

The Steady Rise of Kesterite Solar Cells

Could slow and steady win the race to sustainable energy generation? While perovskite solar cells are currently at the forefront of photovoltaic research activity, we argue in this Viewpoint that devices based on the mineral kesterite could be the dark horse of next-generation solar energy conversion. The most urgent research challenges for this technology are outlined.

Thin-film photovoltaic (PV) technologies offer an economically promising and flexible means to harness solar energy.¹ Compared to silicon, the use of materials that absorb sunlight strongly allows for less material to be used, lowering cost and opening up more possibilities for integrating the solar cell modules with buildings. Only a small number of commercial thin-film technologies have achieved power conversion efficiencies (PCEs) greater than 20%: CdTe and Cu(In,Ga)-(S,Se)₂ (CIGS) have champion device PCEs of 21%.² The toxicity of cadmium and competition in the supply of indium are limiting factors for the large-scale utilization of these technologies.

In the emerging thin-film PV market, hybrid halide perovskites such as methylammonium lead iodide (CH₃NH₃PbI₃) have received an immense amount of research interest, with over 3000 publications in relation to solar cells since 2009. The efficiency of laboratory-scale halide perovskite devices has risen sharply, especially over the course of the first 500 publications focused on the material (see Figure 1). The current record for a perovskite solar cell is 22.1%.² Progress in PCE with respect to the number of publications on this material is beginning to plateau. Furthermore, stability issues and concerns over the lead content of halide perovskites remain as challenges for the commercialization of this technology.³

Solar cells based on the kesterite mineral structure, including Cu₂ZnSnS₄ (CZTS), Cu₂ZnSnSe₄ (CZTSe), and their alloys Cu₂ZnSn(S_xSe_{1-x})₄ (CZTSSe), stand out from other thin-film PV candidates for being composed of earth-abundant and nontoxic elements. Since the first kesterite solar cell was fabricated in 1997, the PCE of the champion device has risen from 0.66%⁴ to the current certified record of 12.6% set in 2013,⁵ with a 13.8% small-area device reported in late 2016.⁶ These efficiencies fall far below the 28% predicted for this technology from the Shockley–Queisser limit. However, kesterites have achieved relatively little attention, with fewer than 1000 publications to date related to photovoltaic applications. A directed focus in research effort may see this sustainable PV technology achieve PCEs approaching those of hybrid perovskites or commercial thin-film PV technologies, perhaps as well with much improved operational stability.

There are numerous synthetic routes to kesterite thin films, including both vacuum-based deposition and nonvacuum-based solution processing. Nonvacuum approaches are desirable for scalability and feasible industrial production, including electrodeposition,^{7–10} nanocrystal dispersion,^{11–13} hydrazine-based deposition,¹⁴ and other pure-solution approaches.^{15–17} The current champion CZTSSe solar cell was fabricated using the hydrazine-based solution method developed at the IBM T. J.

Watson Research Center.⁵ Most record devices since 1997 have been produced by solution-based film deposition approaches,¹⁸ alluding to the potential for large-scale fabrication, which is required to support a terawatt PV industry.

The relatively low efficiency of kesterite-based solar cells is attributed to a large deficit in the open-circuit voltage (V_{OC}) relative to the band gap of the absorber layer. This is universal for high-performance kesterite devices, with the deficit being even larger for the pure sulfide material. While there is a consensus that the V_{OC} deficit is the key limiting factor for devices, the origin remains very much an open question.¹⁹ There are a number of hypotheses to account for the V_{OC} deficit, which can be separated into three categories:

- A non-Ohmic back electrical contact, usually Mo/CZTS, which could result in a high recombination velocity;
- A poorly optimized interface between CZTS and the CdS buffer layer, which could also result in rapid electron–hole recombination;
- Large amounts of defects and disorder in the bulk of the absorber layer, limiting minority charge carrier lifetimes and enhancing recombination processes.

In the best devices, it has been shown that the back contact with Mo is Ohmic in nature.²⁰ The borrowed device architecture from CIGS solar cells involves the use of a CdS buffer layer, and analysis of the conduction band offset between CdS and CZTSSe also does not imply any major limitation on device performance.²¹ This then leaves us with consideration of defects and disorder in the bulk of the absorber layer.

Advances in defect engineering, through modification of synthesis, deposition, and/or annealing procedures, enable a reduction in the impact of extended defects such as grain boundaries, passivation of surfaces, and production of pinhole-free thin films. However, point defects such as site vacancies and antisites will remain present even for carefully processed samples.²² Devices fabricated from high-quality single crystals have demonstrated PCEs of 10%, with a V_{OC} deficit similar to that of thin-film solar cells.²³

Kesterites are an example of a multinary semiconductor, with a zinc-blende-related structure (space group type $\bar{1}4$) and the general chemical formula of Cu₂-M^{II}-M^{IV}-X₄ (X = O, S, Se, Te). A consequence of the many components of the material is an increase in the number of possible lattice defects, with particular concern for cation disorder.²⁴ In CZTS, disorder among Cu and Zn metals would seem particularly likely because of the chemical similarity of the two species, which are neighbors in the periodic table. Indeed, first-principles calculations predict that the neutral defect pair [Cu_{Zn}⁻ + Zn_{Cu}⁺] has a low formation energy,²⁵ implying a high equilibrium concentration, and there is a large body of experimental evidence for Cu/Zn disorder from neutron

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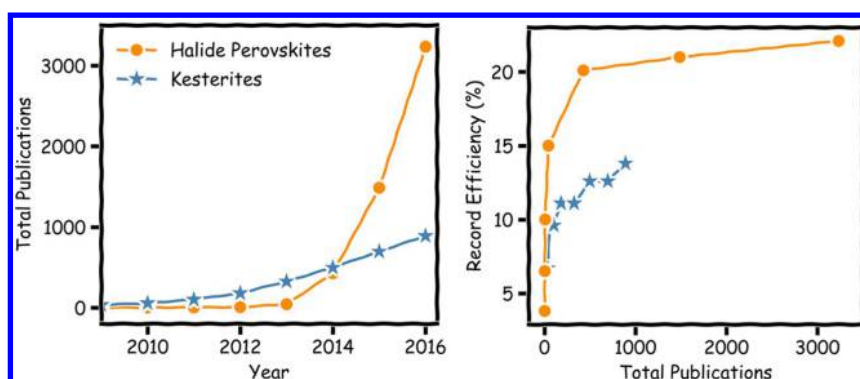


Figure 1. Comparison of the cumulative research output for $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (kesterite) and $\text{CH}_3\text{NH}_3\text{PbI}_3$ (halide perovskite) related photovoltaic technologies against year and the record light-to-electricity conversion efficiency. The publication data has been generated from Web of Science (February 15, 2017) for kesterite (search terms: “kesterite OR stannite” AND “solar cell”) and halide perovskite (search terms: “halide perovskite OR iodide perovskite OR hybrid perovskite” AND “solar cell”) solar cells.

diffraction, synchrotron X-ray diffraction, and near-resonant Raman studies.²² It is now universally accepted that Cu/Zn disorder will be present to a high degree even in high-quality thin films. However, the impact of this type of disorder on device performance is the subject of ongoing debate in the community.^{19,26}

The open-circuit voltage of a PV device is limited by the band gap of the absorber material, but defects can modify the underlying electronic band structure (Figure 2). Lattice

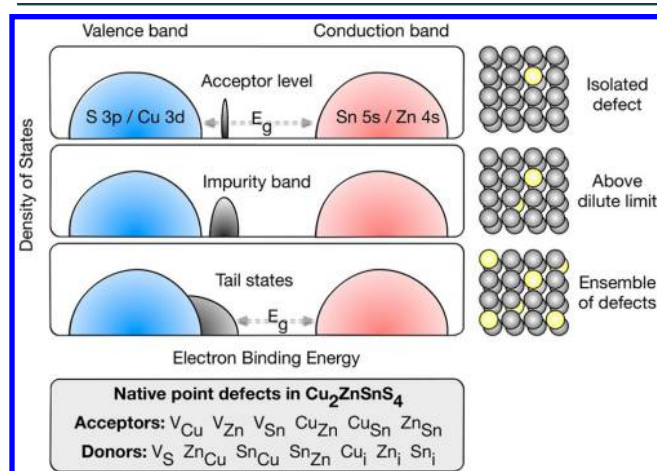


Figure 2. Acceptor defect-induced energy level within the band gap of a semiconductor, broadening to an impurity band with increased defect density until at sufficiently high defect concentrations the band merges with the valence band maximum, resulting in a reduced band gap. Such tail states would limit the open-circuit voltage accessible in a photovoltaic device and could explain the voltage deficit observed in kesterite-based solar cells. Also listed are the range of possible acceptor and donor defects in $\text{Cu}_2\text{ZnSnS}_4$; a large number of possible charge-neutral defect clusters can also be formed.

disorder can result in localized states near the top of the valence band or at the bottom of the conduction band. At sufficiently high concentrations, these interact to form an impurity band. As the density of defects increases, the tail states become more prevalent and penetrate further into the band gap. Localized states and associated band tailing in the electronic structure lead to band gap narrowing.^{22,27} As such, peaks in the photoluminescence spectra are red-shifted to energies below those of the optical band gap obtained from

internal quantum efficiency measurements (which reflects only extended electronic states).²⁸ Band tailing in CZTSSe devices is roughly twice as severe as that in CIGS devices, and it has been suggested that Cu/Zn disorder in CZTSSe is one contributing factor. In comparison, cation disorder in CIGS could be expected to be less prevalent because Cu is less chemically similar to Ga/In than Cu is to Zn, increasing the energy cost associated with making substitutions among any of these two species with Cu compared to that of Zn with Cu. Furthermore, it has been observed that band tailing is less severe in devices made from $\text{Ag}_2\text{ZnSnSe}_4$,²⁹ where cation disorder could be expected to be suppressed because of the greater ionic radii mismatch between Ag^+ and Zn^{2+} than Cu^+ and Zn^{2+} .

To our knowledge no direct connection between bulk disorder in the kesterite absorber layer and photovoltaic performance has yet been made. Postannealing treatments can be used to reduce the prevalence of Cu/Zn antisites.³⁰ Devices of varying degrees of Cu/Zn disorder in the absorber layer produced in this way demonstrated that the V_{OC} changes by the same amount as the optical band gap. The postannealing treatment therefore had no impact on V_{OC} deficit.¹⁹ The lack of direct connection between Cu/Zn antisite concentration and photovoltaic performance could be because, despite reduction in Cu/Zn disorder, the antisite concentration is still high from the perspective of device performance. Alternatively, it could be because there are other defects that are more important for controlling device properties at the current performance level. It is worth noting that the primary factors limiting performance could differ considerably for devices produced using different absorber fabrication procedures or for different performance levels for samples produced using the same approach.

Beyond Cu/Zn antisite defects, another explanation for the V_{OC} deficit is the presence of defects with levels deep in the band gap that could be acting as centers for nonradiative recombination. In particular, defects involving Sn result in deeper charge transition states owing the higher charge and larger radius of Sn relative to Cu and Zn.³¹ Deep-level defects in CZTS have been predicted to have a formation energy that is higher than those of the shallow defects;¹⁶ therefore, it could be expected that they will be less prevalent. However, the presence of “killer centers”³² even in low concentrations could be limiting device performance. It is possible that the formation energy of such centers may be reduced by the specific environmental conditions during synthesis and chemical potentials of the constituent elements.

To summarize, some key challenges and opportunities for kesterite solar cells include the following:

- 1. Missing activation step.** For CdTe, a postdeposition chemical treatment of CdCl₂ or similar is required to “activate” the absorber layer³³ (e.g., passivate grain boundaries, enlarge grain size), while for CIGS a Cu-rich processing stage is needed during the 3-stage evaporation process.³⁴ Identifying a similar activation process for kesterites may enable a step-change in PV action.
- 2. Accurate material and device measurements.** The wide variety of demonstrated growth processes and conditions makes comparison of reported physical properties challenging. Accurate and consistent measurements concerning carrier generation, transport, recombination, and collection for different absorbers would provide valuable insights to overcome device bottlenecks.
- 3. Quantifying defects and disorder.** A number of different descriptors are being used in the field to quantify disorder, including Raman spectra, optical spectra, and neutron diffraction. However, the site disorder averaged over a macroscopic sample does not provide insights into the microscopic cation distribution that will interact with photogenerated electrons and holes. More accurate local structure techniques and materials simulations could provide valuable insights.
- 4. Alternative device architectures.** Relatively little effort has been spent on looking at alternatives to the standard Mo/CZTS/CdS device configuration. Beyond simple component replacement (e.g., Mo for W or ZnS for CdS), other device configurations such as p–i–n could result in enhanced photovoltaic performance.

Two large research consortia have recently been funded to address some of these questions. One is PVTEAM, led by L. M. Peter at the University of Bath (U.K.) that links with the SPECIFIC Innovation and Knowledge Centre for scale-up, and STARCELL, led by E. Saucedo at IREC (Spain) that combines 13 partners across Europe, Japan, and the United States. At a time when further breakthroughs in perovskite solar cells will become increasingly difficult to achieve, a focused effort on kesterites and related materials could have major impacts. While this technology has been relatively slow to emerge, the combination of earth-abundant and nontoxic elements in a chemically stable compound is the solution that sustainable thin-film photovoltaics requires.

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