

Brief review of emerging photovoltaic absorber materials

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Abstract

Photovoltaic solar cells have recently made significant commercial progress and are on track toward meeting more than 1% of global energy demand. However, further research is needed on photovoltaic technologies that face no scalability constraints in generating more than 10% of the world's electricity. This 2017 article briefly reviews emerging photovoltaic absorber materials, focusing on research progress over the past 2–3 years. Particular emphasis is given to emerging solar cell absorbers—for example, SnS, Sb₂Se₃, Cu₂SnS₃, and CuSbSe₂—related to established solar cell technologies such as CdTe, Cu(In,Ga)Se₂, and CH₃NH₃PbI₃. Finally, the general publication and performance trends are discussed, and the promising future research directions are pointed out.

Introduction

Photovoltaic (PV) solar cells are semiconductor-based devices that directly convert sunlight into electricity. The main component of any solar cell device is the PV absorber material, which absorbs sunlight and transports the resulting charge carriers to electrical contacts. Currently, the most commonly used solar cell absorber is thick (~100 μm) multicrystalline silicon (Si) due to its high efficiency (>20%), low cost (<0.5 \$/W), and good reliability (<25 years). The closest commercial competitors for terrestrial application are CdTe and Cu(In,Ga)Se₂ (CIGS) thin-film solar cells that are as efficient yet use ~100x less absorber material compared to Si; another emerging pre-commercial thin-film PV technology is hybrid organic-inorganic perovskite CH₃NH₃PbI₃ (MAPI). For space applications, III-V multijunction PV with higher efficiencies (~40%) is at premium despite higher costs. Substantial progress in research, development, and deployment in each of these solar cell technologies gives confidence that 1 terawatt (TW) of electrical energy (~3% of global demand) will be generated by solar cells in the near future (2020–2030).

Table I. Cost, efficiency, and reliability of PV modules for established solar cell technologies, important for scaling toward 1-TW installation levels; italics indicate yet to be proven projections. (Additional criteria become important for scaling to the 10-W level, and new PV absorbers should have the potential to meet all these criteria.)

Photovoltaic Technology	Module Cost	Module Efficiency	Module Reliability	Capital Expenditures	Environmental Concerns	Elemental Abundance
Si	Low	High	Good	High	No	High
CdTe	Low	High	<i>Good</i>	Medium	Yes	Low
CIGS	Medium	<i>High</i>	<i>Good</i>	Medium	No	Low
III-V	High	Very high	<i>Good</i>	Medium	No	Low
MAPI	<i>Low</i>	<i>High</i>	<i>Bad</i>	<i>Low</i>	Yes	Medium
New absorber	<i>Low</i>	<i>High</i>	<i>Good</i>	<i>Low</i>	No	High

To satisfy 30% of the world's energy demand (~10 TW) by 2040–2050, several other solar cell technology criteria—in addition to efficiency, cost, and reliability—become important. At this scale, an ideal PV absorber technology should also have low capital expenditures (to rapidly finance and build a large number of new solar cell fabrication plants)¹ and be composed of chemical elements that are environmentally friendly, abundant in the Earth's crust, and not concentrated in one geographical region of the planet. Unfortunately, none of the existing solar cell technologies currently meets all these criteria. As shown in Table I, the capital intensity of Si

may be difficult to reduce, environmental friendliness of Cd and Pb are questionable, and Earth-abundance of In, Ga, and Te are under debate. Thus, additional research and development of *emerging PV absorber materials* is needed to diversify the portfolio of incumbent solar cell technologies.

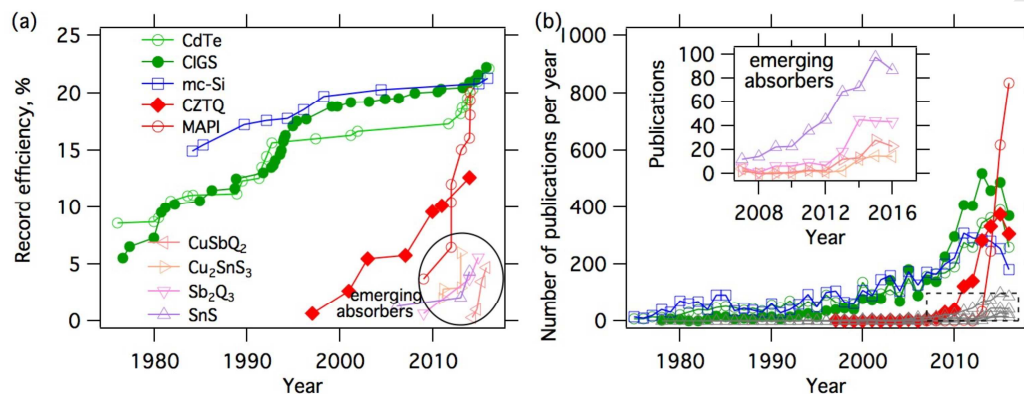


Fig. 1. (a) Record efficiencies and (b) number of publications as a function of year for the established (CdTe, CIGS, multicrystalline Si, MAPI, CZTS—certified) and emerging (SnS, Sb₂Q₃, CuSbSe₂, Cu₂SnS₃—not all certified) PV absorber technologies. The inset in (b) shows the number of publications for the emerging absorbers.

This brief review summarizes the progress in emerging PV absorber materials over the past 2–3 years. Figure 1 shows the emerging PV absorbers, which, for the purposes of this article, are limited to materials that have some resemblance to existing PV technologies. The common feature of these materials is that they have measurable efficiencies (~5%, Fig. 1a) despite the small number of publications per year (usually ~10–40, Fig. 1b). The three specific classes of such emerging PV absorber materials discussed below include binary chalcogenides related to CdTe (e.g., SnS, Sb₂Se₃), copper chalcogenides related to CIGS (e.g., Cu₂SnS₃, CuSbSe₂), and emerging absorber materials related to MAPI. For more details beyond the high-level comparative information provided here, see other reviews on incumbent solar cell technologies such as Si, III-V, CdTe, CIGS, MAPI, dye-sensitized solar cells, and organic PV.

Binary chalcogenides related to CdTe

One emerging class of PV materials under active investigation are binary congruently subliming compounds such as Sb_2Se_3 or SnS (see recent review in Refs. 2,3), which are related to CdTe but made of more environmentally friendly and Earth-abundant elements. Similar to CdTe , their evaporation temperature is below the decomposition temperature. Thus, thin films of these materials can be synthesized using relatively simple vacuum-based evaporation or close-spaced sublimation techniques. Despite the long history of research,^{4,5} SnS heterojunction solar cells achieved 4.4% efficiency only relatively recently (Fig. 1a).⁶ This progress was achieved in part due to changing from CdS to Zn(O,S) heterojunction contacts,^{7,8} but more challenges remain that are related to absorber morphology⁹ and purity.¹⁰ Similar advances in contacts are needed in $\text{Sb}_2\text{Se}_3/\text{CdS}$ solar cells, which are also likely to have high a conduction-band position.

The efficiency of Sb_2Se_3 solar cells has increased very rapidly in the past 2–3 years—from 1%–2%¹¹ to 5%–6%¹² for the absorbers prepared by evaporation (see Fig. 1a and recent review in Ref. 13). Various classical thin-film absorber processing techniques have been attempted, including the addition of oxygen during growth¹⁴ and post-deposition CdCl_2 treatment.¹⁵ It is notable that for the related non-vacuum-based Sb_2S_3 PV technology, the similar efficiencies for electrodeposited $\text{Sb}_2\text{S}_3/\text{Pt}$ planar Schottky junctions had been demonstrated as early as 1994,¹⁶ and confirmed in 2014 in planar $\text{Sb}_2\text{S}_3/\text{TiO}_2$ structures grown by atomic layer deposition.¹⁷ In the interim 20 years, Sb_2S_3 research has focused on mesoscopic sensitized¹⁸ and extremely thin absorber (ETA) cells,¹⁹ reaching similar efficiencies.

One common feature that makes SnS and Sb_2Q_3 ($\text{Q}=\text{S,Se}$) scientifically interesting and distinct from CdTe is their non-cubic crystal structure,²⁰ consisting of pseudo-2-D layers for SnS and pseudo-1-D ribbons for Sb_2Q_3 .¹² These low-dimensional structural features may lead to more electronically passive grain boundaries compared to 3-D bonded materials due to fewer dangling bonds. These pseudo low-dimensional SnS and Sb_2Q_3 absorbers may bridge the knowledge gap between applied development of thin-film solar cells and basis research on truly 2-D materials such as MoSe_2 and SnS_2 (see recent review in Ref. 21). Such 2-D monolayers have recently attracted considerable scientific attention²² and have been proposed for various optoelectronic applications;^{23,24} however, tangible PV conversion efficiencies remain to be demonstrated. The SnS and Sn_2Q_3 materials also provide a fresh perspective on the >30 year old field of binary PV absorbers (e.g. Cu_2S ^{25,26} FeS_2 ^{27,28}), so they fully deserve additional research.

Copper chalcogenides related to CIGS

In 2010–2014, the research on emerging absorbers related to the ternary chalcopyrite $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) alloy has largely focused on the quaternary kesterite $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ (CZTS) alloy that can be derived by cation mutation of In/Ga into Zn/Sn (see recent review in Refs. 29,30 and a book in Ref. 31). In 2010, the 9.6% record efficiency was demonstrated in CZTS,³² eventually reaching 12.6%³³ by solution processing and 11.6% by thermal co-evaporation in 2014–2015 (Fig. 1a).³⁴ Since that time, significant progress has been made in understanding CZTS point defects extrinsic impurities (see Ref. 35 for review), cation disorder,^{36,37} and surfaces/interfaces.^{38,39,40} However, record efficiencies remained constant, possibly due to Cu/Zn disorder on the cation sublattice, which is currently causing research to shift to related quaternary materials that do not contain either Cu or Zn, such as $\text{Ag}_2\text{ZnSn}(\text{S,Se})_4$ (AZTS)⁴¹ and $\text{BaCu}_2\text{Sn}(\text{S,Se})_4$ (BCTS).^{42, 43} A related family of materials—such as $\text{Cu}_{10}\text{Zn}_2\text{Sb}_4\text{S}_{13}$, $\text{Cu}_{11}\text{InSb}_4\text{S}_{13}$, $\text{Cu}_{10}\text{Zn}_2\text{Sb}_4\text{Se}_{13}$, and $\text{Cu}_{10}\text{Te}_4\text{S}_{13}$ —have tetrahedrite crystal structure derived from metallic $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ by substitution of Zn, In, or Sb for Cu, or Te for Sb.⁴⁴

An alternative strategy in copper chalcogenide absorbers is to take a step back from chemically complex quaternaries such as $\text{Cu}_2\text{ZnSnS}_4$ to simpler ternary materials such as Cu_4SnS_4 , $\text{Cu}_4\text{Sn}_7\text{S}_{16}$,⁴⁵ or $\text{Cu}_2(\text{Sn,Ge})\text{S}_3$ (CTS) (see Ref. 46 for recent review). The motivation for CTS is that it has a similar diamond-derived structure as CZTS but one less element (Zn), and thus, less chance for cation disorder. For CTS, the efficiencies of 4%–5% in the Cu_2SnS_3 compound^{47,48} and 6%–7% in $\text{Cu}_2(\text{Sn,Ge})\text{S}_3$ alloy⁴⁹ have been demonstrated (Fig. 1a). However, the CTS structure is composed of two different tetrahedral motifs around S atoms (S- Cu_2Sn_2 and S- Cu_3Sn), leading to a different kind of structural disorder that may be equally detrimental to PV device performance.^{50,37} In addition, the structurally related metallic Cu_3SnS_4 compound⁵¹ and associated Cu_2SnS_3 - Cu_3SnS_4 alloys⁵² may be responsible for high apparent doping density and subpar open-circuit voltages observed in CTS to date.

Another option is to move away from the tetrahedrally bonded materials such as CIGS, CZTS, and CTS to absorbers with other structures such as Cu_3SbS_3 , Cu_3SbS_4 , and CuSbS_2 (see Ref. 53 for a recent review), as well as the Ag/Bi/Se variants. For example, the advantage of the layered chalcostibite CuSbS_2 (CAS) is that the coordination environments of Cu (tetrahedral) and Sb (three short bonds and three long bonds with S) are sufficiently different that the cation disorder is unlikely to occur. In addition, these materials tend to have higher absorption

coefficients than the tetrahedrally bonded counterparts,⁵⁴ albeit at the expense of slightly indirect bandgaps⁵⁵ and higher effective masses.⁵⁶ For CAS, which is the most studied material of the family, tunable properties⁵⁷ and suitable defect physics⁵⁸ have been demonstrated, but the solar cell efficiencies remain close to 1%,^{58,59,60,61} with one exception (3%)⁶². Higher efficiencies of 4 - 5% have been shown in the chalcostibite CuSbSe_2 absorber (Fig. 1a)^{63,64} and up to 6% in chemically related rocksalt-type AgBiS_2 .^{65,66} Overall, these recent results show promise of emerging multinary copper chalcogenides with unusual crystal structures for PV absorber applications and they call for more research in this family of materials.

Absorber materials related to MAPI

Efficiencies of hybrid organic-inorganic perovskites such as $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3 or MAPI) have increased rapidly from 5%–10%^{67,68,69,70} in 2012 to >20% today (Fig. 1a),⁷¹ which is faster than any other PV technology so far (see Refs. 72,73 for recent reviews). This success is accompanied by an unprecedented spike in research activity across the world (Fig. 1b), fueled by the ease of solution processing of the material. The key to efficiency success of this hybrid organic-inorganic PV (HOPV) technology appears to be the long photo-excited charge-carrier diffusion lengths: it is >1 μm in films⁷⁴ and >175 μm in crystals,⁷⁵ indicating recombination lifetimes much longer compared to other absorbers.⁷⁶ The remaining electrical (e.g., charge-carrier mobility, effective mass, doping density) or optical (absorption coefficient, bandgap) properties are comparable to other absorbers.⁷⁷ The logical question to ask is why the recombination lifetimes in HOPV perovskites so long? This question is particularly important to answer in the context of emerging perovskite-related materials, given the concerns about intrinsic thermal instability^{78,79} and environmental toxicity⁸⁰ of MAPI.⁸¹

Several hypotheses have been put forward about the origin of excellent charge-transport properties in MAPI (also see recent review in Ref. 82). One hypothesis is that the long recombination lifetimes in MAPI may result from all electronic states of abundant defects being close to the band edges (shallow).^{83,84} Such “defect tolerance” may originate from the unusual electronic structure with anti-bonding (instead of bonding) valence band maximum,⁸⁵ also present in many other materials with Cu^{1+} , In^{1+} , Pb^{2+} , Sn^{2+} , Sb^{3+} , and Bi^{3+} low-valent cations.⁸⁶ Another hypothesis is that the photoexcited charge carriers are screened by liquid-like molecular reorientation or “large polaron” formation,^{87,88} pointing to a special role of organic molecules in

MAPI. The long photoexcited carrier lifetimes in hybrid halide perovskites were also hypothesized to have a relativistic origin related to large Rashba splitting,^{89,90} leading to slightly indirect-bandgap character under illumination—and hence, suppressed radiative recombination of electrons and holes.⁹¹ One more effect that may contribute to the enhanced performance is ferroelectricity^{92,93} of MAPI due to its polar perovskite-type crystal structure (see Refs. 94,95 for recent reviews).

Following these hypotheses, many new PV materials related to $\text{CH}_3\text{NH}_3\text{PbI}_3$ have been studied recently, with different chemical elements and different crystal structures. On one hand, several Pb-free materials with perovskite crystal structure have been considered (see recent review in Ref. 96). These include different kinds of perovskites, both hybrid organic-inorganic ($\text{CH}_3\text{NH}_3\text{SnI}_3$,⁹⁷ $\text{CH}(\text{NH}_2)_2\text{GeI}_3$ ⁹⁸) and purely inorganic, including single- (e.g., CsSnCl_3 ,^{99,100} CsGeI_3 ^{98,101}) and double- (e.g., $\text{Cs}_2\text{BiAgCl}_6$, $\text{Cs}_2\text{BiAgBr}_6$)^{102,103} halide perovskites. Other perovskite chemistries have also been proposed, including oxides,^{104,105} sulfides/selenides,^{106,107} and nitrides.^{108,109} On the other hand, “perovskite-inspired” materials, with different crystal structures but similar chemical elements, have also been studied (see Ref. 110 for recent review). Examples include Bi/Sb-based halides (BiI_3 ,¹¹¹ $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$,¹¹² $(\text{K,Rb,Cs})_3\text{Bi}_2\text{I}_9$,¹¹³ $\text{Cs}_3\text{Sb}_2\text{I}_9$,³⁰) and mixed-anion compounds ($\text{Bi}(\text{S,Se})\text{I}$,^{114,115} BiOI ,^{114,116} SbSeI ^{117,118}). Currently, these materials show lower solar cell performance (~10%) compared to $\text{CH}_3\text{NH}_3\text{PbI}_3$ (~20%). Nevertheless, the wealth of the chemistries studied across the few publications gives the promise to discover new perovskite-related and perovskite-inspired PV solar cell absorber materials.

Summary, Conclusions, and Outlook

In summary, emerging photovoltaic absorber materials that have some similarities to existing PV technologies have been briefly reviewed, focusing on progress over 2014–2016. The general publication trends include a large spike of activity in research on perovskites and related materials (Fig. 1b), a gradual shift of attention from CZTS to other quaternary (AZTS, BCTS) and ternary (Cu_2SnS_3 , CuSbSe_2) absorbers (Fig. 1b inset), and increased scientific attention to pseudo-low-dimensional binary chalcogenide absorbers (SnS , Sb_2Se_3). The corresponding performance trends include the rise of perovskite efficiencies from ~10% to >20%, and the emergence of several new absorbers with ~5% efficiencies (Fig. 1a).

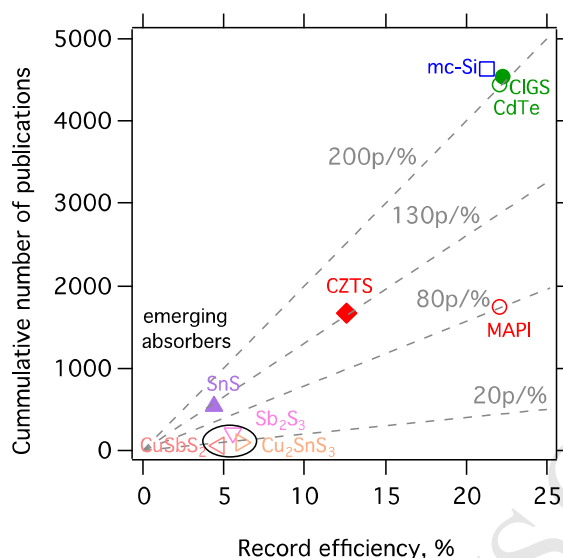


Fig. 2. Cumulative number of publications vs. record efficiency for each incumbent and emerging PV absorber technology from Fig. 1. The dashed lines correspond to an average number of publications required to raise the efficiency by 1%. The emerging PV absorbers are outlined by an ellipse.

These publication and performance trends are summarized in Fig. 2, which shows a scatter plot of the cumulative number of publications vs. record efficiency achieved to date for several incumbent and emerging PV absorber technologies. When plotted in these coordinates, the different PV technologies clearly cluster into several groups—including established absorbers (Si, CdTe, CIGS), emerging absorbers (Sb_2S_3 , Cu_2SnS_3 , CuSbSe_2), and absorbers that are in between (e.g., SnS, CZTS, MAPI). Note that the constant slopes in this correlation plot correspond to the number of papers required to increase the efficiency by 1%, and it ranges from ~20 papers for emerging absorbers to ~200 papers for established solar cell technologies. These numbers can easily be converted to estimates of global investment requirements if the approximate cost of research and development to publish one paper is known. However, the cost per publication may vary between individual technologies and between countries.

As an outlook, a separate topic that was not covered in this review is new PV absorbers for which high-performing prototype solar cells have *not* been reported. The first group includes new absorber chemistries, such as oxides,¹¹⁹ nitrides,¹²⁰ and mixed-anion compounds. The second group is emerging PV technologies that feature new absorber physics, including multiple

exciton generation,¹²¹ hot-carrier extraction,¹²² ferroelectric photovoltaics,⁹⁴ and so on. These two interesting research directions deserve more attention in the future.

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References

- ^{**1} D.M. Powell, R. Fu, K. Horowitz, P.A. Basore, M. Woodhouse, T. Buonassisi, The capital intensity of photovoltaics manufacturing: Barrier to scale and opportunity for innovation, *Energy Environ. Sci.* 8 (2015) 3395–3408. doi:10.1039/c5ee01509j.
- ² J. Andrade-Arvizu, M. Courel-Piedrahita, SnS-based thin film solar cells: Perspectives over the last 25 years, *J. Mater.* (2015). <http://link.springer.com/article/10.1007/s10854-015-3050-z> (accessed November 29, 2016).
- ³ N.K. Reddy, M. Devika, Review on tin (II) sulfide (SnS) material: synthesis, properties, and applications, *Crit. Rev. Solid.* (2015).
- ⁴ M. Devika, N.K. Reddy, K. Ramesh, K.R. Gunasekhar, E.S.R. Gopal, K.T.R. Reddy, Influence of annealing on physical properties of evaporated SnS films, *Semicond. Sci. Technol.* 21 (2006) 1125–1131. doi:10.1088/0268-1242/21/8/025.
- ⁵ H. Noguchi, A. Setiyadi, H. Tanamura, T. Nagatomo, O. Omoto, Characterization of vacuum-evaporated tin sulfide film for solar cell materials, *Sol. Energy Mater. Sol. Cells.* 35 (1994) 325–331. doi:10.1016/0927-0248(94)90158-9.
- ^{*6} P. Sinsermsuksakul, L. Sun, S.W. Lee, H.H. Park, S.B. Kim, C. Yang, R.G. Gordon, Overcoming efficiency limitations of SnS-based solar cells, *Adv. Energy Mater.* 4 (2014) 1400496. doi:10.1002/aenm.201400496.
- ⁷ P. Sinsermsuksakul, K. Hartman, S. Bok Kim, J. Heo, L. Sun, H. Hejin Park, R. Chakraborty, T. Buonassisi, R.G. Gordon, Enhancing the efficiency of SnS solar cells via band-offset engineering with a zinc oxysulfide buffer layer, *Appl. Phys. Lett.* 102 (2013) 53901. doi:10.1063/1.4789855.
- ⁸ L.A. Burton, A. Walsh, Band alignment in SnS thin-film solar cells: Possible origin of the low conversion efficiency, *Appl. Phys. Lett.* 102 (2013) 132111. doi:10.1063/1.4801313.
- ⁹ V. Steinmann, R. Chakraborty, P.H. Rekemeyer, K. Hartman, R.E. Brandt, A. Polizzotti, C. Yang, T. Moriarty, S. Gradečak, R.G. Gordon, T. Buonassisi, A two-step absorber deposition approach to overcome shunt losses in thin-film solar cells: Using tin sulfide as a proof-of-concept material system, *ACS Appl. Mater. Interfaces.* 8 (2016) 22664–22670. doi:10.1021/acsami.6b07198.
- ¹⁰ V. Steinmann, R.E. Brandt, R. Chakraborty, R. Jaramillo, M. Young, B.K. Ofori-Okai, C. Yang, A. Polizzotti, K.A. Nelson, R.G. Gordon, T. Buonassisi, The impact of sodium contamination in tin sulfide thin-film solar cells, *APL Mater.* 4 (2016) 26103. doi:10.1063/1.4941713.
- ¹¹ X. Liu, J. Chen, M. Luo, M. Leng, Z. Xia, Y. Zhou, S. Qin, D.-J. Xue, L. Lv, H. Huang, D. Niu, J. Tang, Thermal evaporation and characterization of Sb₂Se₃ thin film for substrate Sb₂Se₃/CdS solar cells, *ACS Appl. Mater. Interfaces.* 6 (2014) 10687–10695. doi:10.1021/am502427s.
- ^{**12} Y. Zhou, L. Wang, S. Chen, S. Qin, X. Liu, J. Chen, D.-J. Xue, M. Luo, Y. Cao, Y. Cheng, E.H. Sargent, J. Tang, Thin-film Sb₂Se₃ photovoltaics with oriented one-dimensional ribbons and benign grain boundaries, *Nat. Photonics.* 9 (2015) 409–415. doi:10.1038/nphoton.2015.78.
- ¹³ K. Zeng, D.-J. Xue, J. Tang, Antimony selenide thin-film solar cells, *Semicond. Sci. Technol.* 31 (2016) 63001. doi:10.1088/0268-1242/31/6/063001.
- ¹⁴ X. Liu, C. Chen, L. Wang, J. Zhong, M. Luo, J. Chen, D.-J. Xue, D. Li, Y. Zhou, J. Tang, Improving the performance of Sb₂Se₃ thin film solar cells over 4% by controlled addition of oxygen during film deposition, *Prog. Photovoltaics Res. Appl.* 23 (2015) 1828–1836. doi:10.1002/pip.2627.

- ¹⁵ L. Wang, M. Luo, S. Qin, X. Liu, J. Chen, B. Yang, M. Leng, D.-J. Xue, Y. Zhou, L. Gao, H. Song, J. Tang, Ambient CdCl₂ treatment on CdS buffer layer for improved performance of Sb₂Se₃ thin film photovoltaics, *Appl. Phys. Lett.* 107 (2015) 143902. doi:10.1063/1.4932544
- ¹⁶ O. Savadogo, K. Mandal, Low cost Schottky barrier solar cells fabricated on CdSe and Sb₂S₃ films chemically deposited with silicotungstic acid, *J. Electrochem. Soc.* (1994). <http://jes.ecsdl.org/content/141/10/2871.short> (accessed November 29, 2016).
- *¹⁷ D. Kim, S. Lee, M. Park, J. Kang, J. Heo, S. Im, Highly reproducible planar Sb₂S₃-sensitized solar cells based on atomic layer deposition, *Nanoscale*. (2014). <http://pubs.rsc.org/en/content/articlehtml/2014/nr/c4nr04148h> (accessed November 29, 2016).
- ¹⁸ S.-J. Moon, Y. Itzhaik, J.-H. Yum, S.M. Zakeeruddin, G. Hodes, M. Grätzel, Sb₂S₃-based mesoscopic solar cell using an organic hole conductor, *J. Phys. Chem. Lett.* 1 (2010) 1524–1527. doi:10.1021/jz100308q.
- ¹⁹ Y. Itzhaik, O. Niitsoo, M. Page, G. Hodes, Sb₂S₃-sensitized nanoporous TiO₂ solar cells, *J. Phys. Chem. C* 113 (2009) 4254–4256. doi:10.1021/jp900302b.
- ²⁰ V. Steinmann, R.E. Brandt, T. Buonassisi, Photovoltaics: Non-cubic solar cell materials, *Nat. Photonics*. 9 (2015) 355–357. doi:10.1038/nphoton.2015.85.
- ²¹ C. Xia, J. Li, Recent advances in optoelectronic properties and applications of two-dimensional metal chalcogenides, *J. Semicond.* 37 (2016) 51001. doi:10.1088/1674-4926/37/5/051001.
- *²² Q.H. Wang, K. Kalantar-Zadeh, A. Kis, J.N. Coleman, M.S. Strano, Electronics and optoelectronics of two-dimensional transition metal dichalcogenides, *Nat. Nanotechnol.* 7 (2012) 699–712. doi:10.1038/nnano.2012.193.
- ²³ M.-Y. Li, Y. Shi, C.-C. Cheng, L.-S. Lu, Y.-C. Lin, H.-L. Tang, M.-L. Tsai, C.-W. Chu, K.-H. Wei, J.-H. He, W.-H. Chang, K. Suenaga, L.-J. Li, Epitaxial growth of a monolayer WSe₂-MoS₂ lateral p-n junction with an atomically sharp interface, *Science* (80-.). 349 (2015).
- ²⁴ B. Radisavljevic, A. Kis, Mobility engineering and a metal–insulator transition in monolayer MoS₂, *Nat. Mater.* 12 (2013) 815–820. doi:10.1038/nmat3687.
- ²⁵ K.L. Chopra, S.R. Das, Cu₂S based solar cells, in: *Thin Film Solar Cells*, Springer US, Boston, MA, 1983: pp. 349–390. doi:10.1007/978-1-4899-0418-8_7.
- ²⁶ A.B. Wong, S. Brittman, Y. Yu, N.P. Dasgupta, P. Yang, Core–shell CdS–Cu₂S nanorod array solar cells, *Nano Lett.* 15 (2015) 4096–4101. doi:10.1021/acs.nanolett.5b01203.
- ²⁷ A. Ennaoui, H. Tributsch, Iron sulphide solar cells. *Solar cells* 13 (1984) 197
- ²⁸ L. Luo, W. Luan, B. Yuan, C. Zhang, L. Jin, High efficient and stable solid solar cell: Based on FeS₂ nanocrystals and P3HT: PCBM, *Energy Procedia*. 75 (2015) 2181–2186. doi:10.1016/j.egypro.2015.07.368.
- ²⁹ X. Liu, Y. Feng, H. Cui, F. Liu, X. Hao, G. Conibeer, D.B. Mitzi, M. Green, The current status and future prospects of kesterite solar cells: A brief review, *Prog. Photovoltaics Res. Appl.* 24 (2016) 879–898. doi:10.1002/pip.2741.
- ³⁰ A. Polizzotti, I.L. Repins, R. Noufi, S.-H. Wei, D.B. Mitzi, The state and future prospects of kesterite photovoltaics, *Energy Environ. Sci.* 6 (2013) 3171. doi:10.1039/c3ee41781f.
- ³¹ K. Ito, ed., *Copper Zinc Tin Sulfide-Based Thin-Film Solar Cells*, John Wiley & Sons Ltd, Chichester, UK, 2014. doi:10.1002/9781118437865.
- ³² T.K. Todorov, K.B. Reuter, D.B. Mitzi, High-efficiency solar cell with earth-abundant liquid-processed absorber, *Adv. Mater.* 22 (2010) E156–E159. doi:10.1002/adma.200904155.
- *³³ W. Wang, M.T. Winkler, O. Gunawan, T. Gokmen, T.K. Todorov, Y. Zhu, D.B. Mitzi, Device characteristics of CZTSSe thin-film solar cells with 12.6% efficiency, *Adv. Energy Mater.* 4 (2014) 1301465. doi:10.1002/aenm.201301465.
- ³⁴ Y.S. Lee, T. Gershon, O. Gunawan, T.K. Todorov, T. Gokmen, Y. Virgus, S. Guha, Cu₂ZnSnSe₄ thin-film solar cells by thermal co-evaporation with 11.6% efficiency and improved minority carrier diffusion length, *Adv. Energy Mater.* 5 (2015) 1401372. doi:10.1002/aenm.201401372.
- ³⁵ M. Kumar, A. Dubey, N. Adhikari, S. Venkatesan, Q. Qiao, Strategic review of secondary phases, defects and defect-complexes in kesterite CZTS–Se solar cells, *Energy Environ. Sci.* 8 (2015) 3134–3159. doi:10.1039/C5EE02153G.
- *³⁶ J.J.S. Scragg, L. Choubrac, A. Lafond, T. Ericson, C. Platzer-Björkman, A low-temperature order-disorder transition in Cu₂ZnSnS₄ thin films, *Appl. Phys. Lett.* 104 (2014) 41911. doi:10.1063/1.4863685.
- **³⁷ P. Zawadzki, A. Zakutayev, S. Lany, Entropy-driven clustering in tetrahedrally bonded multinary materials, *Phys. Rev. Appl.* 3 (2015). doi:10.1103/PhysRevApplied.3.034007.

- ³⁸ J. Kim, H. Hiroi, T.K. Todorov, O. Gunawan, M. Kuwahara, T. Gokmen, D. Nair, M. Hopstaken, B. Shin, Y.S. Lee, W. Wang, H. Sugimoto, D.B. Mitzi, High efficiency $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ solar cells by applying a double $\text{In}_2\text{S}_3/\text{CdS}$ emitter, *Adv. Mater.* 26 (2014) 7427–7431. doi:10.1002/adma.201402373.
- ³⁹ S. Siol, T.P. Dhakal, G.S. Gudavalli, P.P. Rajbhandari, C. DeHart, L.L. Baranowski, A. Zakutayev, Combinatorial reactive sputtering of In_2S_3 as an alternative contact layer for thin film solar cells, *ACS Appl. Mater. Interfaces.* 8 (2016) 14004–14011. doi:10.1021/acsami.6b02213.
- ⁴⁰ C. Yan, F. Liu, N. Song, B.K. Ng, J.A. Stride, A. Tadich, X. Hao, Band alignments of different buffer layers (CdS , $\text{Zn}(\text{O},\text{S})$, and In_2S_3) on $\text{Cu}_2\text{ZnSnS}_4$, *Appl. Phys. Lett.* 104 (2014) 173901. doi:10.1063/1.4873715.
- ^{*41} E. Chagarov, K. Sardashti, A.C. Kummel, Y.S. Lee, R. Haight, T.S. Gershon, $\text{Ag}_2\text{ZnSn}(\text{S},\text{Se})_4$: A highly promising absorber for thin film photovoltaics, *J. Chem. Phys.* 144 (2016) 104704. doi:10.1063/1.4943270.
- ⁴² D. Shin, B. Saparov, T. Zhu, W.P. Huhn, V. Blum, D.B. Mitzi, $\text{BaCu}_2\text{Sn}(\text{S},\text{Se})_4$: Earth-abundant chalcogenides for thin-film photovoltaics, *Chem. Mater.* 28 (2016) 4771–4780. doi:10.1021/acs.chemmater.6b01832.
- ⁴³ J. Ge, Y. Yu, Y. Yan, Earth-abundant orthorhombic $\text{BaCu}_2\text{Sn}(\text{Se}_x\text{S}_{1-x})_4$ ($x \approx 0.83$) thin film for solar energy conversion, *ACS Energy Lett.* 1 (2016) 583–588. doi:10.1021/acsenergylett.6b00324.
- ⁴⁴ J. Heo, R. Ravichandran, C.F. Reidy, J. Tate, J.F. Wager, D.A. Keszler, Design meets nature: Tetrahedrite solar absorbers, *Adv. Energy Mater.* 5 (2015) 1401506. doi:10.1002/aenm.201401506.
- ⁴⁵ P. Zawadzki, L.L. Baranowski, H. Peng, E.S. Toberer, D.S. Ginley, W. Tumas, A. Zakutayev, S. Lany, Evaluation of photovoltaic materials within the Cu-Sn-S family, *Appl. Phys. Lett.* 103 (2013). doi:10.1063/1.4851896.
- ⁴⁶ L.L. Baranowski, P. Zawadzki, S. Lany, E.S. Toberer, A. Zakutayev, A review of defects and disorder in multinary tetrahedrally bonded semiconductors, *Semicond. Sci. Technol.* 31 (2016) 123004. doi:10.1088/0268-1242/31/12/123004.
- ⁴⁷ M. Nakashima, J. Fujimoto, T. Yamaguchi, Cu_2SnS_3 thin-film solar cells fabricated by sulfurization from $\text{NaF}/\text{Cu}/\text{Sn}$ stacked precursor, *Appl. Phys.* (2015). <http://iopscience.iop.org/article/10.7567/APEX.8.042303/meta> (accessed November 29, 2016).
- ⁴⁸ A. Kanai, K. Toyonaga, K. Chino, Fabrication of Cu_2SnS_3 thin-film solar cells with power conversion efficiency of over 4%, *Japanese J.* (2015). <http://iopscience.iop.org/article/10.7567/JJAP.54.08KC06/meta> (accessed November 29, 2016).
- ^{*49} M. Umehara, Y. Takeda, T. Motohiro, T. Sakai, $\text{Cu}_2\text{Sn}_{1-x}\text{Ge}_x\text{S}_3$ ($x = 0.17$) thin-film solar cells with high conversion efficiency of 6.0%, *Appl. Phys.* (2013). <http://iopscience.iop.org/article/10.7567/APEX.6.045501/meta> (accessed November 29, 2016).
- ⁵⁰ L.L. Baranowski, K. McLaughlin, P. Zawadzki, S. Lany, A. Norman, H. Hempel, R. Eichberger, T. Unold, E.S. Toberer, A. Zakutayev, Effects of disorder on carrier transport in Cu_2SnS_3 , *Phys. Rev. Appl.* 4 (2015). doi:10.1103/PhysRevApplied.4.044017.
- ^{*51} L.L. Baranowski, P. Zawadzki, S. Christensen, D. Nordlund, S. Lany, A.C. Tamboli, L. Gedvilas, D.S. Ginley, W. Tumas, E.S. Toberer, A. Zakutayev, Control of doping in Cu_2SnS_3 through defects and alloying, *Chem. Mater.* 26 (2014) 4951–4959. doi:10.1021/cm501339v.
- ⁵² P. Zawadzki, A. Zakutayev, S. Lany, Extended antisite defects in tetrahedrally bonded semiconductors, *Phys. Rev. B - Condens. Matter Mater. Phys.* 92 (2015). doi:10.1103/PhysRevB.92.201204.
- ⁵³ B. Krishnan, S. Shaji, R. Ernesto Ornelas, Progress in development of copper antimony sulfide thin films as an alternative material for solar energy harvesting, *J. Mater. Sci. Mater. Electron.* 26 (2015) 4770–4781. doi:10.1007/s10854-015-3092-2.
- ⁵⁴ L. Yu, R.S. Kokenyesi, D.A. Keszler, A. Zunger, Inverse design of high absorption thin-film photovoltaic materials, *Adv. Energy Mater.* 3 (2013) 43–48. doi:10.1002/aenm.201200538.
- ⁵⁵ D.J. Temple, A.B. Kehoe, J.P. Allen, G.W. Watson, D.O. Scanlon, Geometry, electronic structure, and bonding in CuMCh_2 ($M = \text{Sb}, \text{Bi}$; $\text{Ch} = \text{S}, \text{Se}$): Alternative solar cell absorber materials?, *J. Phys. Chem. C.* 116 (2012) 7334–7340. doi:10.1021/jp300862v.
- ⁵⁶ J.T.R. Dufton, A. Walsh, P.M. Panchmatia, L.M. Peter, D. Colombara, M.S. Islam, Structural and electronic properties of CuSbS_2 and CuBiS_2 : Potential absorber materials for thin-film solar cells, *Phys. Chem. Chem. Phys.* 14 (2012) 7229. doi:10.1039/c2cp40916j.
- ^{*57} A.W. Welch, P.P. Zawadzki, S. Lany, C.A. Wolden, A. Zakutayev, Self-regulated growth and tunable properties of CuSbS_2 solar absorbers, *Sol. Energy Mater. Sol. Cells.* 132 (2014) 499–506. doi:10.1016/j.solmat.2014.09.041.
- ^{*58} B. Yang, L. Wang, J. Han, Y. Zhou, H. Song, S. Chen, J. Zhong, L. Lv, D. Niu, J. Tang, CuSbS_2 as a promising earth-abundant photovoltaic absorber material: A combined theoretical and experimental study, *Chem. Mater.* 26 (2014) 3135–3143. doi:10.1021/cm500516v.

- ⁵⁹ F.W. de Souza Lucas, A.W. Welch, L.L. Baranowski, P.C. Dippo, H. Hempel, T. Unold, R. Eichberger, B. Blank, U. Rau, L.H. Mascaro, A. Zakutayev, Effects of Thermochemical Treatment on CuSbS₂ Photovoltaic Absorber Quality and Solar Cell Reproducibility, *J. Phys. Chem. C*. 120 (2016) 18377–18385. doi:10.1021/acs.jpcc.6b04206.
- ⁶⁰ Y. Rodríguez-Lazcano, M.T.S. Nair, P.K. Nair, CuSbS₂ thin film formed through annealing chemically deposited Sb₂S₃–CuS thin films, *J. Cryst. Growth*. 223 (2001) 399–406. doi:10.1016/S0022-0248(01)00672-8.
- ⁶¹ A.W. Welch, L.L. Baranowski, P. Zawadzki, C. Dehart, S. Johnston, S. Lany, C.A. Wolden, A. Zakutayev, Accelerated development of CuSbS₂ thin film photovoltaic device prototypes, *Prog. Photovoltaics Res. Appl.* (2016). doi:10.1002/pip.2735.
- ⁶² W. Septina, S. Ikeda, Y. Iga, T. Harada, M. Matsumura, Thin film solar cell based on CuSbS₂ absorber fabricated from an electrochemically deposited metal stack, *Thin Solid Films*. 550 (2014) 700–704. doi:10.1016/j.tsf.2013.11.046.
- ⁶³ A. Welch, L. Baranowski, P. Zawadzki, CuSbSe₂ photovoltaic devices with 3% efficiency, *Appl. Phys.* (2015). <http://iopscience.iop.org/article/10.7567/APEX.8.082301/meta> (accessed November 29, 2016).
- ^{**64} A.W. Welch, L. L. Baranowski, H. Peng, H. Hempel R. Eichberger T. Unold, S. Lany, C. Wolden, A. Zakutayev Trade-offs in thin film solar cells with layered chalcostibnite photovoltaic absorbers, under review
- ⁶⁵ D.L. Rodríguez Vela, B. Krishnan, J.A. Aguilar Martínez, S.L. Loredó, S. Shaji, AgSb(S_xSe_{1-x})₂ thin films by rapid thermal processing of Sb₂S₃-Ag-Se thin films for photovoltaic applications, *Phys. Status Solidi*. 13 (2016) 47–52. doi:10.1002/pssc.201510117.
- ^{*66} M. Bernechea, N.C. Miller, G. Xercavins, D. So, A. Stavrinadis, G. Konstantatos, Solution-processed solar cells based on environmentally friendly AgBiS₂ nanocrystals, *Nat. Photonics*. 10 (2016) 521–525. doi:10.1038/nphoton.2016.108.
- ⁶⁷ A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, Organometal halide perovskites as visible-light sensitizers for photovoltaic cells, *J. Am. Chem. Soc.* 131 (2009) 6050–6051. doi:10.1021/ja809598r.
- ⁶⁸ L. Etgar, P. Gao, Z. Xue, Q. Peng, A.K. Chandiran, B. Liu, M.K. Nazeeruddin, M. Grätzel, Mesoscopic CH₃NH₃PbI₃/TiO₂ heterojunction solar cells, *J. Am. Chem. Soc.* 134 (2012) 17396–17399. doi:10.1021/ja307789s.
- ⁶⁹ H. Kim, C. Lee, J. Im, K. Lee, T. Moehl, A. Marchioro, S. Moon, R. Humphry-baker, J.-H. Yum, J.E. Moser, M. Gra, All-solid-state submicron thin film, *Sci. Rep.* 591 (2012) 1–7. doi:10.1038/srep00591.
- ⁷⁰ M.M. Lee, J. Teuscher, T. Miyasaka, T.N. Murakami, H.J. Snaith, Efficient hybrid solar cells based on meso-structured organometal halide perovskites, *Science* (80-.). 338 (2012).
- ⁷¹ M. Saliba, T. Matsui, J.-Y. Seo, K. Domanski, J.-P. Correa-Baena, M.K. Nazeeruddin, S.M. Zakeeruddin, W. Tress, A. Abate, A. Hagfeldt, M. Grätzel, Cesium-containing triple cation perovskite solar cells: Improved stability, reproducibility and high efficiency, *Energy Environ. Sci.* 9 (2016) 1989–1997. doi:10.1039/C5EE03874J.
- ⁷² M.A. Green, A. Ho-Baillie, H.J. Snaith, The emergence of perovskite solar cells, *Nat. Photonics*. 8 (2014) 506–514. doi:10.1038/nphoton.2014.134.
- ⁷³ B. Saparov, F. Hong, J.-P. Sun, H.-S. Duan, W. Meng, S. Cameron, I.G. Hill, Y. Yan, D.B. Mitzi, Thin-film preparation and characterization of Cs₃Sb₂I₉: A lead-free layered perovskite semiconductor, *Chem. Mater.* 27 (2015) 5622–5632. doi:10.1021/acs.chemmater.5b01989.
- ⁷⁴ S.D. Stranks, G.E. Eperon, G. Grancini, C. Menelaou, M.J.P. Alcocer, T. Leijtens, L.M. Herz, A. Petrozza, H.J. Snaith, Electron-hole diffusion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber, *Science* (80-.). 342 (2013).
- ^{*75} Q. Dong, Y. Fang, Y. Shao, P. Mulligan, J. Qiu, L. Cao, J. Huang, Electron-hole diffusion lengths >175 μm in solution-grown CH₃NH₃PbI₃ single crystals, *Science* (80-.). 347 (2015).
- ⁷⁶ S. Johnston, K. Zaunbrecher, R. Ahrenkiel, D. Kuciauskas, D. Albin, W. Metzger, Simultaneous measurement of minority-carrier lifetime in single-crystal CdTe using three transient decay techniques, *IEEE J. Photovoltaics*. 4 (2014) 1295–1300. doi:10.1109/JPHOTOV.2014.2339491.
- ⁷⁷ W.-J. Yin, T. Shi, Y. Yan, Unique properties of halide perovskites as possible origins of the superior solar cell performance, *Adv. Mater.* 26 (2014) 4653–4658. doi:10.1002/adma.201306281.
- ^{*78} G.P. Nagabhushana, R. Shivaramaiah, A. Navrotsky, Direct calorimetric verification of thermodynamic instability of lead halide hybrid perovskites., *Proc. Natl. Acad. Sci. U. S. A.* 113 (2016) 7717–21. doi:10.1073/pnas.1607850113.
- ⁷⁹ Y.-Y. Zhang, S. Chen, P. Xu, H. Xiang, X.-G. Gong, A. Walsh, S.-H. Wei, Intrinsic instability of the hybrid halide perovskite semiconductor CH₃NH₃PbI₃, (2015). <http://arxiv.org/abs/1506.01301> (accessed November 29, 2016).
- ⁸⁰ A. Babayigit, A. Ethirajan, M. Muller, B. Conings, Toxicity of organometal halide perovskite solar cells, *Nat. Mater.* 15 (2016) 247–251. doi:10.1038/nmat4572.

- ⁸¹ T.A Berhe, W.-N. Su, C.-H. Chen, C.-J. Pan, J.-H. Cheng, H.-M. Chen, M.-C. Tsai, L.-Y. Chen, A.A. Dubale, B.-J. Hwang, Organometal halide perovskite solar cells: Degradation and stability. *Energy & Environmental Science*. 9, no. 2 (2016) 323–356.
- ⁸² T.M. Brenner, D.A. Egger, L. Kronik, G. Hodes, D. Cahen, Hybrid organic-inorganic perovskites: Low-cost semiconductors with intriguing charge-transport properties. *Nature Reviews Materials*. 1 (2016) 15007.
- ⁸³ W.-J. Yin, T. Shi, Y. Yan, Unusual defect physics in $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cell absorber, *Appl. Phys. Lett.* 104 (2014) 63903. doi:10.1063/1.4864778.
- ⁸⁴ A. Walsh, D.O. Scanlon, S. Chen, X.G. Gong, S.-H. Wei, Self-regulation mechanism for charged point defects in hybrid halide perovskites, *Angew. Chemie*. 127 (2015) 1811–1814. doi:10.1002/ange.201409740.
- ^{*85} A. Zakutayev, C.M. Caskey, A.N. Fioretti, D.S. Ginley, J. Vidal, V. Stevanovic, E. Tea, S. Lany, Defect tolerant semiconductors for solar energy conversion, *J. Phys. Chem. Lett.* 5 (2014) 1117–1125. doi:10.1021/jz5001787.
- ^{**86} R. Brandt, V. Stevanović, D. Ginley, Identifying defect-tolerant semiconductors with high minority-carrier lifetimes: Beyond hybrid lead halide perovskites, *MRS*. (2015).
http://journals.cambridge.org/abstract_S2159685915000269 (accessed November 29, 2016).
- ⁸⁷ X.-Y. Zhu, V. Podzorov, Charge carriers in hybrid organic–inorganic lead halide perovskites might be protected as large polarons, *J. Phys. Chem. Lett.* 6 (2015) 4758–4761. doi:10.1021/acs.jpcclett.5b02462.
- ^{*88} H. Zhu, K. Miyata, Y. Fu, J. Wang, P.P. Joshi, D. Niesner, K.W. Williams, S. Jin, X.-Y. Zhu, Screening in crystalline liquids protects energetic carriers in hybrid perovskites, *Science* (80-.). 353 (2016).
- ⁸⁹ F. Zheng, L.Z. Tan, S. Liu, A.M. Rappe, Rashba spin–orbit coupling enhanced carrier lifetime in $\text{CH}_3\text{NH}_3\text{PbI}_3$, *Nano Lett.* 15 (2015) 7794–7800. doi:10.1021/acs.nanolett.5b01854.
- ⁹⁰ D. Niesner, M. Wilhelm, I. Levchuk, A. Osvet, S. Shrestha, M. Batentschuk, C. Brabec, T. Fauster, Giant Rashba splitting in $\text{CH}_3\text{NH}_3\text{PbBr}_3$ organic-inorganic perovskite, *Phys. Rev. Lett.* 117 (2016) 126401. doi:10.1103/PhysRevLett.117.126401.
- ^{*91} P. Azarhoosh, S. McKechnie, J.M. Frost, A. Walsh, M. van Schilfgaarde, Research update: Relativistic origin of slow electron-hole recombination in hybrid halide perovskite solar cells, *APL Mater.* 4 (2016) 91501. doi:10.1063/1.4955028.
- ⁹² S. Liu, F. Zheng, N.Z. Koocher, H. Takenaka, F. Wang, A.M. Rappe, Ferroelectric domain wall induced band gap reduction and charge separation in organometal halide perovskites, *J. Phys. Chem. Lett.* 6 (2015) 693–699. doi:10.1021/jz502666j.
- ⁹³ J.M. Frost, K.T. Butler, F. Brivio, C.H. Hendon, M. van Schilfgaarde, A. Walsh, Atomistic origins of high-performance in hybrid halide perovskite solar cells, *Nano Lett.* 14 (2014) 2584–2590. doi:10.1021/nl500390f.
- ^{*94} K.T. Butler, J.M. Frost, A. Walsh, Ferroelectric materials for solar energy conversion: Photoferroics revisited, *Energy Environ. Sci.* 8 (2015) 838–848. doi:10.1039/C4EE03523B.
- ⁹⁵ Z. Fan, K. Sun, J. Wang, Perovskites for photovoltaics: A combined review of organic–inorganic halide perovskites and ferroelectric oxide perovskites, *J. Mater. Chem. A*. 3 (2015) 18809–18828. doi:10.1039/C5TA04235F.
- ⁹⁶ W.-J. Yin, J.-H. Yang, J. Kang, Y. Yan, S.-H. Wei, Halide perovskite materials for solar cells: A theoretical review, *J. Mater. Chem. A*. 3 (2015) 8926–8942. doi:10.1039/C4TA05033A.
- ⁹⁷ C.C. Stoumpos, C.D. Malliakas, M.G. Kanatzidis, Semiconducting tin and lead iodide perovskites with organic cations: Phase transitions, high mobilities, and near-infrared photoluminescent properties, *Inorg. Chem.* 52 (2013) 9019–9038. doi:10.1021/ic401215x.
- ⁹⁸ T. Krishnamoorthy, H. Ding, C. Yan, W.L. Leong, T. Baikie, Z. Zhang, M. Sherburne, S. Li, M. Asta, N. Mathews, S.G. Mhaisalkar, Lead-free germanium iodide perovskite materials for photovoltaic applications, *J. Mater. Chem. A*. 3 (2015) 23829–23832. doi:10.1039/C5TA05741H.
- ⁹⁹ I. Chung, B. Lee, J. He, R.P.H. Chang, M.G. Kanatzidis, All-solid-state dye-sensitized solar cells with high efficiency, *Nature*. 485 (2012) 486–489. doi:10.1038/nature11067.
- ¹⁰⁰ L. Huang, W.R.L. Lambrecht, Electronic band structure, phonons, and exciton binding energies of halide perovskites CsSnCl_3 , CsSnBr_3 , and CsSnI_3 , *Phys. Rev. B*. 88 (2013) 165203. doi:10.1103/PhysRevB.88.165203.
- ¹⁰¹ W. Ming, H. Shi, M.H. Du, Large dielectric constant, high acceptor density, and deep electron traps in perovskite solar cell material CsGeI_3 , *J. Mater. Chem. A*. 0 (2016) 1–7. doi:10.1039/C6TA04685A.
- ¹⁰² G. Volonakis, M.R. Filip, A.A. Haghighirad, N. Sakai, B. Wenger, H.J. Snaith, F. Giustino, Lead-free halide double perovskites via heterovalent substitution of noble metals, *J. Phys. Chem. Lett.* 7 (2016) 1254–1259. doi:10.1021/acs.jpcclett.6b00376.

- ¹⁰³ A.H. Slavney, T. Hu, A.M. Lindenberg, H.I. Karunadasa, A bismuth-halide double perovskite with long carrier recombination lifetime for photovoltaic applications, *J. Am. Chem. Soc.* 138 (2016) 2138–2141. doi:10.1021/jacs.5b13294.
- ¹⁰⁴ I. Grinberg, D.V. West, M. Torres, G. Gou, D.M. Stein, L. Wu, G. Chen, E.M. Gallo, A.R. Akbashev, P.K. Davies, J.E. Spanier, A.M. Rappe, Perovskite oxides for visible-light-absorbing ferroelectric and photovoltaic materials, *Nature*. 503 (2013) 509–512. doi:10.1038/nature12622.
- *¹⁰⁵ R. Nechache, C. Harnagea, S. Li, L. Cardenas, W. Huang, J. Chakrabartty, F. Rosei, Bandgap tuning of multiferroic oxide solar cells, *Nat. Photonics*. 9 (2014) 61–67. doi:10.1038/nphoton.2014.255.
- ¹⁰⁶ Y.-Y. Sun, M.L. Agiorgousis, P. Zhang, S. Zhang, Chalcogenide perovskites for photovoltaics, *Nano Lett.* 15 (2015) 581–585. doi:10.1021/nl504046x.
- ¹⁰⁷ W. Meng, B. Saparov, F. Hong, J. Wang, D.B. Mitzi, Y. Yan, Alloying and defect control within chalcogenide perovskites for optimized photovoltaic application, *Chem. Mater.* 28 (2016) 821–829. doi:10.1021/acs.chemmater.5b04213.
- *¹⁰⁸ R. Sarmiento-Pérez, T.F.T. Cerqueira, S. Körbel, S. Botti, M.A.L. Marques, Prediction of stable nitride perovskites, *Chem. Mater.* 27 (2015) 5957–5963. doi:10.1021/acs.chemmater.5b02026.
- ¹⁰⁹ A. Fuertes, Chemistry and applications of oxynitride perovskites, *J. Mater. Chem.* 22 (2012) 3293–3299. doi:10.1039/C2JM13182J.
- ¹¹⁰ R. L. Z. Hoy, Perovskite-inspired photovoltaic materials: Toward best practices in materials characterization and calculations, under review
- ¹¹¹ R.E. Brandt, R.C. Kurchin, R.L.Z. Hoye, J.R. Poindexter, M.W.B. Wilson, S. Sulekar, F. Lenahan, P.X.T. Yen, V. Stevanović, J.C. Nino, M.G. Bawendi, T. Buonassisi, Investigation of bismuth triiodide (BiI₃) for photovoltaic applications, *J. Phys. Chem. Lett.* 6 (2015) 4297–4302. doi:10.1021/acs.jpcclett.5b02022.
- ¹¹² M. Lyu, J.-H. Yun, M. Cai, Y. Jiao, P. V. Bernhardt, M. Zhang, Q. Wang, A. Du, H. Wang, G. Liu, L. Wang, Organic–inorganic bismuth (III)-based material: A lead-free, air-stable and solution-processable light-absorber beyond organolead perovskites, *Nano Res.* 9 (2016) 692–702. doi:10.1007/s12274-015-0948-y.
- ¹¹³ A.J. Lehner, D.H. Fabini, H.A. Evans, C.-A. Hébert, S.R. Smock, J. Hu, H. Wang, J.W. Zwanziger, M.L. Chabynyc, R. Seshadri, Crystal and electronic structures of complex bismuth iodides A₃Bi₂I₉ (A = K, Rb, Cs) related to perovskite: Aiding the rational design of photovoltaics, *Chem. Mater.* 27 (2015) 7137–7148. doi:10.1021/acs.chemmater.5b03147.
- ¹¹⁴ H. Shi, W. Ming, M.-H. Du, Bismuth chalcogenides and oxyhalides as optoelectronic materials, *Phys. Rev. B*. 93 (2016) 104108. doi:10.1103/PhysRevB.93.104108.
- ¹¹⁵ A.M. Ganose, K.T. Butler, A. Walsh, D.O. Scanlon, Relativistic electronic structure and band alignment of BiSI and BiSeI: Candidate photovoltaic materials, *J. Mater. Chem. A*. 4 (2016) 2060–2068. doi:10.1039/C5TA09612J.
- ¹¹⁶ A.M. Ganose, M. Cuff, K.T. Butler, A. Walsh, D.O. Scanlon, Interplay of orbital and relativistic effects in bismuth oxyhalides: BiOF, BiOCl, BiOBr, and BiOI, *Chem. Mater.* 28 (2016) 1980–1984. doi:10.1021/acs.chemmater.6b00349.
- ¹¹⁷ A.C. Wibowo, C.D. Malliakas, Z. Liu, J.A. Peters, M. Sebastian, D.Y. Chung, B.W. Wessels, M.G. Kanatzidis, Photoconductivity in the chalcogenide semiconductor, SbSeI: A new candidate for hard radiation detection, *Inorg. Chem.* 52 (2013) 7045–7050. doi:10.1021/ic401086r.
- ¹¹⁸ K.T. Butler, S. McKechnie, P. Azarhoosh, M. van Schilfgaarde, D.O. Scanlon, A. Walsh, Quasi-particle electronic band structure and alignment of the V-VI-VII semiconductors SbSI, SbSBr, and SbSeI for solar cells, *Appl. Phys. Lett.* 108 (2016) 112103. doi:10.1063/1.4943973.
- **¹¹⁹ S. Rühle, A.Y. Anderson, H.-N. Barad, B. Kupfer, Y. Bouhadana, E. Rosh-Hodesh, A. Zaban, All-oxide photovoltaics, *J. Phys. Chem. Lett.* 3 (2012) 3755–3764. doi:10.1021/jz3017039.
- ¹²⁰ A. Zakutayev, Design of nitride semiconductors for solar energy conversion, *J. Mater. Chem. A*. (2016). <http://pubs.rsc.org/en/content/articlehtml/2016/ta/c5ta09446a> (accessed April 30, 2016).
- ¹²¹ M.C. Beard, Multiple exciton generation in semiconductor quantum dots, *J. Phys. Chem. Lett.* 2 (2011) 1282–1288. doi:10.1021/jz200166y.
- ¹²² D. König, K. Casalenuovo, Y. Takeda, G. Conibeer, J.F. Guillemoles, R. Patterson, L.M. Huang, M.A. Green, Hot carrier solar cells: Principles, materials and design, *Phys. E Low-Dimensional Syst. Nanostructures*. 42 (2010) 2862–2866. doi:10.1016/j.physe.2009.12.032.

