schematically in Fig. 1. ''Optical type 1 (OT1)'' is the case when the DA direct gap is the lowest energy transition and the next direct-but-forbidden transition is above it (i.e., $E_g^{da} \leq E_g^{df}$). ''Optical type 2 (OT2)'' is the case where the lowest transition is direct-but-forbidden, i.e., when $E_g^{da} > E_g^{df}$. Accordingly, ''optical type 3 (OT3)'' and ''optical type 4 (OT4)'' are two types of indirect gap materials, corresponding to cases with $E_g^i < E_g^{da} \leq E_g^{df}$ and $E_g^i < E_g^{df} < E_g^{da}$, respectively. Each of these four optical types has different characteristic absorption profile near threshold, depending on the order and energy separation between allowed and forbidden states. Subsequent, quantitative spectroscopic calculations (below) will demonstrate this classification on a class of materials.

The SLME is generalized from the SQ limiting efficiency. The power conversion efficiency [7] of a thin film solar cell depends on the fraction of the radiative electron-hole recombination current (f_r) and the photon absorptivity [$a(E)$]. SLME improves upon the SQ efficiency formula in the description of both f_r and $a(E)$. SQ efficiency assumes $f_r = 1$; i.e., the radiative recombination is the only recombination process for all optical types of materials. This could be a good approximation for OT1 materials such as GaAs [8] where radiative recombination dominates. However, for other types of materials where E_g^{da} is not the minimum band gap, the nonradiative recombinations (e.g., Auger recombination) is frequently much more significant [f

some compounds with non-(1:1:2) stoichiometry could be also good for PV absorbers.

The calculated *GW* band gaps of considered 256 compounds are given in the Supplemental Material, Table S1 [15]. Figure 2 shows the *GW* gaps of 215 compounds [25] classified into four optical types. Some clear trends emerge here. (i) Within the same structure type, the band gap of materials decreases with increasing atomic number of one atom when the other two atoms are held fixed. For instance, for OT1 materials, $E_g^{GW}(\mathrm{InAs_2}) > E_g^{GW}(\mathrm{InSb_2}) > E_g^{GW}(\mathrm{InBi_2})$. (ii) The optical types can change if the stoichiometry changes within the same element set. For example, $\mathrm{In_3Te_2}$ (OT3) → $\mathrm{In_5Te_3}$ (OT4) → $\mathrm{In_7Te_4}$ (OT1) → $\mathrm{InTe_2}$ (OT2). (iii) For the same

the same minimum gap (1.17 eV), but their SLMEs vary significantly, being 27.6%, 22.6%, and 7.5%, respectively. From the inset of Fig. 3, it can be seen that the SLME difference between A I Te_2 and 1 7T S_4 originates from different onset absorption spectra. For 1 ¶ Te_2, the E_g^{da} is about 1 eV larger than E_g, i.e., = 1 , and hence the nonradiative recombination loss dominates. This large leads to a much smaller overlap between absorption spectrum and solar spectrum. Hence, although the absorption near E_g^{da} (2.2 eV) is very strong in 1 ¶ Te_2, the SLME is still rather small. Therefore, a material with the minimum gap being around 1.0–1.5 eV does not necessarily mean it is a good PV absorber.

From Fig. 4, we can find that there are about 25 materials with SLME higher than 20% (see Table S3 [15] for details). These high-SLME materials have the band gaps ranging from 0.8 to 1.75 eV. Most of them—18 out of 25—are OT1. Seven of them are OT3. None of them have been found to be OT2 or OT4. The common character among these OT3 materials is that E_g^i is only slightly smaller than E_g^{da}, i.e., small . For example, = 0.07 for 3

identification of hitherto overlooked, promising candidate materials in different optoelectronic technology areas.

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