoms have a positive moment for the Fe and Ni doped CuGaS$_2$. The magnetic moment on the Ga atoms is very small in all the doped materials.

### 3.2 Optical properties

We compare the optical absorption coefficients and optical conductivities of the host CuGaS$_2$ semiconductor with the M doped systems in polarizations, which has a close connection with the dielectric function. We used the following computational formulas:

$$\epsilon_1(\omega) = n^2(\omega) - k^2(\omega)$$

**Table 2** The average magnetic moment, $\mu_p$, per atom for the M, Ga, Cu and S atoms in the Cu$_4$Ga$_3$MS$_8$ systems (in $\mu_B$)

<table>
<thead>
<tr>
<th>Cu$_4$Ga$_3$MS$_8$</th>
<th>Ga</th>
<th>Cu</th>
<th>S</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.039</td>
<td>0.222</td>
<td>0.498</td>
<td>3.833</td>
</tr>
<tr>
<td>Co</td>
<td>0.015</td>
<td>−0.346</td>
<td>−0.204</td>
<td>2.401</td>
</tr>
<tr>
<td>Ni</td>
<td>0.013</td>
<td>0.361</td>
<td>0.727</td>
<td>1.550</td>
</tr>
</tbody>
</table>

![Fig. 4](a) DOS and (b) PDOS of M (Fe, Co and Ni) doped CuGaS$_2$. The vertical dashed line is the Fermi level.

![Fig. 5](Scheme showing the orbital occupation of the 3d electron for the M dopants in CuGaS$_2$.)

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where the $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real part and the imaginary part, respectively. They are connected through the Kramers–Kronig relationship. From $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$, the other optical properties, such as the refractive index $n(\omega)$, the extinction coefficient, $k(\omega)$, and the absorption coefficient, $\alpha(\omega)$, can be evaluated.

The $\alpha(\omega)$, as a function of the incident energy, is shown in Fig. 6 (a)–(c) for the energy range relevant to the absorption of solar light. Since CuGaS$_2$ belongs to the tetragonal system, we consider the optical absorption only in two directions. Obviously, the optical absorption in the zz direction (along the $c$ axis) is stronger than that in the xx direction (along the $a$ axis). Therefore, the subsequent discussion will be focused on the zz direction. The spectrum of the host chalcopyrite CuGaS$_2$ has the usual absorption peak at the theoretical value of the band gap about 2.0 eV. However, for the Fe doped CuGaS$_2$ compound, except for the peak at 2.0 eV, two additional new absorption peaks appear at around 1.0 eV and 1.7 eV, corresponding to the electron transition from the VB to the IB for both spin components. Besides, the optical absorption begins at almost zero energy, largely extending to the infrared portion of the solar

\[
\varepsilon_2(\omega) = 2n(\omega)k(\omega)
\]

\[
\alpha(\omega) = \frac{2\omega n(\omega)}{c} = \frac{\omega}{c} \sqrt{2 \left( \varepsilon_2^2(\omega) + \varepsilon_1^2(\omega) - \varepsilon_1(\omega) \right)}
\]
spectrum, and the overall optical absorption intensity is greatly enhanced compared to that of host CuGaS₂. The result is in good agreement with the experimental result, showing that two absorption peaks are observed at 1.2 eV and 1.9 eV. Co doped CuGaS₂ turns into a half-metal with the disappearance of the absorption peak at 2.0 eV. The absorption enhancement at a lower energy is caused by the electron transition from occupied states to unoccupied states around the Fermi level. As for the Ni substituted CuGaS₂, one absorption peak is located at about 1.75 eV, which resulted from the same spin electron transition from the VB to the IB (see Fig. 6). The absorption spectrum of the Ni doped CuGaS₂ is also largely enhanced in intensity, though with a relatively narrow energy range. Furthermore, the optical conductivity (Fig. 6(d)–(f)) shows the same trend with the absorption coefficient according to \( \sigma \propto \omega \varepsilon_2(\omega) \).

Strictly speaking, the IB needs to be partially filled so that a three-photon absorption process can happen. Though the IB obtained by doping Fe or Ni is empty, which can only enable VB–CB and VB–IB optical transitions, a design with a third electrode for extracting the current from the IB can relax the stringent requirement. Besides, electrons excited from the VB to the IB can transfer to the CB through a nonequilibrium transition, by absorbing a second photon. In a word, the Fe or Ni doped CuGaS₂ compound exhibits excellent characteristics, such as the extended absorption energy range and the enhanced optical absorption intensity, due to the existence of isolated IBs. Thus, the Fe or Ni doped CuGaS₂ may realize IBSCs with high quantum efficiencies.

4 Conclusions

In this work, we investigated the electronic structures and optical properties of host CuGaS₂ and 25% M (Fe, Co, and Ni) doped CuGaS₂, by employing the range-separated hybrid functional, Heyd–Scuseria–Ernzerhof (HSE06). Our results revealed that HSE06 can give a much better description of the host CuGaS₂ than DFT. Isolated intermediate bands (IBs), with an optimal position and width, appeared in Fe and Ni doped CuGaS₂ compounds, which originated from the M-3d states with a weak hybridization of the S-3p and Cu-3d states. Benefitted by the two photon process induced by the IBs, additional peaks appeared in the spectrum. Furthermore, the optical absorption coefficients were greatly enhanced and the absorption energy ranges were largely extended in the M doped CuGaS₂ systems. However, Co doping turned the system into a half-metal. Therefore, Fe and Ni doped CuGaS₂ semiconductors will be potential candidates for photovoltaic materials. Additionally, these materials may also be useful in other applications, such as photon up/down converters, spintronics and so on.

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References