OPTICAL PROPERTIES OF NOVEL INTERMEDIATE BAND INDIUM THIOSPINEL MATERIALS BY QUANTUM MECHANICAL CALCULATIONS

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ABSTRACT: In this work we present quantum mechanic calculations using the Density Functional Theory for several transition metal substituted octahedral thiospinels derivatives of the In_2S_3 and $MgIn_2S_4$ compounds. The calculations predict that these materials will have a partially filled band inside the band-gap of the aforementioned semiconductors and due to that can be proposed as a novel class of high efficiency photovoltaic materials for intermediate band solar cells. The new band enables absorption of additional photons with energies lower than those of the band-gap, increasing in this way the photocurrent. Results of calculations show the enhancement of the optical absorption properties. The purpose of the work is to develop a material which can be used to create a more efficient photovoltaic solar cell.

Keywords: Spinels, Fundamental, ab-initio

1 INTRODUCTION

In last years our group has presented several materials [1-4] as candidate materials which properties fulfill the intermediate-band (IB) material concept [5]. The proposed materials must have a partially filled band formed inside the band-gap of an appropriate semiconductor. All these studies have been made theoretically using the Density Functional Theory (DFT).

The first proposed candidates to obtain this intermediate band were transition metal-doped III-V materials based on GaAs or GaP [1]. Later we proposed other systems as I-III-VI$_2$ chalcopyrite semiconductors (CuGaS$_2$)[2,3]. In these two material families we have made substitutions of the Ga atoms (III type) with some transition metal atoms. We have calculated them at different dilution levels and with metallic substitutions at several sites. The substitutes are 3d metal elements like Titanium, Vanadium, Chromium and Manganese. The environment around the metals results to be tetrahedral and we consider that the metal is in a M^{3+} oxidation state and its 3d states are partially filled and splitted in two manifolds according to the aforementioned coordination.

For these chalcopyrite type systems we have also studied the energetics of the substitution with these metals using chemical energy balances, to ascertain the practical feasibility of formation of this IB material [4]. The IB concept is postulated as able to enhance the efficiency of photovoltaic (PV) cells.

The IB is due to the transition metal. In order to obtain good quantum efficiencies in the light absorption, these new metal levels must form a real band and must be isolated from the ordinary valence (VB) and conduction bands (CB) of the host semiconductor. In our systems the transition metal IB is used to enhance the use of sub-band gap energy photons. Using the IB an electron can be excited from the valence band (VB) to the conduction band (CB) as usual but we have also the possibility of two more excitations from the VB to the IB and from the IB to the CB. These lower energy transitions will be the responsible for the light absorption enhancement. The IB concept has an ideal solar energy conversion limit of up to 63.2% at maximum concentration.

The aim of this work is to show a new family of systems which are indium-based thiospinels. They main difference with the previous approaches is that the substitution is now made in an octahedral coordination, so we will have six atoms around the metal. This situation should be thermodynamically more favorable than the previous approaches because these metal atoms in a M^{3+} oxidation state prefer to be coordinated in that way [6].

Our studies have been done in the framework of quantum mechanic calculations, using the DFT at the local density approximation (LDA) and the generalized gradient approximation (GGA) levels including spin polarization. In this work we have made electronic structure calculations and presenting electronic density of states with several projections for selected elements. Using the energy values of each state we have made calculations of the absorption coefficient of V-substituted $MgIn_2S_4$ and In_2S_3 systems. We will also identify which transitions corresponds to each peak in the absorption coefficient using the a projection of the imaginary part of the dielectric function.

2 MODELS

Spinels are a family of compounds whose chemical formula is II-III_2-VI_4 which crystallizes in Fd3m space group. In their structures, anions form a face centered cubic lattice, surrounded by tetrahedral and octahedral sites which are occupied by the cations. In direct spinels, II type atoms are on tetrahedral sites and the III-type atoms are on octahedral sites. In inverse spinels, the cations situation change, so half of the III-type atoms are on tetrahedral sites and all the II-type atoms and the other half of the III-type atoms are now on octahedral sites.

The $MgIn_2S_4$ spinel has some degree of inversion but, for simplicity, we have studied its direct spinel structure where the Indium atoms occupy the octahedral and the Magnesium atoms the tetrahedral sites. The studied spinel derivative was obtained by substitution of one Indium by a transition metal (Titanium or Vanadium) with a $Mg_2In_3S_8M$ final formula. Its crystal structure is shown in Fig. 1.

The In_2S_3 ($In_{16}S_{24}$ primitive unit cell) lattice can be considered as a defect structure of the above $MgIn_4S_8$ spinel with Mg vacancies and with a ¼ of Indiums at tetrahedral sites and the rest at the octahedral ones. The intermediate band system has been made by substitution of two octahedrally coordinated Indiums by a transition metal and has a $In_{14}S_{24}M_2$ formula. Its crystal structure is shown in Fig. 1.
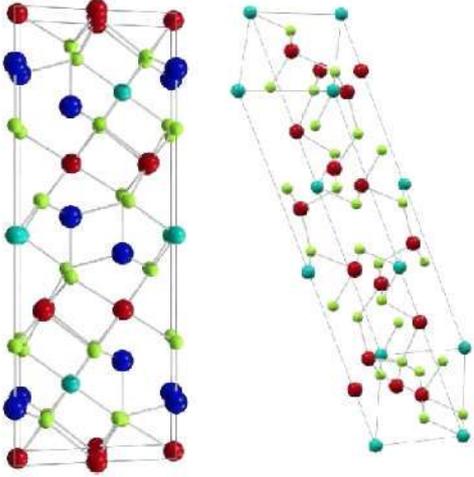

Figure 1: $Mg_2In_3S_8M$ (left) and $In_{14}S_{24}M_2$ (right) crystal structure, being M a metal= Ti or V. Mg (dark blue), In (red), S (green), M (light blue)

3 METHODS

We have made spin-polarized DFT calculations mainly at the Perdew and Wang functional (PW91) level using the plane-wave VASP program with PAW potentials [7]

Convergence tests of kinetic cutoff and k-points sampling were done. For $MgIn_2S_4$ the final energy cutoff was 198.0 eV. The Brillouin zone (BZ) was sampled with an 8x8x8 Monkhorst-Pack (MP) k-point mesh. For In_2S_3 the energy cutoff was 280 eV and the BZ was sampled with a 4x4x4 MP mesh. For the $Mg_2In_3S_8M$ spinel alloys we used the same energy cutoffs as for the semiconductor but using a 10x10x10 MP mesh. The $In_{14}S_{24}M_2$ alloy system used it has the same convergence parameters than the host semiconductor In_2S_3. The PDOS is obtained through integration inside atom-centered spheres having the standard atomic radii of the corresponding species. In our cases the radii used were 1.66 1.60 1.27 Å for Mg, In and S respectively and 1.47 and 1.34 Å for the metallic species Ti and V.

Concerning the calculation of the optical properties we have used the so-called Random Phase Approximation (RPA) consisting in obtaining the imaginary part of the dielectric function (and so other optical properties) from the microscopic properties of the system (wavefunctions, eigenvalues, and occupations of the electronic states). The practical implementation of this approximation consists in the following. We can write the elements of the imaginary part of the dielectric tensors as a sum over occupied and unoccupied states in Eq.(1)

$$\varepsilon_{\alpha\beta}^{(2)}(\omega) = \frac{4\pi^2 e^2}{\Omega m^2 \omega^2} \sum_{knn'\sigma} f_{n\sigma}^k \left(1 - f_{n'\sigma}^k\right) \delta\left(\xi_{kn'} - \xi_{kn} - \hbar\omega\right)$$
$$x \left\langle \psi_{nk\sigma} \mid p_\alpha \mid \psi_{n'k\sigma} \right\rangle \left\langle \psi_{n'k\sigma} \mid p_\beta \mid \psi_{nk\sigma} \right\rangle$$

(1)

where $\psi_{nk\sigma}$ and $\psi_{n'k\sigma}$ are the crystal wavefunctions corresponding to the initial and final states at the k-point k. Respectively, e, m and Ω are the electron charge, its mass and the volume of the unit cell, and $f_{n\sigma}^k$ is the occupation of the level, according to the Fermi distribution.

With this, we can compute the real part of the dielectric function by the Kramers-Kronig equations Eq. (2), and with both ε components we obtain the fundamental optical properties; such as absorption, reflectance, refraction index, etc.; by simple relations. More details of this method can be found in reference [8].

$$\varepsilon_{\alpha\beta}^{(1)}(\omega) = 1 + \frac{2}{\pi} \wp \int \frac{\omega'}{\omega'^2 - \omega^2 + i\eta} \varepsilon_{\alpha\beta}^{(2)}(\omega') \, d\omega'$$

(2)

We use equations (1) and (2) as implemented in the post-processing tool of VASP called OPTIC [9]. For these calculations we found converged optical properties by sampling the BZ with a 12x12x12 MP grid.

4 RESULTS

4.1 $MgIn_2S_4$ and derivatives.

We have previously presented calculations for the parent spinel [10,11]. The cell parameters compared quite well with experimental results. The In-S computed distance is 2.63 Å (exptl.: c.a 2.58 Å) and the Mg-S distance 2.46 Å (exptl.: c.a 2.48 Å).

When an Indium atom is replaced by a transition metal atom (Titanium or Vanadium) an intermediate band appears at the spin up channel in the band diagram for both systems. These can be clearly seen in Fig. 2.
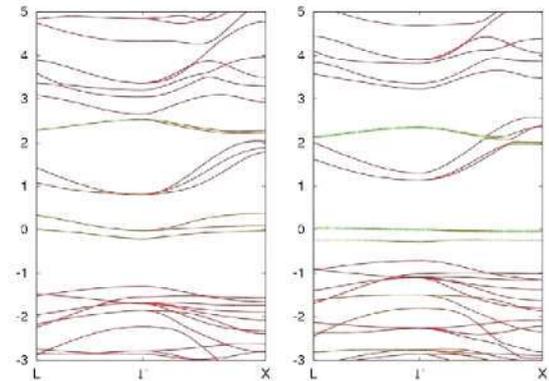

Figure 2: GGA band diagrams for the $Mg_2In_3S_8M$, (M= Ti, V) system. E=0 marks the Fermi level.

The optical absorption as well as other optical properties have been calculated for the semiconductor as well as for the substituted alloys. The most interesting

conclusion of this work is that with the transition metal we get a significant increase of the absorption of low energy photons compared to that of the semiconductor. This increase occurs at the main region of the solar spectrum as is required for an intermediate band material for photovoltaic purposes. In the inset of Fig. 3 we can see this enhancement by comparing the V-substituted compound with the host spinel.

To understand the peaks in the absorption spectrum and to interpret which transitions contribute to each peak, we calculated the ω-weighted imaginary part of the total dielectric function and its partial contribution to the different transitions. The peaks of this magnitude don't have exactly the same relative intensities as those of the absorption but they are in the same positions, therefore, we can understand any of the latter by means of the former. We can see in Fig. 3 how an intraband IB-IB transition appears first (this transition will not contribute to the photocurrent since the intermediate band is isolated); next the transitions between the VB and the IB, beginning at ca. 0.7 eV; after this we see the contribution of transition between the IB and the CB, starting at c.a 1.2 eV and peaking at 2.5 eV and finally the usual one between the VB and the CB.
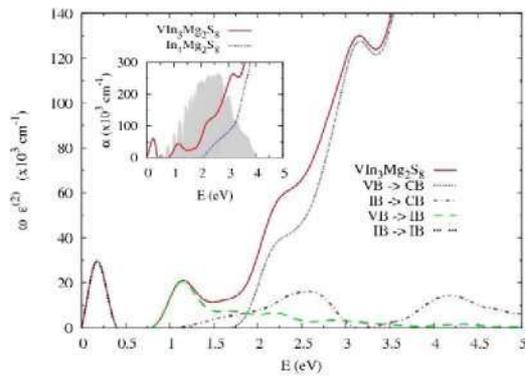

Figure 3: ω-weighted imaginary part of the dielectric function of $Mg_2In_3S_8V$. Inset: computed total absorption coefficient compared to that of the host semiconductor.

4.2 In_2S_3 and derivatives.

As in the case of the Magnesium thiospinel, we have first made calculations for the undoped system (In_2S_3). This system is commonly used as a window layer in thin-film photovoltaic systems so the substituted system preparation is expected to be easier than for $Mg_2In_3S_8M$. After geometry relaxation the geometranion positions compare very well with experimental results [12].
A theoretical band gap width of ca. 0.86 eV is observed while the experimental value is 2.1eV; such underestimation is expected in GGA calculations. In Fig. 4 we show the total and projected density of states for this semiconductor. The top of the valence band is mainly due to Sulphur p-type orbitals and the bottom of the conduction band has a mix between Indium s and p-type and Sulphur p-type orbitals.
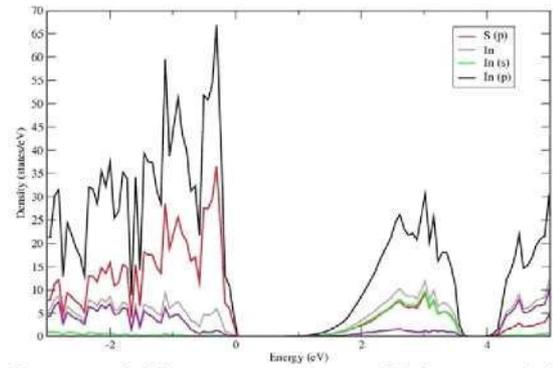

Figure 4: GGA total and projected DOS for the In_2S_3 semiconductor.

For the $In_{16}S_{24}$ semiconductor we have substituted two of the octahedrally coordinated Indiums by transition metal atoms. We have found intermediate bands in the Titanium and Vanadium cases. In Fig. 5, we show a density of states for the $In_{14}S_{24}V_2$
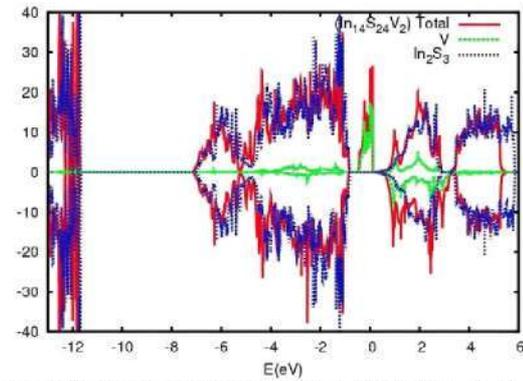

Figure 5: GGA total and projected DOS for the $In_{14}S_{24}V_2$ compared with the total DOS for In_2S_3 semiconductor.

In the same way as for the compounds with Mg, we can compute the optical properties of the In_2S_3 and its derivatives. In this case we also show the enhancement in the absorption due to the intermediate band. In the inset of Fig. 6 we compare the ab-initio calculated absorptions of the V-alloy and the In_2S_3 but also we compare the latter with available experimental results for this compound. In this case, we show the predicting capabilities of the used approach, since our calculation is in good agreement with the experimental measures of Guillen et al. [13].

The decomposition in the partial contributions to the imaginary part of the dielectric function has been also carried out (Fig. 6).
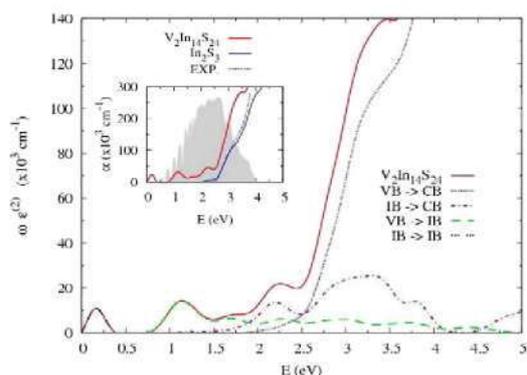
Figure 6: ω-weighted imaginary part of the dielectric function of $In_{14}S_{24}V_2$. Inset: computed total absorption coefficient compared to that of the host semiconductor.

4.3 Experimental Results.

The In_2S_3 semiconductor and its V-substituted derivative have been obtained experimentally by a solvothermal method and their diffuse reflectance UV-Visible-Near IR (NIR) spectra have been recorded [14]. NIR data show a good correspondence between the experimental and theoretical peaks. These results validate our calculations. See Fig.7.
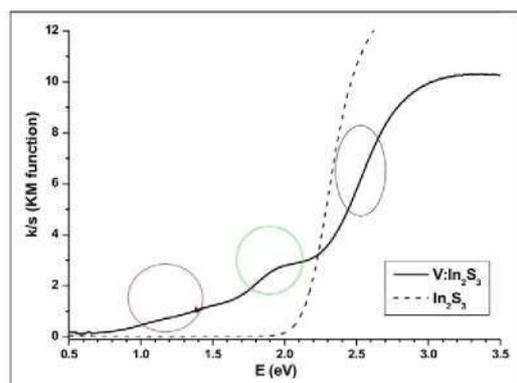

Figure 7: NIR diffuse reflectance spectrum of the substituted vanadium alloy ($In_{14}S_{24}V_2$).

5   CONCLUSIONS

We have made DFT calculations for $MgIn_2S_4$ and In_2S_3 systems and their Indium substituted derivatives. The results show that systems which have incorporated transition metals to their structures can have an intermediate band. By means of this intermediate band, we can allow the absorption of photons of sub-band-gap energy in the main region of the solar spectrum. That being the basis of the intermediate band photovoltaic material concept. In this work we have confirmed the effect of the enhancement in the optical properties of the material resulting from the intermediate transition metal band.

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