Intermediate band materials for more efficient solar energy use: quantum modeling and experimental realizations

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The intermediate band (IB) solar cell (Fig. 1) has been proposed[1] to increase photovoltaic efficiency by a factor above 1.5, based on the absorption of two sub-bandgap photons to promote an electron across the bandgap. To realize this principle, that can be applied also to obtain efficient photocatalysis with sunlight, we proposed in recent years several materials where a metal or heavy element, substituting for an electropositive atom in a known semiconductor that has an appropriate band gap width (around 2 eV), forms inside the gap the partially filled levels needed for this aim. After studying Ga(As,P) with Ga partially substituted by Ti or Cr[2], we proposed several systems that could be made in thin film form:

a) Ti- or Cr- substituted $CuGaS_2$ or similar chalcopyrite (Fig. 2), where the thermodynamics of formation is seen to be less disfavourable than e.g. insertion of Mn in GaAs[3];

b) In_2S_3 and other sulphides containing octahedral In, which when doped with Ti or V form also the IB according to quantum calculations[4] (Fig. 3). The V-doped In_2S_3 material is particularly promising. Being based on a binary compound host, controlling its stoichiometry should be easy. In addition In_2S_3, with E_g= 2.0 eV, is used as buffer layer in thin film CIGS PV cells, so that the known technology to make it in thin film form could be used. Besides, we have synthesized it in nanocrystalline form[5] and shown that its optical absorption spectrum has the features predicted by quantum calculations for the IB structure (Fig. 4). Furthermore, recent photocatalytic tests made with it[6] show that the V dopant extends its spectral response down to the IR range without increasing recombination, which would decrease its efficiency.

c) Octahedral Sn^{IV} sulphide and other similar compounds show also, according to DFT modeling (Fig. 5), the formation of an IB with the desired characteristics when V, Nb or similar metals are introduced at Sn sites[7]. The experimental synthesis of such sulphide is in progress, and first results obtained show optical absorption spectra matching again the expectations for an IB material (Fig. 6).

d) Another class of IB materials consists of Si heavily doped with certain elements. With Ti as dopant the desired IB electronic structure appears (Fig. 7) if Ti lies at interstitial sites[8]. Such material has been prepared by ion implantation methods, and its electrical properties[9] show uncommon features that can be explained assuming the formation of a partially filled band a few tenths of eV below the conduction band, as predicted by the DFT calculations. Although its band gap is not optimum to get high efficiency, it can serve as benchmark to study the behaviour of IB materials in single-crystal form. We could also show that substitution of Si by S or Se, accompanied by hole doping, provides an IB material as well[10].

e) Finally we showed with DFT calculations that a clathrate-type silicon polymorph, that in pure form has E_g=1.9 eV and for which some thin film preparation recipes exist, forms an IB material when a metal as Ag is occluded in its cavities or some of its Si atoms are substitued by a transition metal as V[11] (Fig. 8).

An overview of these systems, including results obtained on them using high level, state-of-the-art quantum calculation methods as e.g. GW, will be presented.

References

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[3] P. Palacios *et al*. Thin Solid Films **515** (2007) 6280; *ibid.* J. Phys. Chem. C **112** (2008) 9525
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[6] R. Lucena and J.C. Conesa, in preparation
[7] P. Wahnón *et al.*, in preparation
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Figures

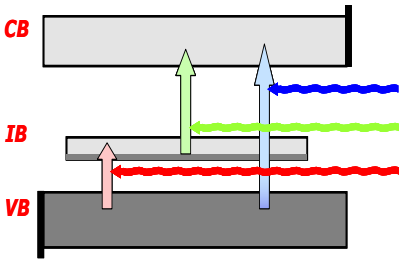

Figure 1- Scheme of operation of an intermediate band photovoltaic cell

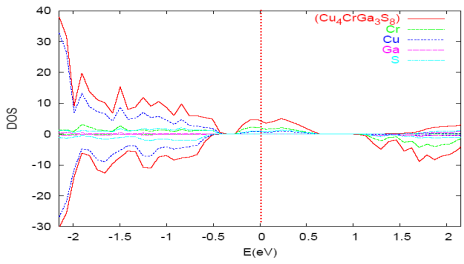

Figure 2 - Density of states (computed with DFT) of $CuGaS_2$ with Ga partially substituted by Cr

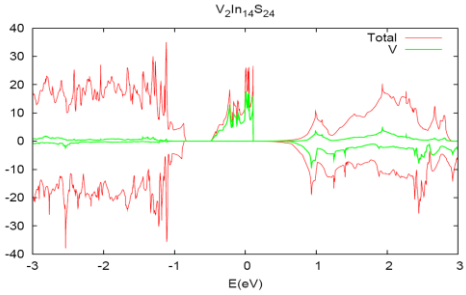

Figure 3 - Density of states (computed with DFT) of In_2S_3 with octahedral In partially substituted by V

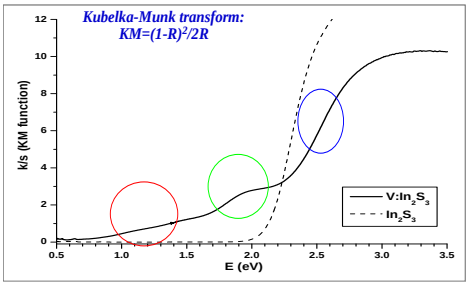

Figure 4 - Experimental diffuse reflectance spectrum of pure and V-doped nanocrystalline In_2S_3

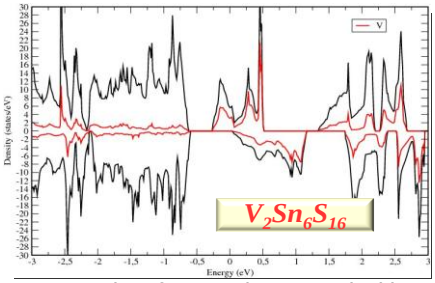

Figure 5 - Density of states (computed with DFT) of SnS_2 with Sn partially substituted by V

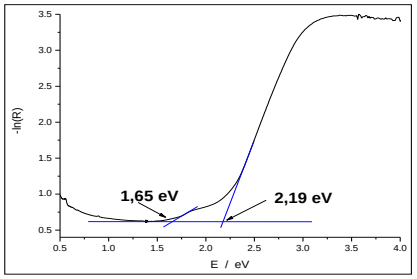

Figure 6 - Experimental diffuse reflectance spectrum of V-doped nanocrystalline SnS_2

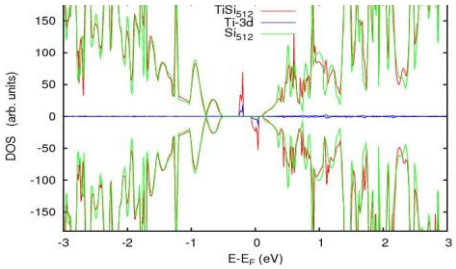

Figure 7 - Density of states (computed with DFT) of Si with Ti located in an interstitial site

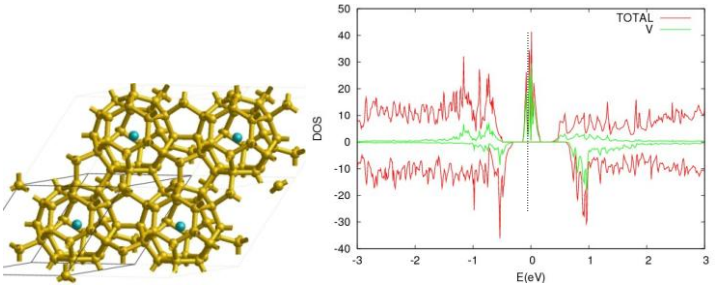

Figure 8 – Estructure of Si clathrate, and density of states computed for it when V substitutes for Si atoms in the lattice