

# Thermodynamics of zinc insertion in $\text{CuGaS}_2\text{:Ti}$ , used as a modulator agent in an intermediate-band photovoltaic material

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## A B S T R A C T

An intermediate-band photovoltaic material, which has an isolated metallic band located between the top of the valence band and bottom of the conduction band of some semiconductors, has been proposed as third generation solar cell to be used in photovoltaic applications. Density functional theory calculations of Zn in  $\text{CuGaS}_2\text{:Ti}$  have previously shown that, the intermediate-band position can be modulated in proportion of Zn insertion in such a way that increasing Zn concentration can lead to a band-gap reduction, and an adjustment of the intermediate-band position. This could be interesting in the formation of an intermediate-band material, that has the maximum efficiency theoretically predicted for the intermediate-band solar cell. In this work, the energetics of several reaction schemes that could lead to the decomposition of the modulated intermediate-band photovoltaic material,  $\text{CuGaS}_2\text{:Ti:Zn}$ , is studied in order to assess the thermodynamic stability of this material. Calculations of the total free energy and disorder entropy have been taken into account, to get the reaction energy and free energy of the compound decomposition, which is found to be thermodynamically favorable.

### Keywords:

DFT  
Intermediate-band  
Solar cell  
Thermodynamics

## 1. Introduction

In standard solar cells (SC) efficiency losses are unavoidable. In order to obtain an enhanced conversion of solar radiation into electricity, some theoretical hypotheses have been proposed, among which is the intermediate-band (IB) concept. In this solar cell, the existence of an isolated, partially-filled band, in the host semiconductor band-gap, allows two extra low energy photons to be absorbed, which gives an increase in efficiency as high as 63.2% [1], greater than the maximum theoretical value predicted for a single gap solar cell, 40.6% [1,2]. This photovoltaic material could be obtained by doping over the Mott limit a semiconductor, which has a band-gap of around 2 eV.

In order to predict an IB-SC that could be synthesized, our group had carried out calculations of electronic and optical properties of some doped semiconductors, which have the desired characteristics [3–10], and among these IB materials, one of the proposed is  $\text{CuGaS}_2\text{:Ti}$ . Chalcopyrites, used in thin film technology, have efficiencies and stabilities comparable with those found in

conventional crystalline silicon cells [11]. Besides,  $\text{CuGaS}_2$  has an experimental wide gap, near the theoretical band-gap found for the most efficient IB material.

Furthermore, some experimental evidences of Zn occupying cationic positions in  $\text{CuGaS}_2$  show that, the semiconductor band-gap reduces from 2.53 eV [12], to 2.1–2.3 eV [13,14] in doped compound, taking the form of  $(\text{CuGaS}_2)_{1-x}-2(\text{ZnS})_x$ , with  $x$  ranging from 0.05 to 0.0005 respectively. This demonstrates that Zn insertion in  $\text{CuGaS}_2$ , in moderated proportions, can modulate the band-gap value of this wide gap chalcopyrite. The Zn modulation effect can be seen as well in  $\text{CuGaS}_2\text{:Ti}$  [15], where Zn insertion in the IB material,  $\text{CuGaS}_2\text{:Ti}$ , not only modulates the band-gap value, but also the position of the IB and consequently the sub band-gaps created by the IB.

Nevertheless, even though other doped chalcopyrite synthesis, including Ti doped ones, have been reported in literature [18,16,17], and  $\text{CuGaS}_2\text{:Ti}$  formation has also been theoretically predicted [19], an experimental synthesis of  $\text{CuGaS}_2\text{:Ti}$  has not yet been reported. Some of these doped-chalcopyrites, using binary sulfides as precursors in thin film chalcopyrite solar cell obtainment [20,21], can also be found in literature. In this work, we intend to predict, using the energetics of several reaction schemes, whether Zn in  $\text{CuGaS}_2\text{:Ti}$  is termodinamically stable.

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## 2. Models and methods

Modeled supercells were made using 32 atoms, in which Zn and Ti substitute Ga atom positions and starting with  $\text{CuGaS}_2$  experimental parameters.

The constructed structures were relaxed in both atomic coordinates and lattice dimensions using density functional theory (DFT) with GGA PW91 functional [22] implemented in `VASP` program [23,24], where the presence of spin polarization was also considered. Atomic core regions of the electronic structure in the periodic systems were represented with PAW potentials [25,26].

The cut-off energy used, 374 eV, was high enough to evaluate the convergence of each of the studied materials, and the reciprocal space was sampled according to a dense Monkhorst–Pack grid increased until total energy difference was less than 1 meV. After relaxation, the calculations were taken as a starting point to obtain energy minimization using tetrahedron method. The k-point values were also increased to confirm that convergence was achieved.

## 3. Results and discussion

### 3.1. First decomposition scheme studied

The straightforward way of assessing the compound stability, is to compare its energy with that of a sum of simpler known compounds, in which it could possibly decompose. Besides, it is well known that the type of crystalline structure could have an influence on the reaction dynamics. According to this, a combination of  $\text{ZnS}$ ,  $\text{Cu}_2\text{S}$ ,  $\text{TiS}_2$  and  $\text{CuGaS}_2$  might be found favorable and the first  $\text{CuGaS}_2$ :Ti:Zn decomposition reaction scheme proposed is,



DFT computational calculation of the compound total energy involved, gives a negative energy difference of  $\text{ZnTi}_2\text{Cu}_8\text{Ga}_5\text{S}_{16}$  decomposition (Table 1). This negative energy difference,  $\Delta E$ , means that  $\text{CuGaS}_2$ :Ti:Zn compound decomposition is predicted favorably.

Different Ti–Ti and Ti–Zn distances and the same Zn–Zn distance, 7.53 Å, were modeled in the 32 atom supercells (Fig. 1), to compare the influence of substituent distances in total energy difference of reaction (2). In these supercells, the substituent distances were taken as is shown in Table 1.

The total energy in supercell A was 0.013 eV lower than this value in modeled supercell B. This means that the largest possible Ti–Ti distance gives a more stable compound formation, but in decomposition processes the smallest Ti–Ti distance is preferred. In the following,  $\Delta E$  values will refer to the most stable supercell A.

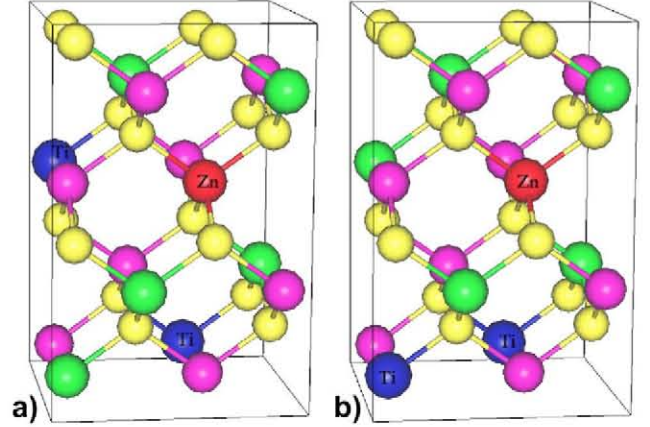
### 3.2. Two decomposition schemes using non-binary sulfides

We may also consider decomposition schemes using more complex compounds, such as  $\text{Cu}_{2/3}\text{TiS}_2$ , suggested in our previous study of Ti insertion in  $\text{CuGaS}_2$  [19], and others like  $\text{Cu}_4\text{TiS}_4$  [27] or  $\text{ZnGa}_2\text{S}_4$  [28], which are tetragonal chalcogenides as  $\text{CuGaS}_2$ .

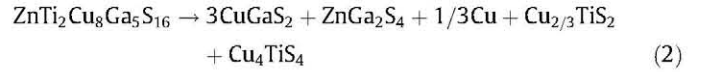
As an example of a decomposition path of reaction using the aforementioned compounds, we calculated the following reaction scheme,

**Table 1**  
Substituent distances in two  $\text{ZnTi}_2\text{Cu}_8\text{Ga}_5\text{S}_{16}$  supercells in Å, and corresponding  $\Delta E$  of Eq. (1) in eV (1 eV correspond to 96.51 kJ/mol).

	Zn–Ti	Ti–Ti	$\Delta E$
Supercell A	5.3	6.6	–0.43
Supercell B	6.6	5.3	–0.44

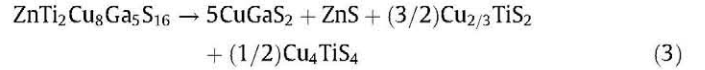


**Fig. 1.** Zn and Ti substitution in different Ga positions of  $\text{ZnTi}_2\text{Cu}_8\text{Ga}_5\text{S}_{16}$  where (a) corresponds to supercell A and (b) is labeled supercell B.



For the energy balance of reaction (2) the DFT calculations give  $\Delta E = -0.87$  eV, confirming that  $(\text{Zn}_y\text{Ti}_{1-y})_x\text{CuGa}_{1-x}\text{S}_2$  compounds are metastable and only exist under kinetically controlled conditions.

Another possible decomposition scheme has also been analyzed,



and the result of the calculation shows that this is even more spontaneous than the two previous ones:  $\Delta E = -1.30$  eV.

However, this energy difference is negative as that previously found for the  $\text{CuGaS}_2$ :Ti decomposition [19]. This  $\Delta E$  is also negative as that found for decomposition of IB material such as  $\text{In}_2\text{S}_3$ :V [29],  $-0.58$  eV/V atom, or for a doped semiconductor such as Mn substituting Ga in GaAs [30], and we have to remark that these two systems have been successfully synthesized [31,32].

Nevertheless, we have to point out that, even though the proposed reaction schemes in this work could constitute viable decomposition paths of  $\text{CuGaS}_2$ :Ti:Zn systems, other reaction proposals might make decomposition energy balances somewhat less negative, i.e. more favorable. The present results can be taken therefore as a lower limit for free energy balances.

### 3.3. Configurational entropy contribution to the free energy balance, of disordered compounds in reactions 2 and 3

We know that  $\text{Cu}_{2/3}\text{TiS}_2$ , a disordered compound, and the structure of our Zn- and Ti-substituted material (which if synthesized should also be disordered), would introduce configurational entropy to the whole system and, in order to show the possible effects on thermodynamical stability, we calculated the configurational entropy contribution following the standard equation,

$$S = -k[x_1 \ln(x_1) + (1 - x_1) \ln(1 - x_1)] \quad (4)$$

This configurational entropy formula can be applied, due to the presence of a disordered Cu in interstitial positions of  $\text{Cu}_{2/3}\text{TiS}_2$  and, in this case the  $x_1$  value in (4) correspond to  $x_1 = 2/3$ . In  $(\text{Zn}_y\text{Ti}_{1-y})_x\text{CuGa}_{1-x}\text{S}_2$ , on the other hand, random Ga positions are occupied by Zn and Ti atom substituents, and as a result of this argument the configurational entropy has a more complex equation,

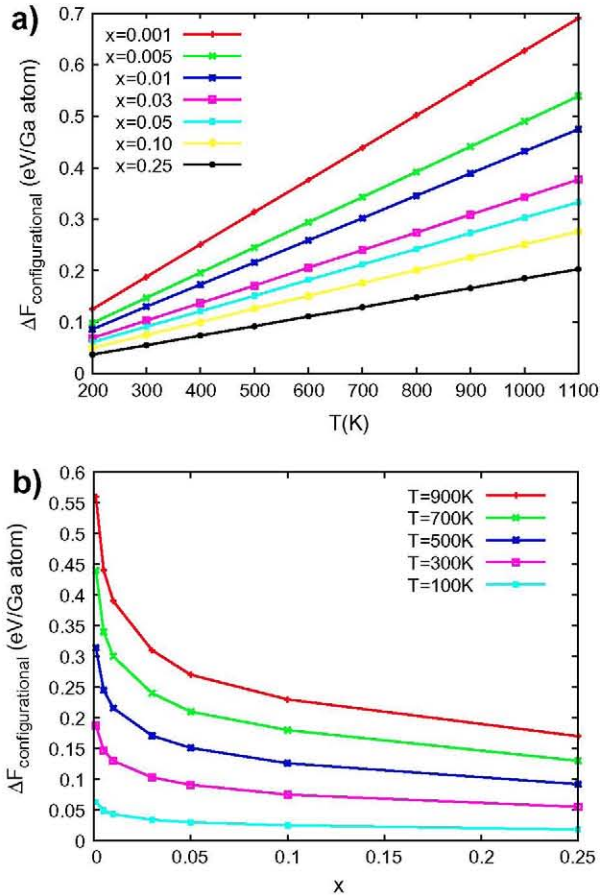
$$S = -k\{[x \ln(x) + (1 - x) \ln(1 - x)] + x[y \ln(y) + (1 - y) \ln(1 - y)]\} \quad (5)$$

In this equation the complexity of evaluating configurational entropy includes, not only the effect of substituents localized in random Ga positions, but also a competition between Zn and Ti atoms to occupy a minimal energy Ga site. In agreement with these two factors, and regarding  $(\text{Zn}_y\text{Ti}_{1-y})_x\text{CuGa}_{1-x}\text{S}_2$  stoichiometry, in Eq. (5) we evaluated  $x = 3/8$ , and  $y = 1/3$  of the total random positions in these systems.

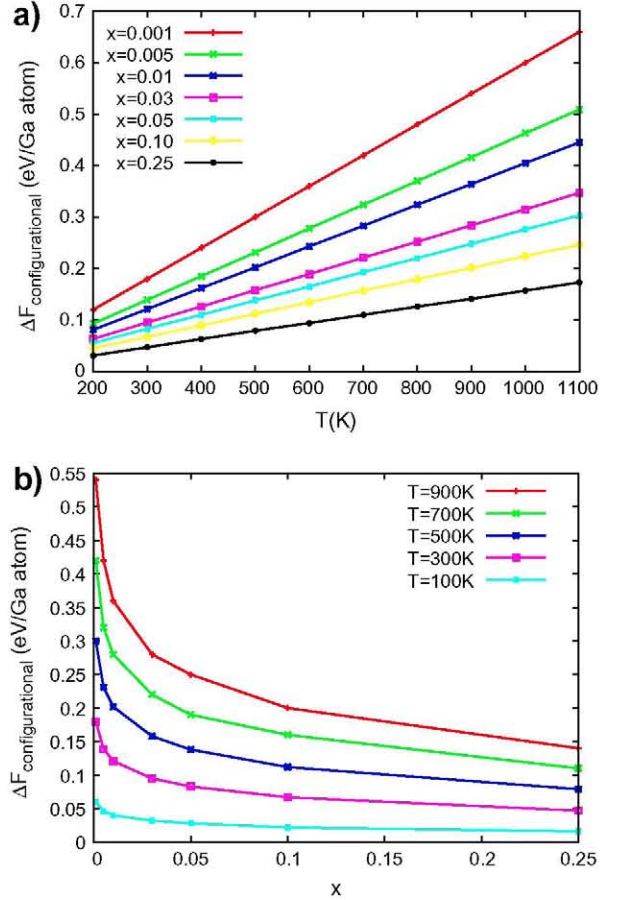
The Helmholtz free energy,  $\Delta F$ , calculation results of Eq. (2) in Fig. 2a show, the configurational entropy contribution to the free energy, when the temperature rises, and in Fig. 2b the configurational free energy,  $\Delta F_{\text{configurational}}$ , when  $x$  concentration of Zn and Ti atoms located at random positions rises, is shown.

Fig. 3 shows these results for Eq. (3), in which the configurational entropy contribution is smaller than that corresponding to Eq. (2).

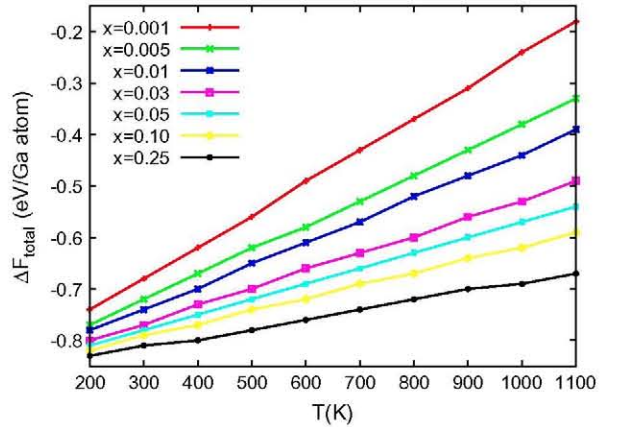
This leads us to infer that,  $\Delta F_{\text{configurational}}$  contribution reduces instability in the whole system of interest, when the temperature rises and also using low Ti and Zn concentrations. As was previously found for a  $\text{CuGaS}_2\text{:Ti}$  formation [19], vibrational entropy might also be involved here as another factor that contributes to instability reduction, but this factor is likely to be negligible in total free energy calculations. The resulting total free energy of Eq. (3),  $\Delta F_{\text{total}}$  (Fig. 4), which is the more negative one of the two proposed reaction scheme having disordered  $\text{Cu}_{2/3}\text{TiS}_2$ , shows that  $(\text{Zn}_y\text{Ti}_{1-y})_x\text{CuGa}_{1-x}\text{S}_2$  compounds are unstable, even at high temperatures.



**Fig. 2.** Thermodynamical parameters of reaction Eq. (2) (a)  $\Delta F_{\text{configurational}}$  at different  $x$  dilutions of Zn and Ti atoms substituting Ga atoms. (b)  $\Delta F_{\text{configurational}}$  at different temperatures  $T$ .



**Fig. 3.** Thermodynamical parameters of reaction Eq. (3) (a)  $\Delta F_{\text{configurational}}$  at different  $x$  dilutions of Zn and Ti atoms substituting Ga atoms. (b)  $\Delta F_{\text{configurational}}$  at different temperatures  $T$ .



**Fig. 4.**  $\Delta F_{\text{total}}$  of Eq. (3) at different  $x$  dilutions.

#### 4. Conclusions

Different proposals of spontaneous  $(\text{Zn}_y\text{Ti}_{1-y})_x\text{CuGa}_{1-x}\text{S}_2$  system decomposition, analyzed through the calculation of thermodynamical parameters, were considered. We observed that the reaction scheme of binary sulfides gives, the least negative  $\Delta E$  value of all the studied reaction. We can conclude that the decomposition scheme via non-binary sulfides, is an spontaneous process even at high temperatures and at low Zn and Ti concentrations.

However, the energy of reaction, considered per substituent atom, is smaller than that found for previous predicted IB materials, which have also been synthesized.

The results presented in this work show that it is thermodynamically unfavorable to obtain the Zn- and Ti-substituted CuGaS<sub>2</sub>, but this does not exclude that the material may be obtained using kinetically controlled methods.

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