



# Ionization energies of amphoteric-doped $\text{Cu}_2\text{ZnSnS}_4$ : Photovoltaic application



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## ABSTRACT

The substitution of Cu, Sn or Zn in the quaternary  $\text{Cu}_2\text{ZnSnS}_4$  semiconductor by impurities that introduce intermediate states in the energy bandgap could have important implications either for photovoltaic or spintronic applications. This allows more generation–recombination channels than for the host semiconductor. We explore and discuss this possibility by obtaining the ionization energies from total energy first-principles calculations. The three substitutions of Cu, Sn and Zn by impurities are analyzed. From these results we have found that several impurities have an amphoteric behavior with the donor and acceptor energies in the energy bandgap. In order to analyze the role of the ionization energies in both the radiative and non-radiative processes, the host energy bandgap and the acceptor and the donor energies have been obtained as a function of the inward and outward impurity-S displacements. We carried out the analysis for both the natural and synthetic CZTS. The results show that the ionization energies are similar, whereas the energy band gaps are different.

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## 1. Introduction

The quaternary  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) semiconductor has a variety of interesting physical properties and with a wide range of potential applications in device technology. Among these properties, the bandgap energy (1.4–1.6 eV) and high absorption coefficient ( $\alpha \sim 10^4 \text{ cm}^{-1}$ ) stand out. In addition CZTS have relatively abundant constituents, at a low-cost, and are non-toxic.

CZTS has been experimentally obtained and prepared by several methods: the sulfurization of sputtered [1–3] or evaporated [4] stacked films, spray method [5,6], sol–gel method [7], hydrazine deposition [8], and electrode deposition [9]. Their properties have been extensively studied both experimentally [10–18] and theoretically [19–26]. The experimental samples mainly crystallize in the kesterite structure, although a stannite-type structure can be formed through a two step process [27].

Although the kesterite- and the stannite-type structures do show any differences, it is rather difficult to distinguish one from the other experimentally as these structures have similar cell volumes and internal atomic positions. In addition, both structures are nearly degenerated energetically [21–23]. Therefore, it is likely that the two structures coexist in experimental samples [14,15] leading to phase mixing.

Even in undoped CZTS the cation substructure turns out to be intrinsically disordered. The exchange between Cu and Zn only

results in a minimal energy penalty and causes a significant lowering in symmetry [21–23]. The Cu/Zn disorder is difficult to measure experimentally since the atomic scattering form factors are proportional to the atomic number, and the Cu and Zn positions are not easy to differentiate. Therefore, although the CZTS structure without cation disorder has been predicted to be the most stable [21,22], possible a Cu/Zn cation disorder in experimental samples cannot be excluded [21–23].

Intrinsic disorder in CZTS, i.e. the presence of vacancies, anti-site atoms, etc., are what gives rise to the doping behavior [21–24]. The observed *p*-type conductivity comes mainly from the intrinsic  $\text{Cu}_{\text{Zn}}$  antisite with a relatively deeper acceptor level. In addition, the inter-mixing of host atoms with different oxidation states, such as the Sn/Zn cation disorder [24] can give rise to deeper levels in the energy band gap.

Therefore, systematic control of intrinsic defects in growing and non-equilibrium growth techniques may be required to avoid the formation of secondary phases by using kinetic energy barriers [20]. This would improve the crystallinity and the solar cell performance.

Because of the large variety of isolated intrinsic point defects and structures, the experimental and theoretical studies are currently focusing on the impact of structural modifications. However, there are few studies on the isolated substitutional impurities.

The insertion of intermediate states into the energy bandgap of a host semiconductor can modify the optoelectronic properties of the host. In particular, it could provide additional paths for optical transitions making these compounds interesting for optoelectronic

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applications. For example, solar-cell devices based on a material with three defined absorption bands in a simplified one-junction structure can increase the efficiency as regards single-gap solar cells [28]. The absorption of photons is more efficient than in conventional single-gap cells because the absorption of low energy photons causes transitions from the valence band (VB) to the partially filled intermediate band (IB) and from there to the conduction band (CB). These transitions generate additional carriers to those generated for the usual process through photon absorption, promoting electrons from the VB to the CB.

Some host semiconductors and impurities have been analyzed in order to insert intermediate states into the energy band gap: doped chalcopyrites [29–32], II–VI compound doped with isoelectronic oxygen impurities, Cr-doped zinc chalcogenides [33,34], etc. In particular, the isoelectronic doping with oxygen of some II–VI semiconductors has shown that oxygen gives rise to deep traps [35–38] in which carriers recombine radiatively [39–43]. Cr-doped zinc chalcogenides [44–46] have been used as broadly tunable continuous wave lasers with negligible non-radiative decay at room temperature. Cr-doped CZTS present several recombination paths depending on the IB occupation and on the cation substitution [26].

However, the influence of the impurities on the lattice dynamic has not attracted as much attention, despite its importance in radiative and non-radiative processes. For example, in the interaction of impurity electrons with light, the Coulomb field of the charged impurity center displaces the nearest neighboring atoms via a breathing mode, which may affect its properties. When the impurity acceptor energy crosses the CB because of the breathing mode, an electron in the CB can be captured non-radiatively by the impurity (Fig. 1). Similarly, when the impurity acceptor energy crosses the VB, an electron in the impurity can be captured non-radiatively by the VB. In this way it closes the cycle of non-radiative recombination from an electron in the CB to an electron in the VB [47,48].

In addition, the energetic positions of the donor ( $e_D$ ) and acceptor ( $e_A$ ) ionization energies allow an easy characterization of the impurity as a donor ( $e_D$  lies in the gap but  $e_A$  does not) an acceptor ( $e_A$  lies in the gap but  $e_D$  does not) or with amphoteric behavior (both  $e_D$  and  $e_A$  i.e., the lower and upper Hubbard bands, are found within the gap). This behavior can be very important for the radiative and non-radiative transitions [49,50], as well as in the application of these compounds for optoelectronic devices. It could have a negative effect because these deep localized defect states at low concentration act as effective non-radiative recombination centers as previously mentioned. However, at high concentration the defect states lead to bands. If the bands corresponding to the ionization energies overlap, there is the possibility of forming a partially filled IB. For a partially filled IB the donor and acceptor energies coincide with the Fermi energy, i.e. the IB has amphoteric behavior. On the other hand, the limits of the IB for a larger impurity concen-

tration would lead to two energy levels for lower impurity concentration via a metal–insulator transition. In order to form a band, the impurity concentration should exceed the threshold set by the Mott's transition ( $\sim 10^{19} \text{ cm}^{-3}$  [49]). Then, the modification of the charge density around the impurity as consequence of the electronic capture of the non-radiative mechanism is redistributed among all the impurities [49] or with the host semiconductor [50], and the negative non-radiative recombination would be decreased. Experimental evidence supporting this theory was reported by measuring the lifetime of titanium implanted silicon wafers [51].

The technological importance of CZTS as an absorbent material for low-cost thin-film solar cells together to the possible additional improvement in their optoelectronic properties for inserting states into the energy band gap leads us to explore the effect of the substitution of first row transition-metal atoms at cation substitutional CZTS sites. After a general screening, V, Cr and Ir have been identified as interesting impurity candidates, i.e. with amphoteric behavior at the nuclear equilibrium configuration, to obtain intermediate states within the main gap of the modified CZTS. In order to analyze the effect on the non-radiative processes (Fig. 1), the ionization energies have been obtained at the nuclear equilibrium configurations corresponding to a breathing mode.

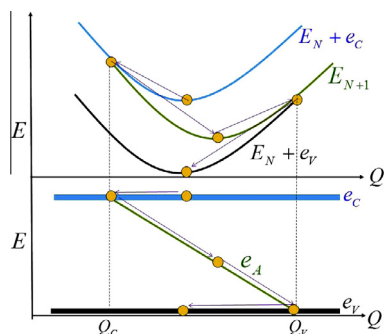
The results in this work refer to ideal stoichiometric CZTS lattice structures, in the sense that no intrinsic point defects nor combinations of them other than the specific substitution proposed have been allowed. It is assumed that the substitutional impurities have no interaction with other intrinsic point defects. Hence, the substitutional impurity results also add to the results of isolated point defects and complexes. It is expected that these results may guide future experimental work in CZTS compounds for optoelectronic applications. Even if some impurities do not have attractive optoelectronic properties, they could have potential applications in spintronic devices. To achieve this objective, firstly, the position in energy of the donor and the acceptor ionization levels will be determined for both the natural and synthetic CZTS, comparing the results with the literature. Secondly, the evolution of the ionization levels with respect to the M–S distance will be obtained. From these results, the relative influence of radiative and non-radiative processes will be analyzed.

## 2. Calculations

Defect levels are usually characterized using a single-particle picture. But these single-particle eigenvalues do not account for the excitation aspect inherent in the ionization or recharging of the defect. Therefore, in order to obtain the donor ( $e_D$ ) and acceptor ( $e_A$ ) ionization energies we used total-energy differences [52,53] instead of single-particle energies.

The formation energy needed to incorporate one positive (negatively) charged M atom into place B ( $M_B$  substitution) in the host H semiconductor, and thus form a donor (acceptor), is  $\Delta H_f(M_B^\pm) = E(M_B^\pm) - E_H + \mu_B - \mu_M \pm E_F$ , where  $E(M_B^\pm)$  denotes the total incorporation energy,  $E_H$  is the total energy of the host,  $E_F$  is the Fermi energy, and  $\mu_B$  and  $\mu_M$  denote the chemical potentials of the B and M. These chemical potentials represent the energy of the reservoirs with which atoms are being exchanged. Therefore the incorporation will be favored if more M atoms are available (higher  $\mu_M$ ), if more B places are available (lower  $\mu_B$ ), and if the position of  $E_F$  is lower (higher). The ionization energies correspond to the value of  $E_F$  at which the impurity or defect changes from  $M_B^+$  to  $M_B$ , i.e.  $e_A = E(M_B^-) - E(M_B)$  and  $e_D = E(M_B) - E(M_B^+)$ . For the host semiconductor, when B = M, the acceptor and donor energies correspond with the CB and VB edge energies, i.e.  $e_c$  and  $e_v$ , and the gap is  $E_g = e_c - e_v = E(M_M^-) - 2E_H + E(M_M^+)$ .

In order to obtain the total energies needed to obtain the ionization levels, we use the density-functional theory. The standard Kohn–Sham [54] equations are solved self-consistently [55]. The standard Troullier–Martins [56] pseudopotential for the core orbitals is adopted and expressed in the Kleinman–Bylander [57] factorization. The valence wave functions are expanded in a localized pseudoatomic orbital basis set [58]. The pseudopotentials used to describe the exchange correlation energy were carried out with the generalized gradient approximation (GGA) from Perdew, Burke, and Ernzerhof [59]. All calculations were made with periodic boundary conditions and spin polarization.



**Fig. 1.** Schematic representation of the non-radiative recombination with respect to the configuration coordinate  $Q$ .  $Q_c$  ( $Q_v$ ) is the crossing point of the ionization  $e_A$  and CB (VB) edge  $e_c$  ( $e_v$ ) energies.

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