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First-principles analysis of the spectroscopic limited maximum efficiency of photovoltaic absorber layers for CuAu-like chalcogenides and silicon

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Chalcopyrite semiconductors are of considerable interest for application as absorber layers in thin-film photovoltaic cells. When growing films of these compounds, however, they are often found to contain CuAu-like domains, a metastable phase of chalcopyrite. It has been reported that for CuInS_2 , the presence of the CuAu-like phase improves the short circuit current of the chalcopyrite-based photovoltaic cell. We investigate the thermodynamic stability of both phases for a selected list of I-III-VI₂ materials using a first-principles density functional theory approach. For the CuIn-VI_2 compounds, the difference in formation energy between the chalcopyrite and CuAu-like phase is found to be close to 2 meV/atom, indicating a high likelihood of the presence of CuAu-like domains. Next, we calculate the Spectroscopic Limited Maximum Efficiency (SLME) of the CuAu-like phase and compare the results with those of the corresponding chalcopyrite phase. We identify several candidates with a high efficiency, such as CuAu-like CuInS_2 , for which we obtain an SLME of 29% at a thickness of 500 nm. We observe that the SLME can have values above the Shockley-Queisser (SQ) limit, and show that this can occur because the SQ limit assumes the absorptivity to be a step function, thus overestimating the radiative recombination in the detailed balance approach. This means that it is possible to find higher theoretical efficiencies within this framework simply by calculating the J - V characteristic with an absorption spectrum. Finally, we expand our SLME analysis to indirect band gap absorbers by studying silicon, and find that the SLME quickly overestimates the reverse saturation current of indirect band gap materials, drastically lowering their calculated efficiency.

1 Introduction

The conventional search for potential absorber materials in photovoltaic devices is expensive and time consuming. Inverse design methods have the power to screen materials relatively quickly, providing valuable information that allows experimental work to focus on promising compounds¹. In order to accurately screen materials, however, a proper selection metric is required. Traditionally, the Shockley-Queisser (SQ) limit² has been used as a theoretical gauge of the potential efficiency of absorbers. The Spectroscopic Limited Maximum Efficiency³ (SLME) goes beyond the SQ limit by including the absorption spectrum and film thickness in the determination of the efficiency. Since its conception, the SLME has been successfully applied to perovskites⁴⁻⁷, chalcogenides^{8,9}, direct band gap silicon crystals^{10,11} and other materials¹²⁻¹⁵.

Ternary I-III-VI₂ semiconductors, such as the well known Cu(In,Ga)(S,Se)_2 compounds, are commonly used as absorber materials to produce highly flexible and lightweight solar cells. The high absorption coefficient of these compounds allows for

cost-efficient absorber layers that are particularly suited for deposition on flexible substrates¹⁶. Laboratory values for the efficiency of CuIn(S,Se)_2 thin film solar cells have recently reached a record value of 22.3%¹⁷. Furthermore, CuIn(S,Se)_2 is also considered a suitable material for the top cell in tandem structures¹⁸ and quantum dot based luminescent solar concentrators¹⁹. The rapid succession of new record efficiencies indicates that there is still room for improvement in these applications.

I-III-VI₂ compounds are stable at room temperature in the chalcopyrite (CH) structure (space group $I\bar{4}2d$). However, Su and Wei²⁰ have used TEM to demonstrate the presence of CuAu-like (CA) orderings (space group $P4_2m$) in thin films of CuIn(S,Se)_2 , grown by vapor-phase epitaxy on Si and GaAs substrates. Alvarez et al.²¹ also analyzed films of CuInS_2 , using XRD to estimate the relative amount of phase domains. They found that the total amount of CA ordered phase in samples grown under Cu-poor conditions was between 8% and 25%. By growing films of CuInS_2 on various Si substrates, Su et al.²² discovered that although the CA phase is always present, the amount of CA domains is influenced by the substrate orientation. Moreover, Hahn et al.²³ found that by using a Si(001) substrate, the CA phase will

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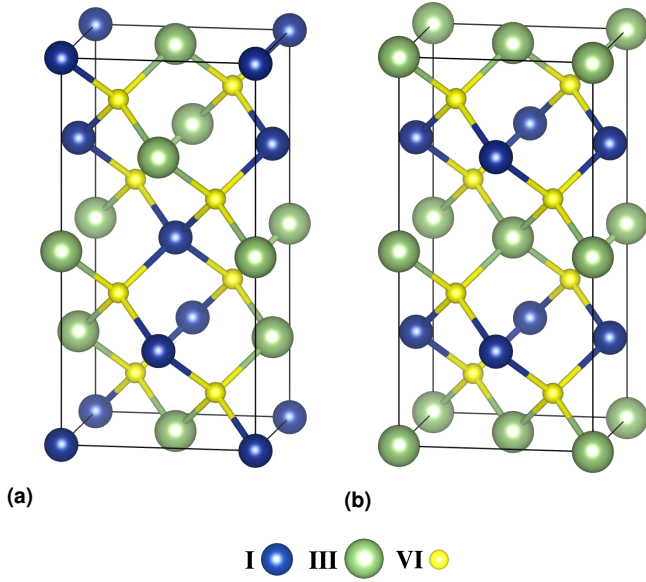


Fig. 1 Chalcopyrite (a) and CuAu-like (b) structure of ternary I-III-VI₂ compounds.

dominate the orderings of the cation sublattice. Recently, Moreau et al.²⁴ have stated that for the CuInS₂ compound, introducing domains of CA phase can lead to a reduction of strain in the absorber layer, resulting in an increased carrier mobility and reduced recombination. Despite the fact that this phase is often found together with CH in thin films, little research has been done to determine its properties. Figure 1 shows the CH and CA structure of the ternary I-III-VI₂ materials.

In this paper we present a first-principles investigation of the efficiency of the CA phase for a selection of compounds. First, we analyze the thermodynamic stability in order to determine the likelihood of the presence of CA domains within a CH-based solar cell. We continue by presenting the optoelectronic properties of the CA phase materials. Next, we use these results to calculate the SLME and discuss the obtained efficiencies of specific compounds. For one of the compounds, the SLME is above the SQ limit. Similar results have been observed by Sarmadian et al.⁹. We analyze this surprising result in more detail by taking a closer look at how the calculated efficiency depends on the thickness and band gap of the material, as well as the temperature of the device. We deduce that the detailed balance approach for the radiative recombination current allows for higher open circuit voltages at lower thicknesses, producing a higher SLME than the corresponding SQ limit. In order to broaden our analysis to indirect band gap materials, we study the SLME of silicon. We find that in the SLME model, the fraction of non-radiative recombination is such that many indirect band gap absorber layers have a very high reverse saturation current, resulting in an unreasonably low calculated efficiency.

2 Computational Details

We make a selection of ten compounds for which we can compare the calculated efficiency of the CA phase with the CH results of Yu and Zunger³. The CA and CH structure

are studied using a first-principles approach within the Density Functional Theory (DFT) formalism, as implemented in the Vienna Ab initio Simulation Package^{25–27} (VASP). The Projector Augmented Wave (PAW) method²⁸ is applied, and the electrons that are treated as valence electrons are underlined in Table 1. The exchange-correlation functional is calculated using the Generalized Gradient Approximation (GGA) of Perdew-Burke-Ernzerhof (PBE)²⁹. The energy cutoff for the plane wave basis is set to 350 eV, and a 4×4×4 Monkhorst-Pack³⁰ (MP) mesh is used for sampling the first Brillouin zone. Electronic convergence is obtained when the energy difference between two electronic steps is smaller than 10⁻⁴ eV. The structure is considered converged when the forces on the atoms are all below 10⁻² eV/Å.

Table 1 Electron configuration of the atoms.

Element	Configuration
Cu	[Ar] 3d ¹⁰ 4s ¹
Ag	[Kr] 4d ¹⁰ 5s ¹
Ga	[Ar] 3d ¹⁰ 4s ² 4p ¹
In	[Kr] 4d ¹⁰ 5s ² 4p ¹
S	[Ne] 3s ² 3p ⁴
Se	[Ar] 3d ¹⁰ 4s ² 4p ⁴
Te	[Kr] 4d ¹⁰ 5s ² 5p ⁴

Because an accurate band gap is important for the correct evaluation of the efficiency, we perform single shot G₀W₀³¹ calculations on top of HSE06³². However, in order to accurately update the quasiparticle energies within the G₀W₀ approximation, it is necessary to consider the semi-core electrons as valence electrons within the PAW framework³³. Hence, we treat the 3s, 3p and 3d (4s, 4p and 4d) orbitals as valence states for the Ga (In) atoms for the G₀W₀@HSE06 calculations of the band gap. In addition, we use a well converged 8×8×8 MP mesh, an increased energy cutoff of 400 eV and a large amount of unoccupied bands (600 in total).

The optical properties are calculated within the Random Phase Approximation (RPA), using the long wavelength expression for the imaginary part of the dielectric tensor^{35,36}. The real part of the dielectric tensor is determined using the Kramers-Kronig relation*. In order to get an accurate description of the energy levels, the exchange-correlation energy is calculated with the HSE06 functional, which has been reported³⁷ to produce optical properties close to those obtained from experiment for CuIn(S_xSe_{x-1})₂. We found that it is enough to sample the Brillouin zone using a 12×12×12 MP mesh to obtain a converged dielectric tensor. The number of unoccupied bands is increased to at least three times the number of occupied bands. Because of the tetragonal symmetry of the CA structure, the resulting

* The Kramers-Kronig relation is calculated by VASP using a complex shift (“CSHIFT”). After calculating the real part, however, VASP also recalculates the corresponding imaginary part. Since the complex shift introduces a broadening, this causes an earlier onset of the imaginary part, and consequently in the absorption coefficient. In order to prevent this, we commented out the line in the VASP code that recalculates the imaginary part.

Table 2 Lattice parameters of the CuAu-like (CA) and chalcopyrite (CH) phase of the considered compounds

Material	CA			CH			CH(Ref ³⁴)		
	a (Å)	c (Å)	c/a	a (Å)	c (Å)	c/a	a (Å)	c (Å)	c/a
AgGaSe ₂	5.702	12.663	2.221	6.045	11.267	1.864	5.973	10.88	1.823
AgGaTe ₂	6.220	13.060	2.100	6.403	12.327	1.925	6.283	11.94	1.897
AgInS ₂	5.780	12.132	2.100	5.925	11.554	1.950	5.816	11.17	1.920
AgInTe ₂	6.511	13.224	2.031	6.570	13.000	1.979	6.406	12.56	1.962
CuGaS ₂	5.341	10.861	2.033	5.384	10.669	1.982	5.349	10.47	1.958
CuGaSe ₂	5.662	11.436	2.020	5.683	11.277	1.984	5.607	10.99	1.960
CuGaTe ₂	6.109	12.170	1.992	6.091	12.160	1.996	5.994	11.91	1.987
CuInS ₂	5.636	11.129	1.975	5.598	11.274	2.014	5.517	11.06	2.005
CuInSe ₂	5.914	11.710	1.980	5.881	11.840	2.013	5.773	11.55	2.001
CuInTe ₂	6.323	12.590	1.991	6.313	12.681	2.009	6.167	12.34	2.000

dielectric tensor is diagonal and has two independent components ϵ_{xx} ($=\epsilon_{yy}$) and ϵ_{zz} . Since we make no assumptions about the direction from which the photons enter the absorber layer, we average the diagonal components to derive the dielectric function $\epsilon(E) = \epsilon^{(1)}(E) + i\epsilon^{(2)}(E)$ at energy E . Finally, in order to obtain a more accurate onset of the absorption spectrum, we shift the imaginary part of the dielectric function to the $G_0W_0@HSE06$ band gap, and recalculate the real part using the Kramers-Kronig relations.

Once we have acquired the dielectric function, we can calculate the absorption coefficient

$$\alpha(E) = \frac{4\pi E}{hc} \hat{k}(E), \quad (1)$$

with h Planck's constant and c the speed of light, from the extinction coefficient $\hat{k}(E)$:

$$\hat{k}(E) = \sqrt{\frac{|\epsilon(E)| - \epsilon^{(1)}(E)}{2}}. \quad (2)$$

This allows us to determine the absorptivity $a(E) = 1 - e^{-2\alpha(E)L}$ for an absorber layer of thickness L with a reflecting back surface³⁸.

The theoretical maximum solar cell efficiency is defined as

$$\eta = \frac{P_m}{P_{in}}, \quad (3)$$

where P_m is the maximum power density and P_{in} is the total incident power density from the solar spectrum. For the SLME, the maximum power density is derived using the J - V characteristic of the solar cell:

$$P = JV = \left(J_{sc} - J_0 \left(e^{\frac{eV}{kT}} - 1 \right) \right) V, \quad (4)$$

with J the total current density, V the potential over the absorber layer, k Boltzmann's constant, T the temperature of the device and e the elementary charge. The short circuit current density J_{sc}

and the reverse saturation current density J_0 are calculated from the absorptivity $a(E)$ of the material, as well as the AM1.5G solar spectrum $I_{sun}(E)$ and the black-body spectrum $I_{bb}(E, T)$:

$$J_{sc} = e \int_0^\infty a(E) I_{sun}(E) dE, \quad (5)$$

$$J_0 = \frac{J_0^r}{f_r} = \frac{e\pi}{f} \int_0^\infty a(E) I_{bb}(E, T) dE,$$

where J_0^r is the radiative recombination current density. The fraction of radiative recombination f_r is modeled using a Boltzmann factor:

$$f_r = \exp\left(\frac{E_g^{da} - E_g}{kT}\right), \quad (6)$$

where E_g and E_g^{da} are respectively the fundamental and direct allowed band gap.

3 Structure and Formation energy

To estimate the likelihood of finding a significant amount of CA domains in CuInSe₂, Wei et al.³⁹ used first-principles calculations to determine the difference in formation energy $\Delta E_f = E_{tot}^{CA} - E_{tot}^{CH}$ between the CH and CA phases of the compound. They found a very small energy difference of 2 meV/atom, which led them to predict the coexistence of the CH and CA structures in CuInSe₂. This was confirmed experimentally by Su and Wei²⁰, supporting the idea that the presence of CA domains is a result of bulk thermodynamics. In order to determine the formation energy difference, we first optimize the structure of the CA and CH phase for each compound as described in Section 2.

We show the calculated lattice parameters and c/a ratio in Table 2, as well as the corresponding experimental values for the CH phase of the compounds[‡]. We can see that the calculated c/a

‡ No experimental values were found for the CA phase in the literature.

Table 3 Difference in formation energy between the chalcopyrite and CuAu-like structure of the considered ternary I-III-VI₂ compounds.

Material	ΔE_f (meV/atom)
AgGaSe ₂	31.3
AgGaTe ₂	27.8
AgInS ₂	8.9
AgInTe ₂	8.5
CuGaS ₂	8.8
CuGaSe ₂	9.9
CuGaTe ₂	7.0
CuInS ₂	1.6
CuInSe ₂	2.2
CuInTe ₂	2.9

ratios match well with those obtained from experiment. For the CA phase, replacing the cations Ag by Cu or Ga by In decreases the c/a ratio of the unit cell. This trend is reversed for the CH phase. If we compare the c/a ratio of the CA and CH phase, we find a large difference in the c/a ratio for the AgGa-VI₂ compounds. Table 3 presents the difference in formation energy for the selected list of compounds. Our first-principles results for CuInS₂, CuInSe₂ and CuGaSe₂ correspond well with those of Su et al.²². Similar to the results for the c/a ratio, the choice of cations has a large influence on the difference in formation energy. From Table 3, we can see that substituting either In by Ga or Cu by Ag increases the difference in formation energy of the two phases. This means that if we consider the existence of the CA phase to be controlled by bulk thermodynamics, we expect CA domains to be common in the CuIn-VI₂ compounds, and less likely in the AgGa-VI₂ ones.

4 Absorber layer efficiency

For all of the investigated compounds, we find a direct band gap at the Γ -point. Table 4 presents a comparison between the G_0W_0 @HSE06 band gaps calculated for the CA and CH structures[§]. We can see that the G_0W_0 calculated band gaps for the CA phase are lower than those of the CH phase for all compounds besides CuInS₂. Furthermore, the difference is smaller for the I-III-S₂ structures compared to the I-III-(Se,Te)₂ compounds. Table 4 also contains the experimental band gaps of the CH phase of the compounds[‡]. We can see that although the G_0W_0 @HSE06 band gaps correspond quite well to the experimental values for some compounds, there are clear discrepancies for others. This could be a result of the sensitivity of chalcogenide band gaps to the anion displacement u (see the supplementary information for more details). As an example of the dielectric function, we show the result for CA-CuInS₂ in Fig. 2. The results for the other compounds can be found in the

supplementary information.

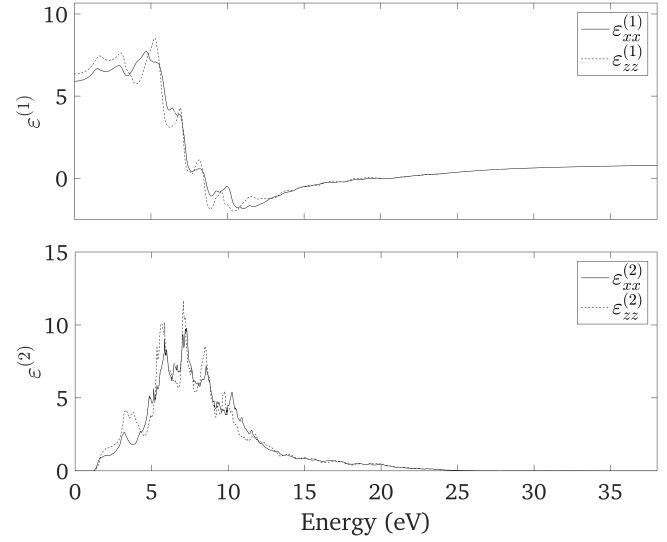


Fig. 2 Real (upper figure) and imaginary (lower figure) parts of the calculated dielectric function of CA-CuInS₂.

After we calculate the band gap and dielectric function for the CA phase of the selected list of compounds, we have all the required information to calculate their SLME. Because we find a direct allowed fundamental band gap for the CA phase of all of the compounds ($E_g^{da} = E_g$), we only have to consider cases where the non-radiative recombination is negligible ($f = 1$, see Eq. (6)). We present the calculated efficiency values in Table 5. In order to compare our results with those of Yu and Zunger, all efficiencies were calculated using thickness $L = 500$ nm and device temperature $T = 300$ K. First, we note that several CH structures that are known to have high device efficiencies, such as CuIn(S,Se)₂, also have a high SLME. Moreover, it is clear that although the band gap has a large influence on the efficiency, some materials, such as CA- and CH-AgInS₂, have a very similar band gap but a significantly different calculated efficiency. This demonstrates the ability of the SLME to provide a more refined selection metric in comparison with the SQ limit. Finally, we see that for several compounds, the CA phase has a higher efficiency than the corresponding CH phase. This is consistent with the findings of Moreau et al.²⁴, who discovered that the presence of CA domains have a positive influence on the efficiency of CuInS₂. We suggest that the efficiency of these devices may have benefited from the presence of the CA phase directly through the optical properties of the material.

In Fig. 3, we show the SLME of the CA and CH phase of the various compounds versus their band gap, as well as the SQ limit. We immediately observe that the SLME value for CA-CuInSe₂ is higher than the corresponding SQ limit. In Section 5 we return to this result and discuss it in detail. The SLME is plotted as a function of the film thickness in Fig. 4. We can see that for most compounds, the efficiency of the CA phase rises quickly for an increasing thickness. This demonstrates the potential of the CA phase compounds as absorber layers in thin-

[§] We calculated the band gap of the CH phase of several compounds ourselves, because of inconsistencies between the tabulated and plotted values for these compounds in Ref. 3. All results taken from Ref. 3 come from Table S3 in their supplementary information.

Table 4 Experimental and calculated band gaps of the CuAu-like(CA) and chalcopyrite (CH) phase of the considered compounds.

Material	CA		CH			
	E_g^{HSE} (eV)	$E_g^{G_0W_0}$ (eV)	E_g^{HSE} (eV)	$E_g^{G_0W_0}$ (eV)	$E_g^{G_0W_0}$ (eV) (Ref. 3)	E_g^{exp} (eV)
AgGaSe ₂	0.84	1.41	-	-	1.80	1.83 ^a
AgGaTe ₂	0.46	0.95	1.14	1.71	1.54	1.1-1.3 ^a
AgInS ₂	1.20	1.69	-	-	1.74	1.87 ^a
AgInTe ₂	0.53	0.92	-	-	1.23	0.96-1.04 ^a
CuGaS ₂	1.77	1.94	-	-	1.99	2.41 ^b
CuGaSe ₂	0.96	1.19	1.29	1.46	1.65	1.64 ^b
CuGaTe ₂	0.77	1.06	-	-	1.47	1.23 ^a
CuInS ₂	1.14	1.13	1.14	1.05	1.54	1.53 ^b
CuInSe ₂	0.59	0.58	0.67	0.66	1.33	1.04 ^b
CuInTe ₂	0.76	0.94	-	-	1.03	0.96 ^a

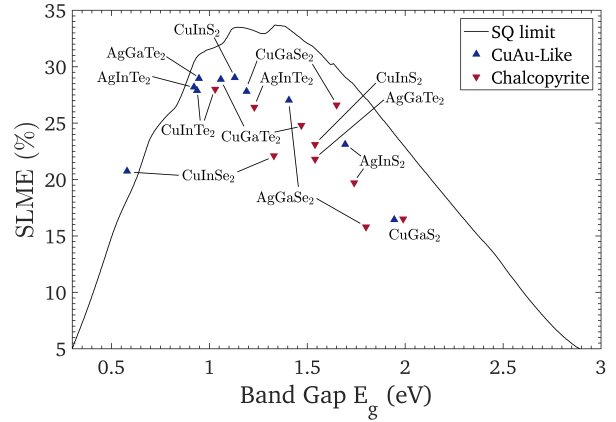
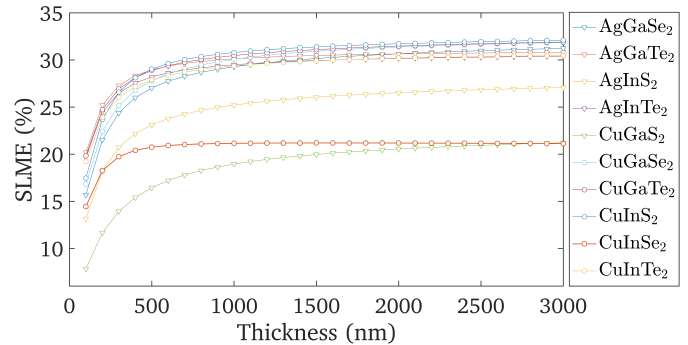
^a Ref. 40, ^b Ref. 41**Table 5** Calculated SLME for both the CuAu-like and chalcopyrite³ structures. The SQ limit of the corresponding band gap is also given as a reference.

Material	SLME(%)	SQ(%)	SLME(%)	SQ(%)
	(CA)	(CA)	(CH)	(CH)
AgGaSe ₂	27.0	33.3	15.8	27.2
AgGaTe ₂	28.9	31.1	21.8	31.6
AgInS ₂	23.1	29.1	19.7	28.4
AgInTe ₂	28.2	30.5	26.4	33.2
CuGaS ₂	16.4	24.1	16.5	23.1
CuGaSe ₂	27.8	33.4	26.6	29.9
CuGaTe ₂	28.9	32.0	24.8	32.5
CuInS ₂	29.0	33.5	23.1	31.6
CuInSe ₂	20.7	18.3	22.1	33.6
CuInTe ₂	27.9	30.9	28.0	31.7

film solar cells. Finally, we discuss the issue of the possible discrepancy between the calculated and experimental band gaps for some of the compounds. Looking at Fig. 3, we expect the influence of the band gap to be small in the 1-1.5 eV interval. In case the calculated and experimental band gap are not in this region, however, any discrepancy between the calculated and experimental band gap is likely to influence the SLME.

5 SLME Analysis

During the discussion of the SLME results of the CA phase, we noted that CA-CuInSe₂ has an SLME value above the SQ limit. This result is surprising because the SQ limit is widely considered to be a theoretical maximum efficiency of a single junction absorber layer[¶], and the SLME is based on the same detailed

**Fig. 3** SLME of the CuAu-like and chalcopyrite³ phase of the compounds versus the band gap. All of the efficiencies were calculated using thickness $L = 500$ nm and device temperature $T = 300$ K. The black line represents the Shockley-Queisser limit.**Fig. 4** Calculated maximum efficiencies of the CuAu-like phase materials as a function of film thickness.

¶ There are a number of considerations that could allow the efficiency of a single-junction solar cell to exceed the SQ limit, such as multiple-exciton generation, photon recycling, etc., however none of these are implemented by the SLME.

balance approach as the SQ limit. Due to the construction of the SLME, the calculated efficiency returns to the SQ limit for $L \rightarrow \infty$, since for an infinitely thick absorption layer the absorptivity becomes a step function. However, looking at the thickness dependence of the SLME for CA-CuInSe₂ and CA-CuInS₂ (Fig. 5), we see that the way they approach the SQ value is different. More specifically, the SLME of the compound CuInSe₂ crosses the SQ limit, whereas that of CuInS₂ does not.

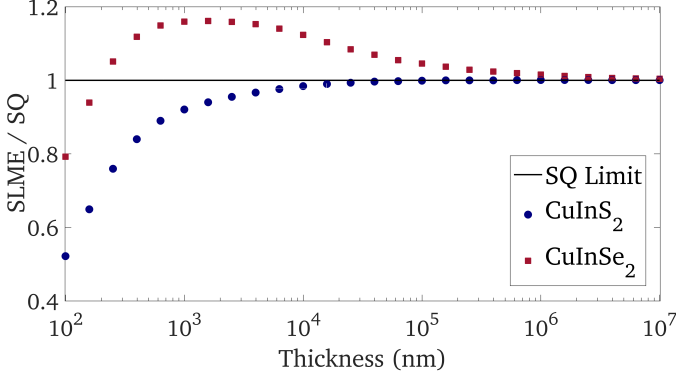


Fig. 5 Thickness dependence of the SLME of CA-CuInSe₂ and CA-CuInS₂ at 300 K versus their SQ limit.

We can understand the origin of this behavior by considering how the short-circuit current density J_{sc} and reverse saturation current density J_0 are used to calculate the power density of the absorber layer (Eq. (4)). In Fig. 6 we show the calculated J - V characteristic of CA-CuInS₂. We can see that the total current density J remains close to J_{sc} up to a certain voltage. The value of this voltage, and hence the value of the open circuit voltage V_{oc} and the voltage that maximizes the power density V_m , depends strongly on J_0 . When we look at both current densities as a function of the thickness in Fig. 7, it is clear that for both compounds J_{sc} converges to the corresponding SQ value much quicker than J_0 . The relatively low value for J_0 at certain thicknesses allows for a higher open circuit voltage V_{oc} . This is the case for both CA-CuInS₂ and CA-CuInSe₂. However, the order of magnitude of J_0 is much larger for CA-CuInSe₂ than for CA-CuInS₂.

The SLME crosses the SQ limit when its maximum power density is higher than the one calculated using the SQ values for J_{sc} and J_0 :

$$J_m V_m = P_m > P_m^{SQ} = J_m^{SQ} V_m^{SQ} \quad (7)$$

$$\Leftrightarrow \frac{V_m}{V_m^{SQ}} > \frac{J_m^{SQ}}{J_m}.$$

Because the order of magnitude of J_0 is much larger for CA-CuInSe₂, the value of the fraction V_m/V_m^{SQ} at low thicknesses is higher for CA-CuInSe₂ when compared to that for CA-CuInS₂ (Fig. 8). In comparison, the convergence of the fraction J_m^{SQ}/J_m is similar for both compounds. From Eq. (7), it is clear that when V_m/V_m^{SQ} is larger than J_m^{SQ}/J_m , the maximized power density is higher than its SQ value, which means that the SLME will be higher than the Shockley-Queisser limit for that thickness.

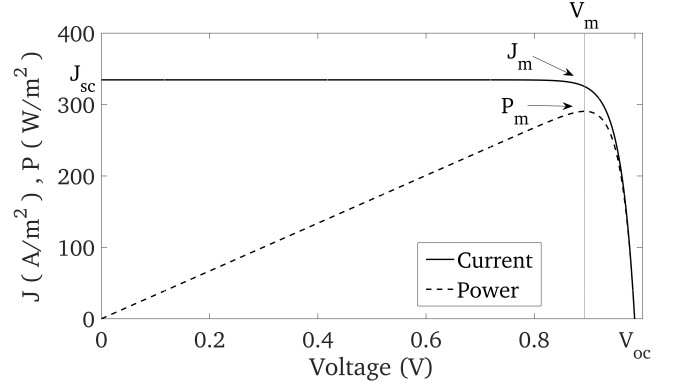


Fig. 6 Calculated J - V characteristic of CA-CuInS₂ at $T = 300$ K and $L = 500$ nm (full line), as well as the corresponding power density (dashed line).

Looking at Fig. 8, we can see that at $T = 300$ K, this happens for CuInSe₂.

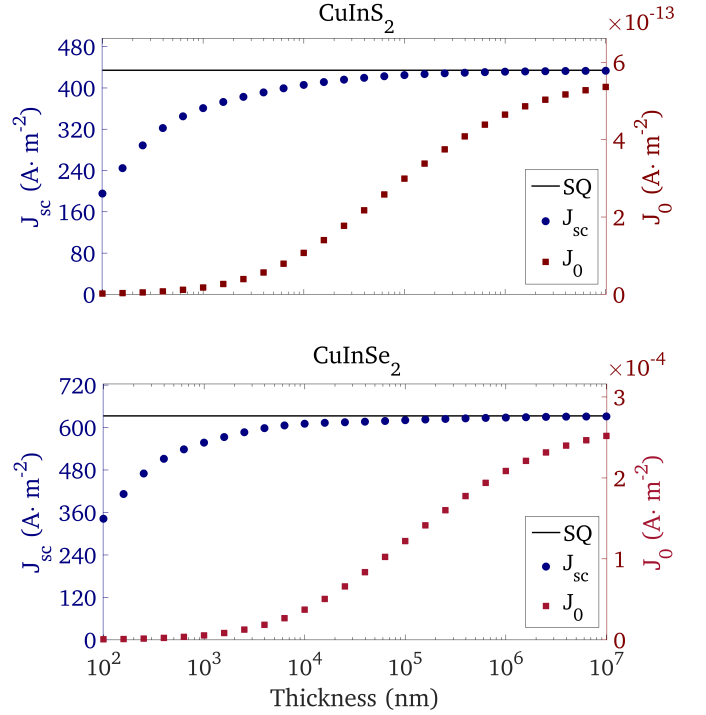


Fig. 7 Thickness dependence of the current densities of CuInS₂ (upper figure) and CuInSe₂ (lower figure) versus their respective SQ values.

For direct band gap absorbers, $f_r = 1$, and J_0 is calculated from the overlap of the black-body spectrum $I_{bb}(E, T)$ and the absorptivity $a(E)$ of the material. From Eq. (5), we can understand that lowering the band gap increases J_0 . As a result, materials with a low band gap are more likely to have an SLME value above the SQ limit at a specific thickness. It is also clear, however, that J_0 increases at higher temperatures. This raises the relative increase of V_{max} at lower thicknesses, potentially producing calculated efficiencies above the SQ limit. For example, looking at the thickness dependence of the SLME of CA-CuInS₂ at

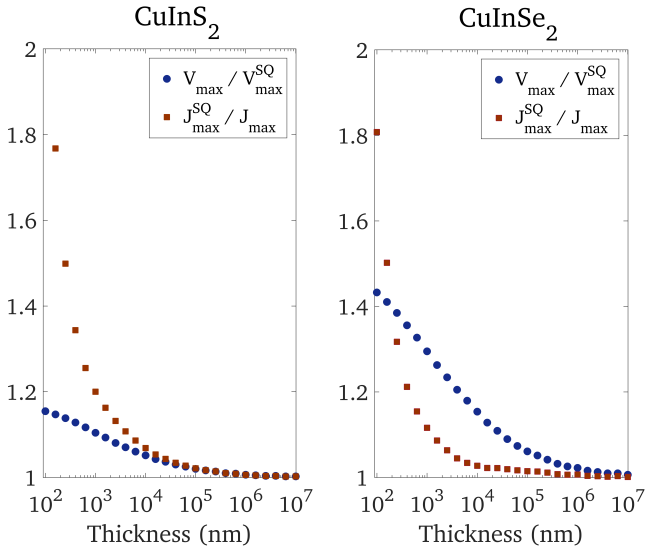


Fig. 8 Comparison of the relative increase of the voltage that maximizes the power density ($V_{\max}/V_{\max}^{\text{SQ}}$) with the relative decrease of the corresponding current density ($J_{\max}^{\text{SQ}}/J_{\max}$).

$T = 450\text{K}$ (Fig. 9), we see that at this temperature the calculated efficiency also crosses the Shockley-Queisser limit.

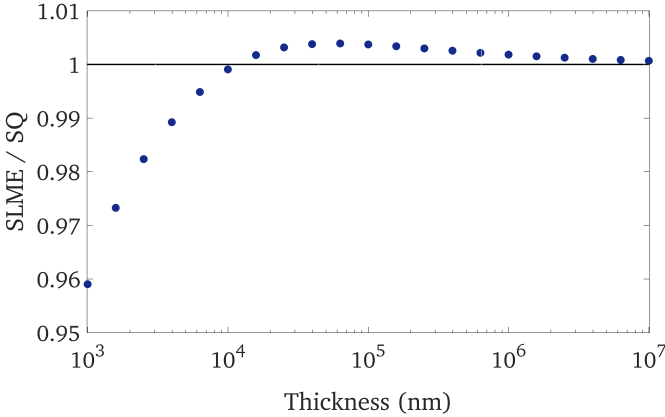


Fig. 9 Thickness dependence of the SLME of CA-CuInS₂ at $T = 450\text{K}$.

Since the calculation of the SLME only deviates from the SQ limit by the introduction of an *ab initio* calculated absorption spectrum, these results show that the SQ limit is not a theoretical upper limit within the assumptions of the detailed balance approach. This is because considering an infinite thickness for the solar cell, i.e. taking a step function for $a(E)$, overestimates J_0 as it is calculated in the detailed balance framework. As a result, it is possible that for a material with a certain band gap and absorptivity, J_0 is very low compared to its SQ value, which allows for a high V_{oc} . In case V_{oc} is increased sufficiently, the total power density can go above that of the SQ limit, even though the calculated J_{sc} is lower than its SQ value. In other words, if we consider all of the assumptions made in the Shockley-Queisser approach and introduce an absorption spectrum, it is possible to obtain efficiencies above the SQ limit.

6 Indirect band gap absorbers

So far, we have only considered materials which have a direct band gap. For completeness, we expand our analysis to indirect band gap absorbers. We choose to calculate the SLME of silicon, which is currently the material that is still used the most for the production of solar cells. In Fig. 10, we show the experimental^{||} absorption coefficient of crystalline silicon⁴². Notice the onset of the indirect and direct absorption at $E_g = 1.17\text{ eV}$ and $E_g^{da} = 3.4\text{ eV}$, respectively.

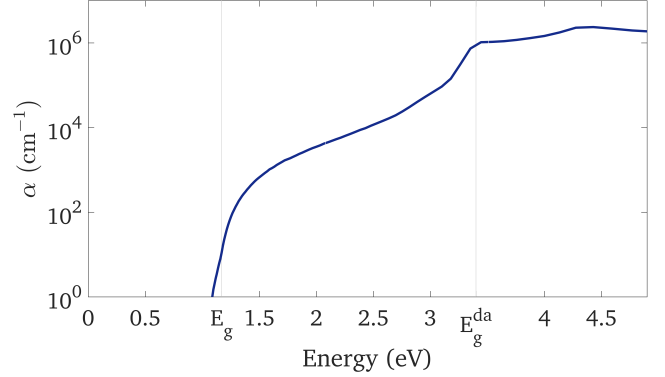


Fig. 10 Experimental absorption coefficient at $T = 300\text{K}$ of crystalline silicon with data taken from⁴².

Calculating the SLME using this optical spectrum produces an efficiency of zero for any value of L and T . The origin of this troubling result is rooted in the fraction of radiative recombination expressed in Eq. (6). Because of the large difference between the direct allowed and fundamental band gap of silicon ($\Delta = E_g^{da} - E_g = 2.23\text{ eV}$), the radiative fraction is of the order 10^{-38} . Since this fraction is used to calculate the reverse saturation current (see Eq. (5)), this results in a J_0 that is unreasonably large. As discussed in Section 5, J_0 has a significant influence on the open circuit voltage V_{oc} . In this case, the high value of J_0 leads to a V_{oc} that is too small to produce any significant power density. However, in case we set $f_r = 10^{-3}$, a more reasonable value for silicon^{43–45}, then we obtain the results shown in Fig. 11.

One could argue that silicon is a special case, and that generally efficient indirect absorbers do not have such a large band gap difference $\Delta = E_g - E_g^{da}$. For thin-film solar cells, indirect absorption also contributes significantly less to the power density. Consequently, indirect band gap materials with a large fundamental band gap are not suitable for these applications in any case. However, even for materials with a small Δ , the modeled fraction of radiative recombination quickly becomes minute. For example, consider the compound Cu_3TlSe_2 , which has been investigated by Yu and Zunger³. The reported difference between the fundamental and direct allowed band gap is 0.24 eV . At 300 K , the fraction of radiative recombination then becomes

^{||} We choose to use an experimental spectrum in order to include the phonon-mediated contributions to the absorption coefficient.

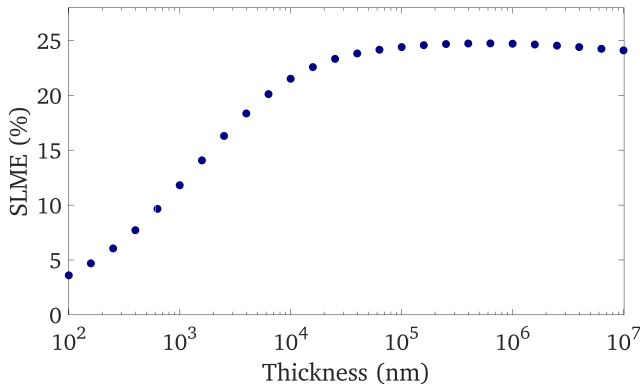


Fig. 11 Thickness dependence of the SLME of silicon.

$f_r = 10^{-4}$. This means that although 99.99 % of the recombination is non-radiative in nature, the reverse saturation current is still derived from an entirely radiative principle, based on the black-body spectrum in Eq. (5). Furthermore, it is clear that because of the exponential function in Eq. (6), the fraction of radiative recombination drops very rapidly with increasing Δ . This indicates that even for materials with a relatively low Δ , the reverse saturation current will rise significantly, which is detrimental for the calculated efficiency. Hence, it is fair to question whether the recombination model of the SLME metric does not judge indirect band gap absorbers unfairly, potentially eliminating good materials during the selection procedure.

7 Summary and Conclusions

We have compared the structural and thermodynamic properties of the CA and CH phase of the compounds. By analyzing the difference in formation energy of the CH and CA phase, we conclude that CA domains are most likely to be present in CuIn-VI₂ compounds, which is in good agreement with experimental results. From the calculated optoelectronic properties of the materials, we have determined their potential as absorbers for solar cells by applying the SLME selection metric. We identify several compounds with a high theoretical efficiency in the CA phase, most notably CA-CuInS₂, which has a significantly higher efficiency than the corresponding CH phase.

After observing an SLME value above the Shockley-Queisser limit for CA-CuInSe₂, we have performed a detailed analysis to find the origin of this result. We find that, within the details balance approach, the reverse saturation current J_0 approaches its SQ value very slowly for an increasing thickness L . This causes the SLME to cross the SQ limit for materials with a J_0 that is relatively high, i.e. materials with a low band gap or at higher temperatures. In other words, because the SQ limit overestimates J_0 , it is not an effective theoretical maximum efficiency of a single junction cell within the detailed balance approach. Finally, we show that the model that introduces non-radiative recombination to the SLME quickly undercuts the efficiency of indirect band gap absorbers.

8 Acknowledgements

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Supplemental information for: First-principles analysis of the efficiency of photovoltaic layers for CuAu-like chalcogenides and silicon

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1 Band gap discrepancy

For some compounds, the calculated band gap of the chalcopyrite (CH) phase does not correspond well to the experimental value. One possible reason for these discrepancies is the sensitivity of the band gap of chalcogenides to the anion displacement u . Jaffe and Zunger [1] used standard DFT to demonstrate the influence of u on the calculated band gap, finding that an increased u leads to higher band gaps for CH-CuInSe₂ and CH-CuAlS₂. Similar results were found by Vidal et al. [2] using HSE06 to calculate the band gap of CH-CuInS₂. In Table 1, we present the u parameter calculated using PBE versus a set of experimental results. We can see that although u corresponds well to experiment for some compounds, there are significant differences for others. For example, the calculated u of both CH-CuInS₂ and CH-CuInSe₂ are below the experimental range. Considering the influence of u on the band gap, it is not unreasonable to assert that the underestimation of the band gap may be related to the low values found for u .

2 Optical properties

For the calculation of the SLME, we require the dielectric tensor of the studied material. For all of the structures considered in this paper, the dielectric tensor is found to be diagonal and has two independent components:

$$\varepsilon_{\alpha\beta}(E) = \begin{pmatrix} \varepsilon_{xx}(E) & 0 & 0 \\ 0 & \varepsilon_{xx}(E) & 0 \\ 0 & 0 & \varepsilon_{zz}(E) \end{pmatrix}, \quad (1)$$

where each component is imaginary (e.g. $\varepsilon_{xx}(E) = \varepsilon_{xx}^{(1)}(E) + i\varepsilon_{xx}^{(2)}(E)$). Figures 1 and 2 show both the real and imaginary part of the calculated tensor components for the CuAu-like phase of the studied

Table 1: Calculated and experimental [1] anion displacement for the chalcopyrite phase of the studied compounds.

Material	u_{PBE}	u_{exp}
AgGaSe ₂	0.278	0.27
		0.276
AgGaTe ₂	0.266	0.26
AgInS ₂	0.256	0.25
		0.250
AgInTe ₂	0.243	0.25
CuGaS ₂	0.237	0.25
		0.275
		0.2539
		0.272
CuGaSe ₂	0.244	0.25
		0.250
		0.243
CuGaTe ₂	0.237	0.25
CuInS ₂	0.218	0.20
		0.214
		0.2295
CuInSe ₂	0.217	0.22
		0.224
		0.235
CuInTe ₂	0.214	0.225

compounds. For completeness, we show the optical dielectric constants in Table 2. It is interesting to note that the choice of the anion (S,Se,Te) in the CuAu-like phase of the I-III-VI₂ compounds has a strong influence on the value of their optical dielectric constants. The computational details can be found in Section 2 of the main text.

Table 2: Optical dielectric constants of the CuAu-phase of the studied compounds.

Material	$\varepsilon_{xx}(\infty)$	$\varepsilon_{zz}(\infty)$
AgGaSe ₂	6.37	6.66
AgGaTe ₂	8.71	8.61
AgInS ₂	5.24	5.53
AgInTe ₂	7.96	8.20
CuGaS ₂	5.72	6.09
CuGaSe ₂	6.99	7.34
CuGaTe ₂	9.00	9.40
CuInS ₂	5.90	6.34
CuInSe ₂	7.18	7.69
CuInTe ₂	8.42	8.99

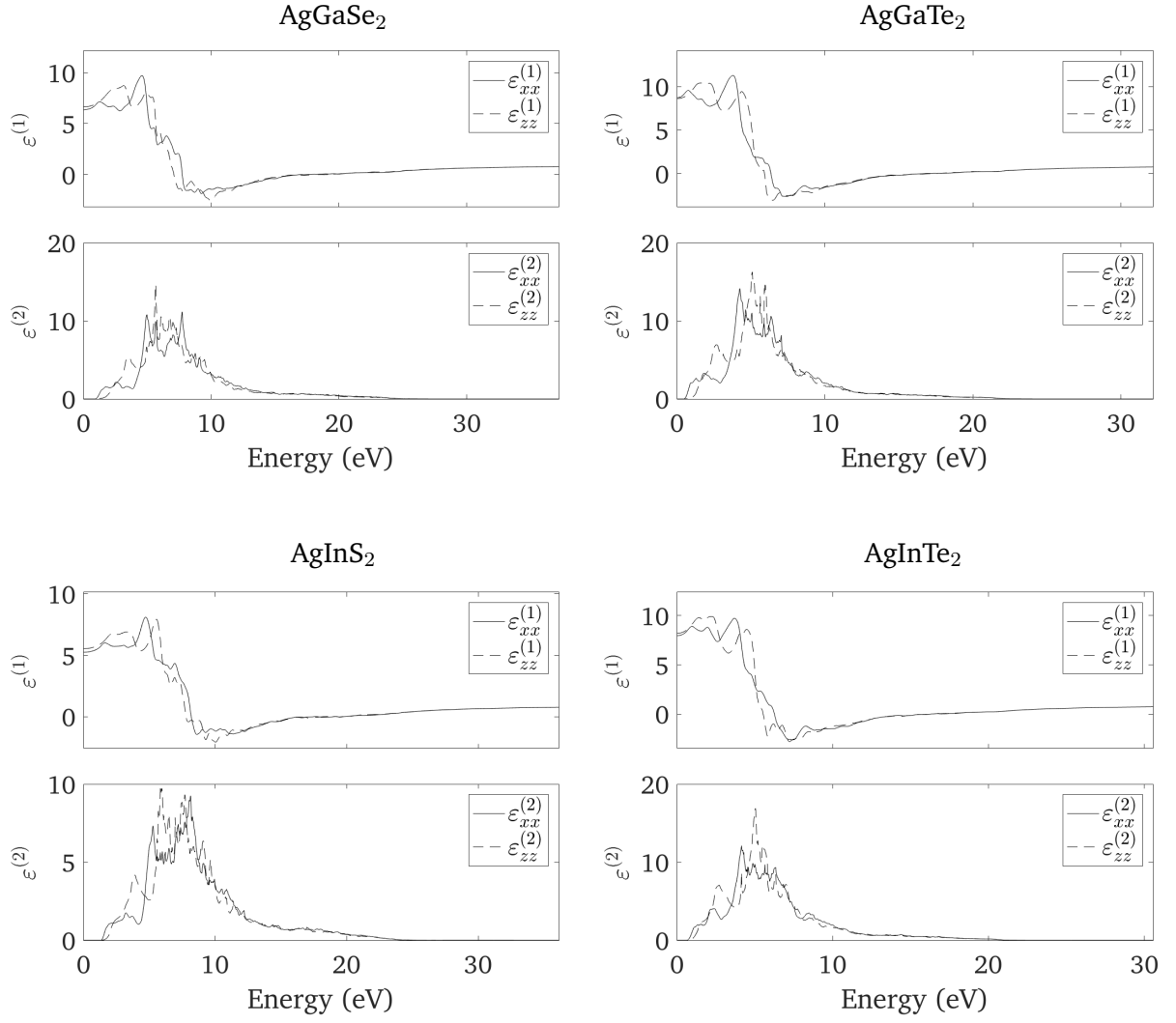


Figure 1: Dielectric functions of the CuAu-like phase of the Ag-III-VI₂ compounds.

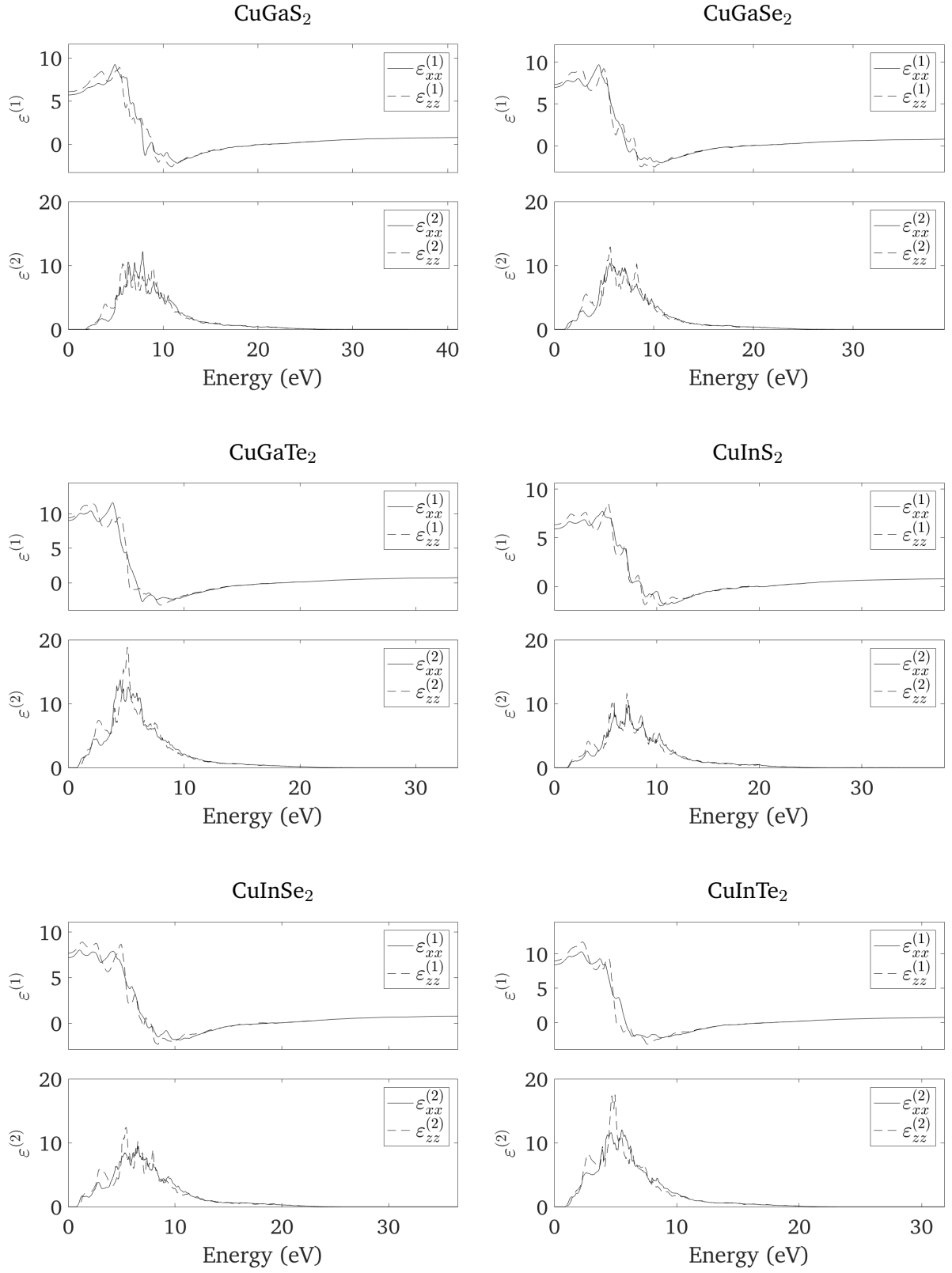


Figure 2: Dielectric functions of the CuAu-like phase of the Cu-III-VI₂ compounds.

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