Inverse Design of High Absorption Thin-Film Photovoltaic Materials

1. Introduction

Enhancement of photocarrier collection by aiding drift through a very thin inorganic absorber film represents a promising route to new, high-efficiency photovoltaic (PV) devices.[1] The realization of such devices is largely predicated on the availability of materials that exhibit strong absorption across the solar spectrum with an abrupt onset at the band gap. Such materials have direct band gaps, but not all direct-band-gap materials are strong absorbers. Currently, ternary I-III-VI$_2$ chalcogenides, typified by CuInSe$_2$, are among the strong direct band-gap absorbers known, establishing the basis for a commercial thin-film solar cell technology. While overall absorption is strong, the measured weak onset absorption near the band gap necessitates the use of rather thick films (~1.5 cationanddesignoftheneededmaterialsrequires an approach beyond the classic one-dimensional Shockley-Queisser criterion,

[4] which selects good PV absorbers solely on the basis of their band gap (direct or indirect) being in the range of 1.0–1.5 eV. This simple one-dimensional metric does not represent material-dependent optical absorption spectra and related radiative/nonradiative recombination losses, which are essential for evaluating a semiconductor as a thin-film absorber. Recently, we have proposed a new and improved

multi-dimensional metric, the so-called Spectroscopic Limited Maximum Efficiency (SLME), for the initial screening of candidate thin-film PV absorbers.[5] While neglecting extrinsic factors (such as dopability, metal contacts, etc.) in the initial stage of material screening, this metric depends explicitly on the calculated absorption spectrum and thickness of the thin-film absorber. It also accounts for the different types of optical transitions, i.e., direct allowed, direct forbidden, and indirect, near the absorption threshold. Our application of SLME[5] to ~300 ternary I-III-VI chalcogenide materials has revealed tens of candidates with SLME values comparable or higher than that of CuInSe$_2$. We also use SLME to identify the underlying phys-

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$^{1+}$, the compound exhibits higher SLME values than those containing high-valence Tl^{3+} element. Whereas in CuInSe$_2$ with its high-valence In the (broadly dispersed) -character is at ; CB , materials with low-valence Tl exhibit a considerable Tl -like orbital density ; B and relatively flat -like bands ; CB . Since Cu -like orbitals (high DOS) contribute mainly to the states near VBM, both $\rightarrow$ and $\rightarrow$ transitions contribute to an enhanced absorption strength in the Cu-Tl^{1+}-VI compounds. Hence, Cu

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chalcogenides containing low-valence ions with an s^2 electron configuration appear to be promising systems for realization of very high absorption coefficients.

Having understood this principle, we can proceed to materials that embody this principle without the toxic and scarce elements Tl and In. We have chosen to consider the system Cu-V-VI (V = P, As, Sb, Bi; VI = S, Se). Group V elements adopt two common oxidation states, namely 5+ and 3+, with valence electron configurations s^0p^0 and s^2p^0, respectively, mirroring the two configurations of the Group III elements (e.g., Tl^{3+} s^0p^0 and Tl^{1+} s^2p^0). Compounds with high Cu/V^{5+} ratios are known, providing an opportunity to examine the effects of high DOS d-orbital contributions near the CBM on the absorption strength. In addition, the low-valence compounds can be studied with respect to the enhancement of absorption through the s-like VBM to p-like contributions near the CBM.

To this end, we have calculated the band gaps, absorption spectra and SLME values for the 30 Cu-V-VI materials listed in Table S1 that have been reported in the inorganic crystal structure database (ICSD).[7] We identify important trends in absorption strength on the basis of projected s, p DOS near the band edges to examine our initial design assumptions. We have also used the ensuing theory-derived design principles to guide initial experiments, allowing us to propose candidate, very thin absorber films for enhancing PV efficiency. The process opens expanded opportunities beyond the Shockley-Queisser construct for identifying new absorbers and motivating their development.

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$$l^{V}_{DOS}(\ ) = \frac{1}{\ } \int_{E_{v-}}^{E_{v}} \ _{l}(E)\,dE,\ \text{or}\ l^{c}_{DOS}(\ ) = \frac{1}{\ } \int_{E_{c}}^{E_{c}+} \ _{l}(E)\,dE$$

(1)

where $_{l}(E) = \sum \ _{l}(E)$ where $_{l}(E)$ is the $\cdot$-projected DOS of atom α which runs over all atoms of interest in the unit cell of volume Ω. We choose $\eta = 2.0$ eV, which effectively covers solar photon absorption for a material with $E_{.}$ near 1 eV. The calculated $,$ integrated DOS contributions of group V atoms near the band edges of 19 compounds are summarized in

dipole-allowed Cu $\rightarrow$ V and V $\rightarrow$ V transitions should contribute to a strong absorption. The less dispersive band character near both the VBM and CBM thus contributes to a high joint DOS, making the low-valence Cu-V-VI materials exceptionally strong absorbers.

These considerations, however, must be tempered by the nature of the band gap, i.e., direct vs. indirect. For example, $CuSb^{3+}S_2$ is an indirect band gap material with a very small Δ value (i.e., the energy difference between indirect gap and dipole-allowed direct gap $\Delta = 0.05$ eV). As seen from Figure 1(a), in comparison with the direct-gap materials $Cu_3Sb^{5+}S_4$ and $CuInSe_2$, $CuSbS_2$ has stronger absorption strength for photons with $\upsilon > E_g + \delta$, where $\delta \approx 0$. For Cu_3SbS_3, however, where Sb is also in the low-valence state, the absorption becomes stronger than $CuInSe_2$ and Cu_3SbS_4 only when $\upsilon > E_g + \delta$ with $\delta > 0.7$ eV. Here, a larger difference ($\Delta = 0.13$ eV) exists between the indirect gap and the dipole-allowed direct gap. This larger Δ means that the absorption coefficient only begins to rise rapidly at an energy near the direct optical transition above E_g. The optical absorption near threshold for a material with large Δ will generally be much weaker than that in a material with very small (or zero) Δ.

6. Spectroscopic Limited Maximum Efficiency Results and Their Correlation to Absorption Strength

A strong optical absorption above a suitable E_g is a necessary condition for realizing highly efficient, thin-film PV performance.[14] Calculated SLME values at a film thickness of 200 nm for 15 Cu-V-VI materials with E_g between 0.5 and 2.5 eV are shown in Figure 3a. Seven of the compounds, namely, $CuSbS_2$, $CuSbSe_2$, Cu_3SbS_4, Cu_3PSe_4, Cu_3AsSe_4, $Cu_6As_4S_9$, and $CuBiS_2$, are found to have comparable or higher SLME ($>20\%$) than $CuInSe_2$. The modeled film thickness is approximately eight times thinner than that commonly found in $CuInSe_2$-type PV cells. As seen in Figure 3b, the SLME metric provides a unique assessment of efficiency as a function of film thickness. Clearly, those materials with high absorption coefficients and rapid onsets near threshold, *., Figure 1 and Figure 3, exhibit the higher efficiencies. They provide unique opportunities for examining cell performance with absorber layers much thinner than those commonly used in current thin-film PV technologies.

7. Comparison of Theory and Experiment

Figure 4a summarizes our calculated band gaps (E_g) for 19 Cu-V-VI compounds distributed across six distinct compositions, deviating by an average of 0.15 eV from experimentally determined values (good agreement). Figure 4b shows the comparison of absorption coefficients between theory and experiment for the materials Cu_3SbS_4, $CuSbS_2$, and $CuInSe_2$ as shown Figure 1a. Consistent with the computed assessment, the Sb compounds are found to have much higher absorption than $CuInSe_2$. Similarly, as predicted, $CuSbS_2$ is found to have the highest overall absorption above threshold. A better agreement between experiment and theory can be also seen if we shift the experimental absorption coefficient curves by about -0.2 eV. In other words, the theoretical absorption strength near the threshold is universally underestimated. For Cu_3SbS_4 and $CuSbS_2$, one can see that the measured absorption
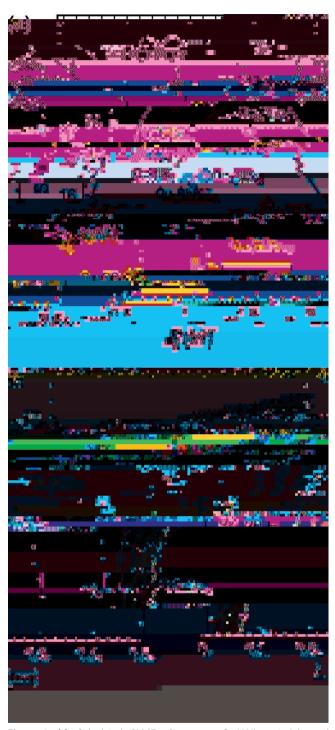

Figure 3. (a) Calculated SLMEs for group Cu-V-VI materials and (b) SLME vs film thickness for selected high-efficiency materials. The open (filled) symbols in (a) represent indirect (direct) band gap materials. In both (a) and (b), red (blue) color denotes for the Cu-V-VI compounds low (high)-valence Group V element.

coefficient rises above 10^5 cm^{-1} at approximately 0.5 eV above threshold, while the xlated absorption reaches the same level only at 0.8 eV above threshold. This might be expected since the excitonic effects and phonon-assisted transitions that also contribute to the absorption near the threshold are neglected