Thermodynamics of the Formation of Ti- and Cr-doped CuGaS₂ Intermediate-band Photovoltaic Materials

Pablo Palacios,^{†,‡} Irene Aguilera,[†] Perla Wahnón,[‡] and José C. Conesa^{*,‡}

Instituto de Energía Solar, Universidad Politécnica de Madrid, ETSI de Telecomunicación, Ciudad Universitaria, 28040 Madrid, Spain and Instituto de Catálisis y Petroleoquímica, CSIC, Marie Curie 2, Cantoblanco, 28049 Madrid, Spain

Following previous electronic structure calculations that indicated that the substitution of part of the Ga atoms in CuGaS₂ chalcopyrite by Ti or Cr produces an intermediate band material that could make new photovoltaic cells of enhanced efficiency possible, new DFT calculations have now been carried out to assess the thermodynamic viability of these substituted structures. Calculations of the total energy, disorder entropy, and vibration (phonon) contributions are combined to obtain the free energy of formation of those materials relative to a combination of the most closely related known stable compounds into which they could decompose. It is found that, except for low substituent concentrations and high temperatures, the substituted structures are less stable than the combination of simpler compounds (the formation of which would thus be more favorable), but to a smaller extent than that previously found for Mn-doped GaAs, which can be prepared in the laboratory. The solubility is computed to be lower for Ti than for Cr; the latter also has a tendency to cluster.

Introduction

For more widespread use, photovoltaic solar cells need to enhance their energy efficiency and/or cost effectiveness above that of the now more frequently used cells based on silicon as the light absorber. Among the several strategies proposed for this, the one deserving attention in recent years is that based on the concept of an intermediate-band (IB) solar cell.¹ In the latter, a relatively narrow (preferably, partially filled) new band (the IB) is inserted into the bandgap of a common semiconductor at an energy position neither overlapping the valence band (VB) nor the conduction band (CB), so that it becomes possible to promote an electron from the VB to the CB not only by absorbing one photon of energy higher than the bandgap width (E_g) but also upon the absorption of two lower energy photons, which, respectively, promote one electron from the VB to the IB and from the IB to the CB. This may allow a higher current to be obtained at the voltage corresponding to the E_g value, increasing the overall efficiency. The ideal upper limit for the latter thus turns out to be 63.2% (achievable for an IB properly placed within a bandgap of $E_g = 1.93$ eV), whereas it is 40.7% for a cell based on a single normal semiconductor as the light absorber.

The present authors have proposed in previous works, on the basis of DFT calculations, that III–V semiconductors such as GaAs or GaP, with Ti partially substituting Ga, can constitute one such IB material,² although an assessment of the energy cost of this insertion, complemented by an estimation of other free energy contributions,³ indicates that this material may be difficult to make, unless experimental synthesis conditions far from the equilibrium are maintained. Subsequent work has shown that the insertion of Ti, and possibly also Cr, into a chalcopyrite semiconductor such as CuGaS₂, with the transition

Figure 1. Basic unit cell used in the simulations of CuGaS₂ with M atoms substituting Ga. Marked are the distances existing between the M substituents in the simulations with two M atoms per cell.

element substituting Ga, may also achieve the desired IB situation, and a preliminary calculation of the insertion energy has suggested that the process could be less unfavorable than in the III–V material.⁴ In the present work a more complete evaluation of the thermodynamic balance of this insertion is presented.

Models and Methods

The crystal model used in all calculations was based on a unit cell derived from the standard centered tetragonal one of chalcopyrite through the vector transformation $\mathbf{a}' = \mathbf{a} + \mathbf{b}$, $\mathbf{b}' = \mathbf{b} - \mathbf{a}$, $\mathbf{c}' = \mathbf{c}$; its 32-atom contents were thus Cu₈Ga₈S₁₆. When two of the Ga atoms in it were substituted by a transition metal M at the positions shown separated by distance d_2 in Figure 1, a face-centered lattice resulted (space group C2). The primitive cell thus had a 16-atom content of Cu₄MGa₃S₈. The calculations were then made on this primitive cell. In other cases, two substituting M atoms were inserted, separated at the shorter distance d_1 , or only one Ga atom was substituted; the calcula-

tions were then made on the aforementioned 32-atom cell, which remained primitive. We have not considered substitution at the Cu site since both Ti and Cr (especially the former) tend to prefer oxidation states higher than +1, which would favor the trivalent element position; furthermore, the ionic radii of Ti^{3+} and Cr^{3+} match that of Ga^{3+} relatively well.

Total energy calculations within density functional theory (DFT) at the gradient-corrected GGA-PBE level were made on these crystal models with the planewave code VASP using PAW potentials.⁵ The planewave cutoff energy (at 375 eV) and the density of the reciprocal space sampling (using gamma point-centered Monkhorst-Pack meshes) were chosen to be high enough to achieve convergences within 10 meV/Ti atom in the total energy balance values computed for reactions 1–3 below. All of the crystal structures considered were fully relaxed in both atomic positions and unit cell parameters.

Phonon densities of states are taken from a previous work.⁶ They were computed for the metal-substituted 16-atom cell also using the VASP code at the GGA PW91 level, determining the dynamic matrix from the second derivatives of the total energy at the geometry giving the energy minimum and obtaining the vibration frequencies from it using the frozen-phonon method. The resulting phonon densities of states $D(\omega)$ were then used to evaluate the vibration contributions to the free energy of each crystal structure using the standard formula shown in the following equation.⁷

$$F_{\text{vib}} = \frac{1}{2} \int \hbar \omega D(\omega) d\omega + kT \int \ln[1 - \exp(-\hbar \omega / kT)] D(\omega) d\omega$$

Results and Discussion

Substitution by Ti. As previously done in similar works of ours,³ in order to assess the stability of Ti substitution in CuGaS_2 the computed total energy of the 16-atom structure $\text{Cu}_4\text{TiGa}_3\text{S}_8$ (based on the 16-atom primitive cell described above) was compared with that of the most closely related stable compounds into which it could conceivably decompose. No stable compound with CuTiS_2 stoichiometry seems to be known in the literature; to the authors' knowledge the closest one is $\text{Cu}_{0.7}\text{TiS}_2$,⁸ describable as a result of randomly intercalating Cu atoms in tetrahedral positions between the sheets of the layered compound TiS_2 . A model of this compound that is tractable using DFT calculations has been built by ordering Cu atoms in a tripled volume supercell of its structure in such a way that the final stoichiometry is $\text{Cu}_{2/3}\text{TiS}_2$. Thus, the most likely relationship between the (potentially existing) $\text{Cu}_4\text{TiGa}_3\text{S}_8$ compound and existing simpler compounds can be modeled through the hypothetical formation process (eq 1).

We consider that this way of assessing the thermodynamic viability of doping (a comparison with a combination of related compounds) is preferable for our purposes than that used by other authors, which is based on a balance including the chemical potentials of the constituent elements and eventually (when analyzing charged defects) the energy of the Fermi level and which has been presented in several reviews.⁹ The latter scheme is useful for understanding the stability of charged defects and guessing which change in the vapor pressure of an element (within a preparative scheme using CVD, MBE, or similar methods) may be more effective to obtain a given phase or doping state.¹⁰ Our procedure, however, addresses just the

stability of the desired material (if it can be formed) against its possible decomposition into experimentally known compounds (which will obviously be more stable than the pure constituting elements) and, therefore, constitutes a more stringent and appropriate stability test.

The DFT computation gives for the energy balance of reaction (1) the value $\Delta E = +0.86$ eV, quite close to that obtained earlier for the same process with the PW91 functional.⁴ Thus, the Ti-substituted compound would be more energetic than the simpler ones, that is, its decomposition is predicted to be a favorable process. This can be ascribed to the preference of Ti^{3+} species for the octahedral coordination, as it occurs in $\text{Cu}_{2/3}\text{TiS}_2$. This energy difference is, however, lower than that previously computed for the substitution of Ga by Ti in GaAs or GaP^3 and is also lower than that found for the substitution of Ga by Mn in GaAs (> 2.0 eV/metal atom).³ Because the latter system is known to be experimentally possible (at least at Ga substitution levels of a few percent) if well-chosen preparation methods are used,¹¹ then the experimental preparation of the Ti-substituted chalcopyrite should be feasible.

A similar calculation was carried out for a more diluted material, considering the process shown in eq 2

where the Ti-containing structure is now that shown in Figure 1 with one Ti atom/cell. This yielded nearly the same ΔE value (differing by just a few meV, quite within the accuracy of the method); this means that a higher dilution does not change the substitution energies. Because this ΔE value is relatively high, one can expect that the concentration of Ti achievable in this system, even when using kinetically controlled synthesis methods, will be modest. Still, the possibility can be considered that the energies could be different if the Ti atoms were located closer to each other than they are in this model. This was assessed by computing the energy balance of eq 1 for a Ti-substituted chalcopyrite structure in which two Ti atoms are positioned in the 32-atom cell depicted in Figure 1 at distance d_1 . The total energy difference between the relative positions d_1 and d_2 was found to be

$$E(d_1) - E(d_2) = -0.015 \text{ eV}$$

This means that the tendency to associate Ti atoms in the chalcopyrite structure is negligible (lower than thermal energy at room temperature).

The proper evaluation of the feasibility of the substitution of Ga by Ti in this chalcopyrite requires the free energy balance (ΔF) of reactions of type 1 or 2 to be estimated. This free energy will have contributions from configurational (disorder) entropy and vibration effects. The former can be computed for any composition $\text{CuTi}_x\text{Ga}_{1-x}\text{S}_2$ having random positioning of the Ti substituent, with the following standard equation (referring to one formula unit).

$$S = -k[x \ln(x) + (1-x) \ln(1-x)]$$

To express the result per atom of transition metal, this expression will be divided by the concentration (x).

In the case of eqs 1 and 2, it is necessary to take into account that the $\text{Cu}_{2/3}\text{TiS}_2$ compound will also have, in reality, its Cu atoms disordered so that it will contain an amount of configuration entropy given by the above formula with $x = 2/3$. The computed overall contribution of this factor to the free energy balance of type 1 and 2 reactions, expressed per Ti atom, is presented in Figure 2A as a function of temperature for several values of x . These data show that for high temperatures and

Figure 2. Contributions of configuration entropy to the free energy of formation (from the simpler compounds indicated in the text, as in eqs 1–3) of (A) $\text{CuGa}_{1-x}\text{Ti}_x\text{S}_2$, and (B) $\text{CuGa}_{1-x}\text{Cr}_x\text{S}_2$.

low x values this factor will significantly contribute to decreasing the instability of the substituted chalcopyrite with respect to a mixture of simpler compounds of the types indicated in reactions 1 and 2.

The vibration contributions (F_{vib}) to the free energies of the different lattices were computed as explained above from the phonon densities of states (DOS) that were calculated in previous work.⁶ As shown in the latter, these DOS show noticeable effects of the metal substitution. The thus obtained balance of F_{vib} corresponding to reaction 1 is presented as a function of temperature in Figure 3. It can be seen that for Ti insertion the vibration contribution to the free energy of the reaction is negative, that is, it partially cancels the unfavorable energies of the process, particularly at high temperatures.

The total free-energy balance for a generic process of the type modeled with reactions of types 1 and 2, computed under the (simplifying) hypothesis that the contribution of vibrations for different Ti dilution levels is similar to that obtained for $\text{Cu}_8\text{TiGa}_7\text{S}_{16}$ (presented in Figure 3), is plotted as a function of temperature and composition in Figure 4A. From these data, the corresponding ones referred to one formula unit of the parent chalcopyrite (i.e., the free energy balance data for the formation of one $\text{CuGa}_{1-x}\text{Ti}_x\text{S}_2$ composition) can be derived through multiplication by the Ti fraction x , but the resulting plots are scarcely informative as they obviously give very small values for high dilution levels; consequently they are not displayed here. In Figure 4A it can be seen that the unfavorable ΔF_{tot} value decreases for decreasing concentrations and increasing temperatures. Ultimately, for each temperature the x value for which ΔF_{tot} becomes zero marks the thermodynamic limit of the concentration of Ti in the Ga sites of this chalcopyrite; Figure 5 shows the temperature dependence of this miscibility limit (a sort of solubility curve) obtained in this way for Ti in

Figure 3. Contributions of vibration terms (evaluated from the phonon densities of states computed in ref 6) to the free energy balance of Ga substitution by Ti and Cr in the 16-atom chalcopyrite cell (processes 1 and 3, respectively).

Figure 4. Total free energy balance, including total energy, configuration entropy, and vibration terms, computed for the formation processes (from the simpler compounds indicated in the text, as in processes 1–3) of (A) $\text{CuGa}_{1-x}\text{Ti}_x\text{S}_2$, and (B) $\text{CuGa}_{1-x}\text{Cr}_x\text{S}_2$.

$\text{Cu}(\text{Ga},\text{Ti})\text{S}_2$. It is rather small even at high temperatures, implying that the preparation of this Ti-substituted material with significant amounts of the transition metal is likely to be successful only when using methods controlled by kinetics, in which thermodynamic equilibrium is not reached.

Substitution by Cr. The stability of Cr-substituted CuGaS_2 , which according to DFT calculations might also have an intermediate band structure of the type desired for photovoltaic application,⁴ was evaluated in a similar way. In this case a stable compound of CuCrS_2 stoichiometry is known to exist, also having a layered structure with the transition metal in octahedral positions and well-ordered Cu in tetrahedral sites.¹² Thus, processes simpler than those in reactions 1 and 2 above can be considered; for example, for a Cr/Ga ratio = 1:3 the relevant reaction is given by eq 3.

The total energy balance (not including vibration effects) is computed in this case to be $\Delta E = +0.61$ eV per Cr atom. Therefore, the Cr-substituted compound would also be unstable against decomposition into simpler compounds, although the energy balance is somewhat smaller, that is, less unfavorable, than in the case of Ti. This latter difference might be related to the fact that, while the ionic radius of hexacoordinated Cr^{3+} is 0.63 Å, practically the same as that of Ga^{3+} (0.62 Å), the Ti^{3+} ionic radius is noticeably larger (0.76 Å), implying some degree of lattice misfit for the substitution with Ti that would be small or absent in the case of Cr. Indeed, in the computed relaxed structures the average Cr–S distance in $\text{Cu}_4\text{CrGa}_3\text{S}_8$ (2.307 Å) is much closer to the Ga–S distance obtained for CuGaS_2 (2.319 Å) than the Ti–S distance computed for $\text{Cu}_4\text{TiGa}_3\text{S}_8$ (2.358 Å). Another possible reason for the less favorable substitution energy balance in the case of Ti might be the reduced stability of the latter in the trivalent state, exemplified by the aforementioned fact that the known Cu–Ti–S compound has a stoichiometry corresponding to a higher average redox state of Ti ($\text{Ti}^{+3.3}$).

The possible effects of concentration in the energies of the substitution of Ga by Cr in the chalcopyrite were also evaluated. As in the case of Ti, the ΔE value per Cr atom obtained for a Cr/Ga ratio = 1:7 was virtually the same as for a 1:3 ratio, implying that the Cr–Cr interaction in the 16-atom cell model is negligible. However, when two Cr atoms were placed in the 32-atom cell at the closest Ga neighboring sites (distance d_1 in Figure 1) the total energy was found to be lower than for the relative location d_2 by 0.14 eV (i.e., by more than 5 times the thermal energy at room temperature). This means that when Cr substitutes Ga in the chalcopyrite it will tend to associate by occupying the nearest Ga positions, a tendency that, as said previously, is negligible for Ti.

For this reason, applying the same thermodynamic analysis directly to the substitution by Cr as was previously made for Ti would be incorrect in the medium-to-large Cr concentration range, in which the probability of having two Cr atoms located at the most closely located sites will be significant. Indeed, the accurate analysis of this situation would require an examination of the energy of the configurations having groups of more than two closely located Cr atoms in a number of different arrangements, as has been done by other authors using different approaches for several cases of substitution or alloying in III–V compounds.¹³ The number of configurations to be evaluated would be, however, clearly larger here, because chalcopyrite has less than cubic symmetry and the number of nonequivalent Ga–Ga distances within a given range is higher. This complex evaluation lies outside the scope of the present work and does not seem necessary for its aims considering that the thermodynamic solubility of Cr will continue to be low (the aforementioned pairing energy is clearly insufficient to compensate for the unfavorable substitution energy balance); therefore, in equilibrium conditions, the Cr concentrations will be small. Thus, disorder entropy considerations will favor the fraction of Cr atoms that will be paired being small; for such cases, an analysis similar to that made for Ti may be considered acceptable and will be completed in the following.

In the first place, the disorder entropy would still be computed as for Ti above, but because the ordered CuCrS_2 compound is stable, no disorder entropy term needs to be considered for it. For that reason, the net balance of disorder entropy is different from that computed for Ti and is shown (for low Cr concentrations only) in Figure 2B. Concerning the vibration contributions

Figure 5. Thermodynamic concentration limits of Ti and Cr in the Ga positions of CuGaS_2 at different temperatures, estimated from the relation $\Delta F_{\text{tot}}=0$ applied to the data represented in Figure 4.

to free energy, they have been computed from the phonon DOS calculated in previous work⁶ as above for Ti. The cell used is still that containing 16 atoms; because the interaction between Cr atoms in this case is small, as previously said, the vibration effects of Cr substitution determined with this calculation can be considered representative of the diluted Cr situation. Thus, the ΔF_{vibr} contribution has been computed in the same way as for Ti and is shown in Figure 3. Compared with that of the Ti-substituted material, this contribution is opposite (i.e., it does not favor the substitution) and is rather smaller, which might be related to the smaller lattice distortion effects resulting from the aforementioned near coincidence of the ionic radii of Cr^{3+} and Ga^{3+} . On this basis, one may expect that vibration effects on free energy will also be small for situations with closely located Cr atoms (the case of distance d_1 in Figure 1), the phonon calculation of which is computationally much more expensive (due to the larger number of atoms involved) and has not been undertaken here.

From all these data, the total free energy balance of the substitution by Cr can be computed as above for Ti, although here, due to the aforementioned tendency to clustering, the calculation can be considered reliable only for lower concentrations; consequently, only data for those lower concentrations have been included in the plots of Figures 4B and 5. It can be seen that the thermodynamic limit for the Cr concentration is low, although it is higher than that of Ti. Again, kinetics-controlled preparation methods will have to be used to obtain this material.

Conclusions

The substitution by Cr or Ti at Ga sites in CuGaS_2 is energetically unfavorable with respect to phase segregation or decomposition into known, simpler stable compounds; this may be due to the preference of both metals when in the trivalent state for octahedral rather than tetrahedral coordination. The contribution of thermal vibrations to the free energy balance is found to be more significant for Ti than for Cr. These contributions may have to be taken into account, rather than being ignored as in some current analysis methods, when thermodynamically assessing semiconductor doping limits.

By estimating all of these contributions, together with the configuration entropy in the ideal mixing limit, values for the net free energy change involved in the aforementioned decompositions have been computed, which allows thermodynamic limits for the Ti and Cr concentrations in those sites of the chalcopyrite to be obtained. These limits are low, indicating

that preparation methods controlled by kinetics must be used to obtain large dopant concentrations in this metal-substituted chalcopyrite. The limit is lower for Ti than for Cr, which might be related to the respective values of the ionic radii and to the different stability of the trivalent state in these elements. Although these unfavorable perspectives for material preparation could be intuitively anticipated purely on chemical grounds, it is proper to recall that these energies are less unfavorable than that of the substitution of Ga by Mn in GaAs (evaluated in a previous work³), a process that has been experimentally achieved; therefore, the results presented here imply that the discussed substitutions in chalcopyrite should not be less feasible.

The validity of the hypothesis that assumes ideal mixing (random substitution) has been checked with preliminary calculations by evaluating the tendency of Cr and Ti to cluster in this system. This tendency appears to be negligible for Ti but not for Cr, which implies that for medium to large substitution levels the results obtained for the latter element must be corrected by taking this factor into account. Also, the value obtained for the Cr–Cr interaction energy suggests that there may be some effect of this interaction on the band structure of the material when the degree of dilution is not small. Both issues, that fall outside the scope of the present work, will be addressed in separate future contributions.

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