AIP | Applied Physics Letters

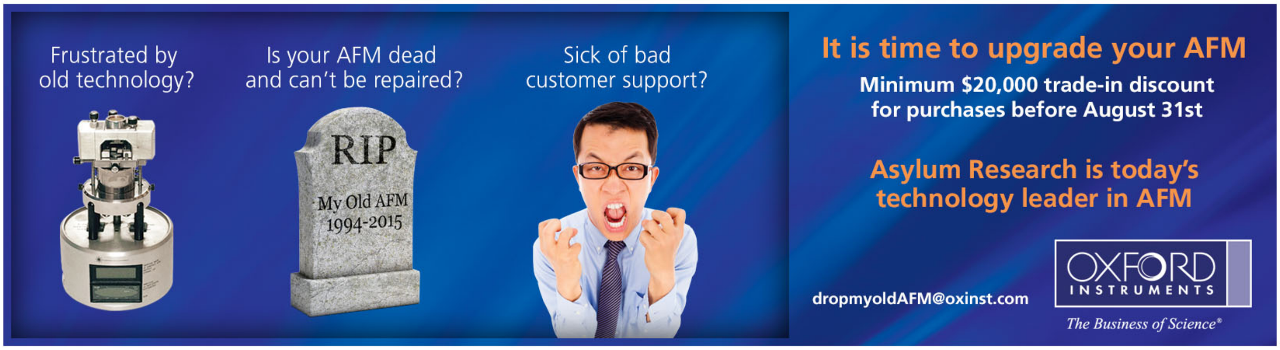
# The electronic consequences of multivalent elements in inorganic solar absorbers: Multivalency of Sn in Cu 2 ZnSnS 4

Koushik Biswas, Stephan Lany, and Alex Zunger

Citation: Applied Physics Letters **96**, 201902 (2010); doi: 10.1063/1.3427433
View online: http://dx.doi.org/10.1063/1.3427433
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/96/20?ver=pdfcov
Published by the AIP Publishing

---

---



APPLIED PHYSICS LETTERS **96**, 201902 (2010)

# The electronic consequences of multivalent elements in inorganic solar absorbers: Multivalency of Sn in $Cu_2ZnSnS_4$

Koushik Biswas, Stephan Lany, and Alex Zunger[a)]
*National Renewable Energy Laboratory, Golden, Colorado 80401, USA*

(Received 12 March 2010; accepted 18 April 2010; published online 18 May 2010)

Multivalent transition metal impurities in semiconductors are known to create deep levels inside the band gap that are associated with changes in the oxidation state. Some emerging functional semiconductor materials now contain multivalent elements not just as impurities, but as part of their structural skeleton ("multivalent semiconductors"). This raises the possibility that the performance of such materials may be affected by those skeleton elements transitioning from one oxidation state to another, in response to charge-altering perturbations such as illumination or doping. Here we address the correlation between multivalency and the electronic properties of these new semiconductor materials. © *2010 American Institute of Physics*. [doi:10.1063/1.3427433]

Main-group elements in the *upper rows* of the periodic table generally utilize all of their outer *s* and *p* valence electrons in forming chemical bonds in solid state compounds, thus, manifesting only in a single, well-defined valence state. This is the case for many divalent (Mg, Ca, Zn, and Cd), trivalent (B, Al, and Ga), or group-IV elements (C and Si).[1] On the other hand, the elements in the *bottom rows* are subjected to relativistic contraction of the outer *s* orbitals,[2] and often form bonds only with their *p* electrons, while accommodating two electrons in a nonbonding $s^2$ state (sometimes called "lone-pair"). The resulting change in valence causes multivalent behavior, as exhibited, for example, by the +I/+III states of In in $InCl/InCl_3$, by the +II/+IV states of Sn in $SnO/SnO_2$, or by the simultaneous existence of the +III/+V states of Bi in $BaBiO_3$.[3] Similarly, transition metals can assume a range of different valence and oxidation states by accommodating a variable number of electrons in (formally) nonbonding *d*-orbitals.[4,5] Here, examples include the +II/+III states of iron ($FeO/Fe_2O_3$) or the +II/+IV states of manganese ($MnO/MnO_2$).

When such multivalent elements are used as *dopant impurities* in semiconductors or insulators, it is not always obvious how many of their valence electrons are available for charge exchange. For example, would Sn doped on the divalent Zn or Mg site donate two electrons (as expected for valence +IV element) or none (as expected for a valence +II element). It is indeed possible that a multivalent impurity would transit from one oxidation state to the other by changing its so-called *defect charge state* and that the transition would occur as a deep level inside the band gap of the material. Such deep levels that are associated with a change in the oxidation state are well known to occur for multivalent transition metal impurities, e.g., Fe(+II)/Fe(+III), in semiconductors,[6,7] which deteriorate the electronic properties by forming recombination centers and carrier traps, therefore necessitating a high level of purification, e.g., of Si for technological applications.[8]

While these questions regarding the effect of multivalency were posed above in the context of such elements appearing as *dilute impurities*, some emerging functional semiconductor materials now contain multivalent elements as part of their *skeletal structure*. One example of such a "multivalent semiconductor" is the $Cu_2ZnSnS_4$ (CZTS) photovoltaic (PV) material,[9] that has recently drawn attention due to the desire to avoid the expensive In in the thin-film absorber $Cu(In,Ga)Se_2$.[10] Thus, the presence of the multivalent element Sn in CZTS raises the question whether functionality-deteriorating deep levels are genetically encoded in the composition of this semiconductor. This is a rather general problem, as numerous inorganic absorbers that are being considered for PV applications contain multivalent elements as part of their skeleton.[11]

In CZTS one can expect that Sn can exist not only on its crystallographic lattice location in the kesterite structure, but also in some fraction on the Zn or Cu lattice sites. This expectation is corroborated by the known existence of different structural modifications of $Cu_2ZnSnS_4$ with distinct ordering of the metal atoms,[12] and by the fact that in the related ternary chalcopyrites such as $CuInSe_2$, antisite substitution among cations, e.g., In-on-Cu ($In_{Cu}$), costs little energy.[13] Thus, the six possibilities due to two possible oxidation states of Sn (+II and +IV) and three different lattice sites provide a rich ground to illustrate the range of electronic behaviors that can be caused by multivalent constituents of a semiconductor. Employing first-principles total energy calculations, we find that Sn displays three distinct behaviors, depending just on its lattice location. (i) It assumes only the +IV oxidation state if located on its native (Sn) site, (ii) substituting for Cu, it assumes only the +II state, and (iii) substituting for Zn, it can assume both the +IV and the +II states depending on the position of the Fermi level in the gap. Indeed, situation (iii) implies that in the presence of an external perturbation, for example photoexcitation in a solar cell device, the Sn atom can change from +IV to +II oxidation by trapping a pair of electrons that will reside in the localized deep gap level instead of occupying the conduction band. This work underscores the electronic consequences of the existence of multivalent elements in semiconductor materials, and the importance of predicting the charge transition levels (inside or outside band gap) due to different possible oxidation states.

In order to quantitatively characterize the multivalent behavior of Sn in CZTS, we performed density functional theory (DFT) supercell calculations (64 atoms), using the projector augmented wave implementation of the VASP code,[14] the exchange-correlation potential of Ref. 15, and

---

[a)] Electronic mail: alex.zunger@nrel.gov.

TABLE I. Nearest neighbor distances $d_{\text{Sn-S}}$ of Sn in $Cu_2ZnSnS_4$ in its two oxidation states.

| | Sn(+IV) | Sn(+II) |
|---|---|---|
| Native Sn-site | $Sn_{Sn}{}^{0}$:2.43 Å | $Sn_{Sn}{}^{2-}$:2.71 Å |
| Cu-site | $Sn_{Cu}{}^{3+}$:2.47 Å | $Sn_{Cu}{}^{1+}$:2.73 Å |
| Zn-site | $Sn_{Zn}{}^{2+}$:2.47 Å | $Sn_{Zn}{}^{0}$:2.72 Å |

on-site Coulomb $U$ energies[16] of 5 eV and 6 eV for the Cu $d$ and Zn $d$ shells, respectively. Band gap and finite supercell corrections were applied as described in Ref. 17. Additionally, we performed self-consistently band gap corrected calculations employing the nonlocal external potentials (NLEP) (Ref. 18) and hybrid-DFT.[19] The presence of potentially detrimental deep levels is addressed by calculating the transition levels $\varepsilon(q/q')$ (see Ref. 17 for details) between the different charge states $q$ and $q'$, which correspond to a respective change in the number of electrons.

When we add (remove) an electron to a given system, like a molecule or a solid, the conventional chemistry rules[20] demand that the oxidation state of one element is reduced (increased) by unity. In a semiconductor, however, these transitions can occur within the continuum of the host crystal bands (outside of the band gap), in that case the electrons or holes occupy the perfectly delocalized state of the CBM or of the VBM. Thus, there is an ambiguity in the assignment of the oxidation state because carriers residing in extended bands cannot be anchored to distinct atoms. In general, this ambiguity needs to be resolved by quantitative evaluation,[7,21,22] which we now address for the three lattice locations that are available for Sn.

*The native* Sn-*on*-Sn ($Sn_{Sn}$) *site*. In the absence of additional carriers (electron or holes), Sn on its native site exists in the +IV oxidation state in $Cu_2ZnSnS_4$. Since, the +III state of Sn is not stable, we have to add two extra electrons to open the possibility of a change in oxidation from +IV to +II, which would proceed by capturing the electrons into the lone pair state of Sn,

$$\text{Sn}(+\text{IV})_{\text{Sn}}{}^{0} + 2\text{e} \rightarrow \text{Sn}(+\text{II})_{\text{Sn}}{}^{2-}. \tag{1}$$

The substitution of the divalent Sn(+II) for the native Sn(+IV) state now accounts for a double acceptor having a 2− charge state and the above reaction corresponds to a transition from 0 to 2− charge state, $\varepsilon(0/2-)$. *Thus, unlike conventional semiconductors, multivalent semiconductors have the intrinsic capability to create electrically active centers, even in the absence of defects.*

How does a change in the Sn oxidation state reveal itself? The first indication is a local lattice relaxation and a large change in the calculated nearest neighbor (NN) distance between Sn and S, as shown in Table I. From an inorganic chemistry point of view, this change is typically interpreted as a change in ionic radius of the Sn based on the assumption that adding two extra electrons increases its radius.[23] Finding that a change in oxidation state of transition metal impurities in semiconductors or insulators is not associated with a local charge accumulation of comparable magnitude, Raebiger *et al.*[7] instead interpreted the increased bond length as arising from the occupation of an *antibonding* state. As illustrated in Fig. 1(a), the lone pair state of Sn(+II) also results from an antibonding interaction of atomic orbitals, i.e., that of Sn $5s$ and S $3p$. Thus, the increased bond length in conjunction with the occupation of the lone pair state, being localized at the Sn atom and its anion neighbors [see Fig. 1(b)], is a clear signature of the Sn(+II) state.

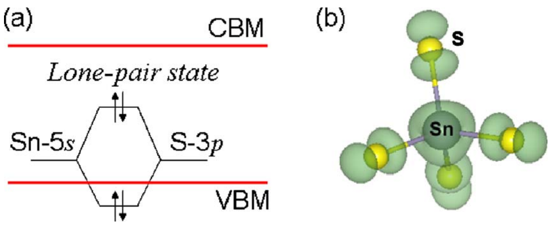


FIG. 1. (Color online) (a) Schematic illustration of the antibonding interaction of atomic orbitals (Sn $5s$/S $3p$) forming the lone pair state of Sn(+II) in CZTS. (b) Isosurface charge density plot of the lone pair state.

The next question to address is whether the transition from Sn(+IV)→Sn(+II) occurs inside or outside the host crystal band gap. If this transition [see Eq. (1)] occurs *inside* the gap, then electrons introduced by doping, or by photoexcitation, would not travel in the free-particle like manner, but would rather occupy the localized state shown in Fig. 1(b), which corresponds to a pair of self-trapped electrons. For solar cells, where one wants to deliver the photoexcited carriers to an external circuit, such self-trapping is detrimental. It is much more desirable that the Sn(+IV)→Sn(+II) transition level occurs *outside* the gap, in that case the free-electron state at the CBM is energetically favorable. Figure 2 shows that the latter situation is present in CZTS, where the double acceptor (0/2−) transition from Sn(+IV) to Sn(+II) occurs when the Fermi level is inside the host conduction band. We find a relatively small separation of the (+IV/+II) transition from the CBM of only 0.2 eV. Indeed, there are examples of other materials where the self-trapped state is energetically inside the band gap. For example, it was recently found in rutile $TiO_2$ that the introduction of an electron via a fluorine donor causes one Ti atom in the neighborhood to change its oxidation state from +IV→+III (single self-trapped electron).[24] Another example is given by $BaBiO_3$,[3,25] where holes self-trap by changing a Bi(+III) site into a Bi(+V) state. Notably, the polaronic Bi(+V) state ob-

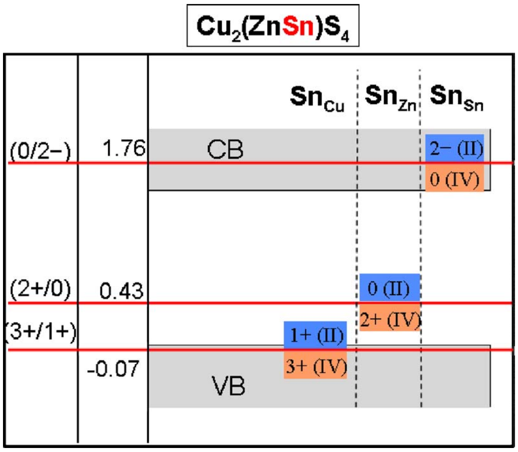


FIG. 2. (Color online) The calculated energetic positions (in electron volt) of the Sn(+IV)→Sn(+II) transitions (shown by horizontal lines) relative to the valence band maximum of CZTS, shown for the different cation sites that can be occupied by Sn. Each Sn(+IV)→Sn(+II) transition also corresponds to charge transitions, viz., $Sn_{Cu}(3+/1+)$, $Sn_{Zn}(2+/0)$, and $Sn_{Sn}(0/2-)$ that are also shown.

served in Ref. 25 has very similar characteristics as the Sn(+II) state shown in Fig. 1(b), which is because it results from a similar atomic orbital interaction as the one shown in Fig. 1(a) [note, however, that the polaronic Bi(+V) state hosts a pair of holes, whereas the Sn(+II) state hosts a pair of electrons]. The close competition between bandlike and polaronic behaviors observed here in CZTS is a reminder that carrier self-trapping is generally an important mechanism in multivalent semiconductors and deserves particular attention when such materials are considered for technological applications.

*The native* Sn-*on*-Cu ($\mathrm{Sn_{Cu}}$) *site*. Being a group-IV element one might expect Sn to act as a triple-donor on the site of the group-Ib element Cu ($\mathrm{Sn_{Cu}}^{3+}$). We however find, that the Sn(+IV) → Sn(+II) transition of Sn lies below the VBM, as shown in Fig. 2, meaning that on the Cu site, Sn exists exclusively in the +II oxidation state. Even under *p*-type conditions (Fermi Energy, $E_\mathrm{F}$ low in the gap), it is energetically favorable when holes stay at the VBM, rather than oxidizing $\mathrm{Sn_{Cu}}$ into the +IV state. Hence, $\mathrm{Sn_{Cu}}$ can be characterized as the case of a divalent element substituting for the monovalent element Cu, thereby forming a *single*-donor having a shallow conduction-band derived state as known from conventional semiconductor models.[26] This stable Sn(+II) is again characterized by the larger Sn–S bond length (see Table I).

*The native* Sn-*on*-Zn ($\mathrm{Sn_{Zn}}$) *site*. Depending on whether Sn assumes the +IV or the +II state, when occupying the Zn site, one expects that it forms either a double-donor ($\mathrm{Sn_{Zn}}^{2+}$) or an isoelectronic center ($\mathrm{Sn_{Zn}}^{0}$). Unlike the cases discussed above, we find that the Sn(+IV) → Sn(+II) transition does occur inside the gap for $\mathrm{Sn_{Zn}}$, which gives rise to a deep (2+/0) charge transition, as shown in Fig. 2. In contrast to the behavior of conventional shallow levels in semiconductors,[26] this transition is associated with large structural relaxations (see Table I), and occurs far away from the conduction band edge. (Note that a group-IV element like Si, which has a much smaller propensity toward the +II oxidation state, would have closely spaced first and second donor ionization energies near the CBM). The existence of such an electronic transition deep inside the gap presents a great concern for the PV properties, since it can lead to recombination of photo-excited electrons and holes.[27] Specifically, the change in oxidation state of multivalent Sn can cause nonradiative recombination of carriers by way of the cycle

$$\mathrm{Sn_{Zn}}^{0} + 2h \rightarrow \mathrm{Sn_{Zn}}^{2+} \quad \text{and} \quad \mathrm{Sn_{Zn}}^{2+} + 2e \rightarrow \mathrm{Sn_{Zn}}^{0}. \tag{2}$$

Thus, CZTS solar cell absorbers should be grown under conditions that minimize the formation of $\mathrm{Sn_{Zn}}$ defect centers. This may be achieved through consideration of the appropriate "doping principles"[13,28] for CZTS.

We note that our present result of a deep level for $\mathrm{Sn_{Zn}}$ differs from a recent theoretical work,[29] where the donor levels of $\mathrm{Sn_{Zn}}$ were placed close to the CBM, as they appear before a correction of the band gap. In order to clarify the dependence of the $\mathrm{Sn_{Zn}}$ donor levels on the magnitude of the band gap, we performed additional self-consistently band gap corrected calculations. Employing the NLEP method[18] and hybrid-DFT,[19] we obtain the $\varepsilon(2+/0)$ level at 0.52 eV and 0.79 eV above the VBM, respectively, i.e., deep inside the $E_\mathrm{g}=1.5$ eV band gap of CZTS. The large lattice relaxations associated with the change in the oxidation state are similar to those given in Table I. Thus, these gap-corrected methods confirm that $\mathrm{Sn_{Zn}}$ is a deep recombination center, and not a shallow donor.

Summarizing the different behaviors of the multivalent element Sn in the PV semiconductor $\mathrm{Cu_2ZnSnS_4}$, we find that Sn assumes only the +IV oxidation state on its native site ($\mathrm{Sn_{Sn}}$), only the +II state on the Cu site ($\mathrm{Sn_{Cu}}$), but on the Zn site, it creates a detrimental deep level due to a +IV → +II transition inside the band gap. This finding highlights the correlation between changes in an atomic oxidation state and the presence of charge transition levels inside the band gap. The occurrence of detrimental deep levels due to different possible oxidation states is a potentially prominent feature in multivalent semiconductors and deserves particular attention when such materials are considered for technological applications.

This work was funded by the U.S. Department of Energy, Office of Energy Efficiency, and Renewable Energy, under Contract No. DE-AC36-08GO28308 to NREL. The use of facilities at the National Energy Research Scientific Computing Center is gratefully acknowledged.

[1] O. Kubaschewski and C. B. Alcock, *Metallurgical Thermochemistry*, 5th ed. (Pergamon, New York, 1979); A. Zunger, Phys. Rev. B **24**, 4372 (1981).

[2] P. Pyykkö, Chem. Rev. **88**, 563 (1988).

[3] D. E. Cox and A. W. Sleight, Solid State Commun. **19**, 969 (1976).

[4] A. F. Wells, *Structural Inorganic Chemistry* (Clarendon, Oxford, 1975).

[5] A. Zunger, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1986), Vol. 39, pp. 275–464.

[6] V. A. Singh and A. Zunger, Phys. Rev. B **31**, 3729 (1985).

[7] H. Raebiger, S. Lany, and A. Zunger, Nature (London) **453**, 763 (2008).

[8] E. R. Weber, Appl. Phys. A: Mater. Sci. Process. **30**, 1 (1983).

[9] K. Ito and T. Nakazawa, Jpn. J. Appl. Phys., Part 1 **27**, 2094 (1988); H. Katagiri, K. Jimbo, W. S. Maw, K. Oishi, M. Yamazaki, H. Araki, and A. Takeuchi, Thin Solid Films **517**, 2455 (2009).

[10] I. Repins, M. A. Contreras, B. Egaas, C. DeHart, J. Scharf, C. L. Perkins, B. To, and R. Noufi, Prog. Photovoltaics **16**, 235 (2008).

[11] C. Wadia, A. P. Alivisatos, and D. M. Kammen, Environ. Sci. Technol. **43**, 2072 (2009).

[12] J. Paier, R. Asahi, A. Nagoya, and G. Kresse, Phys. Rev. B **79**, 115126 (2009).

[13] C. Persson, Y.-J. Zhao, S. Lany, and A. Zunger, Phys. Rev. B **72**, 035211 (2005).

[14] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999); J. Paier, R. Hirschl, M. Marsman, and G. Kresse, J. Chem. Phys. **122**, 234102 (2005).

[15] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[16] A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, Phys. Rev. B **52**, R5467 (1995).

[17] S. Lany and A. Zunger, Phys. Rev. B **78**, 235104 (2008).

[18] S. Lany, H. Raebiger, and A. Zunger, Phys. Rev. B **77**, 241201(R) (2008).

[19] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003).

[20] http://goldbook.iupac.org/O04365.html.

[21] R. Resta, Nature (London) **453**, 735 (2008).

[22] H. Raebiger, S. Lang, R. Resta, and A. Zunger, *Nature Precedings*, hdl:10101/npre.2009.4012.1: Posted 27 Nov 2009.

[23] R. D. Shannon, Acta Crystallogr. **A32**, 751 (1976); R. D. Shannon and C. T. Prewitt, Acta Crystallogr. **B25**, 925 (1969).

[24] S. Yang and L. E. Halliburton, Phys. Rev. B **81**, 035204 (2010).

[25] C. Franchini, G. Kresse, and R. Podloucky, Phys. Rev. Lett. **102**, 256402 (2009).

[26] C. Kittel and A. H. Mitchell, Phys. Rev. **96**, 1488 (1954).

[27] S. Lany and A. Zunger, J. Appl. Phys. **100**, 113725 (2006).

[28] A. Zunger, Appl. Phys. Lett. **83**, 57 (2003).

[29] S. Chen, X. G. Gong, A. Walsh, and S.-H. Wei, Appl. Phys. Lett. **96**, 021902 (2010).