Emerging Earth-Abundant Solar Absorbers

Developing solar absorbers that are efficient, low cost, stable, and comprised of non-toxic, Earth-abundant elements has long been the holy grail of next-generation photovoltaics (PV) research.[1] This effort has been disrupted by the advent and rapid rise in performance of solution-processable lead-halide perovskites.[2] One of the key enabling properties is the ability of these halide perovskites to tolerate point defects, enabling efficient PV performance despite high defect densities.[3,4] This discovery has reinvigorated efforts within the Earth-abundant PV community to design efficient solar absorbers, drawing inspiration from the halide perovskites, with particular focus on defect tolerance and achieving materials with long diffusion lengths. At the same time, the broad families of Earth-abundant solar absorbers provide valuable opportunities to overcome the toxicity and stability limitations of the lead-halide perovskites, without remaining confined solely within the perovskite family of compounds. The merging of these two communities has produced exciting new frontiers, which were explored in the recent symposium on "Earth-abundant next generation materials for solar energy" (Symposium F) at the 2021 Fall European Materials Research Society Meeting (held virtually). Here, we feature some of the key emerging areas discussed at the Symposium: chalcogenide perovskites, II-IV-N_2 compounds, antimony chalcogenides, and the computational search for novel defect-tolerant solar absorbers.

Chalcogenide Perovskites

Whilst much of the effort to discover lead-free perovskite-inspired materials has focussed on halides,[4] there is growing interest in chalcogenide perovskites,[5] including $BaZrS_3$, $SrZrS_3$, $BaHfS_3$ and $SrHfS_3$, among many other Ti-, Zr- and Hf-based compounds.[6,7] These materials have captured attention owing to their: 1) low levels of disorder (Urbach energies between 18-34 meV, see Fig. 1a),[6] 2) high thermal and environmental stability under ambient conditions,[5] and 3) high absorption coefficients on the order of 10^5 cm^{-1}.[8] These materials also hold promise for exhibiting defect tolerance.[5,9] With typical bandgaps close to 2 eV, chalcogenide perovskites are promising for applications as top-cells in tandem with silicon,[10] for indoor photovoltaics,[11] or photoelectrochemical cells.[12] However, directly growing high-quality thin films of these materials face several important challenges: 1) there is a large mismatch in the vapor pressures of the metal cation and chalcogen precursors, 2) chalcogen precursors (e.g., H_2S) are corrosive and damaging to the processing equipment, 3) there is a strong propensity for chalcogenide perovskites (as well as their precursor metal elements) to form oxides instead.[13,14]

Recently, Ravichandran et al.[13] and Jaramillo et al.[14] achieved epitaxial thin films of phase-pure $BaZrS_3$ through pulsed laser deposition (PLD) and molecular beam epitaxy (MBE), respectively, on single-crystalline $LaAlO_3$, $SrLaAlO_4$ or $SrTiO_3$ substrates. The MBE films grew by buffered epitaxy (mode M1; Fig. 1b) or direct epitaxy (mode M2; Fig. 1c), with M1 found to be faster.[14] The PLD films (cross-sectional micrograph in Fig. 1d) were shown to have room temperature photoluminescence (PL; Fig. 1e), along with PL lifetimes up to 8 ns (Fig. 1f), making them promising for PV applications.[13] However, processing temperatures in the range of 700–900 °C were required for the growth of these MBE and PLD films. The high processing temperatures required limits the ability to incorporate these materials in superstrate device architectures, owing to the common transparent conducting oxide substrates used (indium tin oxide and fluorine-doped tin oxide) being compatible with processing temperatures up to only ∼500 °C.

Recent efforts have therefore focussed on developing lower-temperature processing routes for achieving high-quality chalcogenide perovskite thin films. One such route is to pre-synthesize crystalline nanocrystals, which, if colloidally-dispersible, can be deposited to form a thin film. Nag et al. reported that the growth of $BaZrS_3$ nanocrystals colloidally in solution is challenging, and so grew the nanocrystals using a powder synthesis route at 600 °C before dispersing them in solution.[15] More recently, Creutz et al. reported the ability to grow $BaTiS_3$ colloidal nanorods at temperatures as low as 280 °C by using much more reactive amide-based precursors. These nanorods could be precipitated and redispersed in chloroform or toluene, and therefore have potential for forming thin films with standard nanocrystal processing routes.[16]

Thus, the field of chalcogenide perovskites is gaining increasing attention owing to the highly promising optoelectronic properties of these materials. The critical challenge the field is facing is to achieve these desirable properties at processing temperatures compatible with conventional PV device structures. Overcoming this challenge could lead to a new generation of PV and other (opto)electronic devices that are efficient, cost-effective and stable.

II–IV–N_2 Compounds

In recent years, there have been theoretical studies predicting nitrides to have significant potential as light absorbers for photovoltaic applications.[17,18] In particular, the defect-tolerance predicted by the initial theoretical studies and suitable band gaps of some II-IV-N_2, similar to halide perovskites, are noteworthy. Among many II-IV-N_2 compounds, $MgSnN_2$ (MTN) and $ZnSnN_2$ (ZTN) have been drawing attention.[3,17,19–21] MTN, with a bandgap of 1.8 - 3.4 eV, has begun to attract interest as a potential semiconductor material for light emitting diodes (LEDs) and PV (especially as a top sub-cell in tandem with silicon PV). The bandgap of ZTN is 1.0 - 2.4 eV, which is about 1 eV lower than that of MTN, and ZTN is therefore more suitable for solar cell application than MTN, including single-junction PV.

There are several challenges that need to be overcome in order to fully implement ZTN as a promising solar cell material. Firstly, the currently reported values of the carrier concentrations of ZTN are higher than the optimal range for PV applications (10^{13} - 10^{16} cm^{-3}). Secondly, strategies to control impurities, including the unwanted partial oxidation of ZTN forming zinc-tin-oxide, are needed. There is wide variation in the reported values of bandgaps

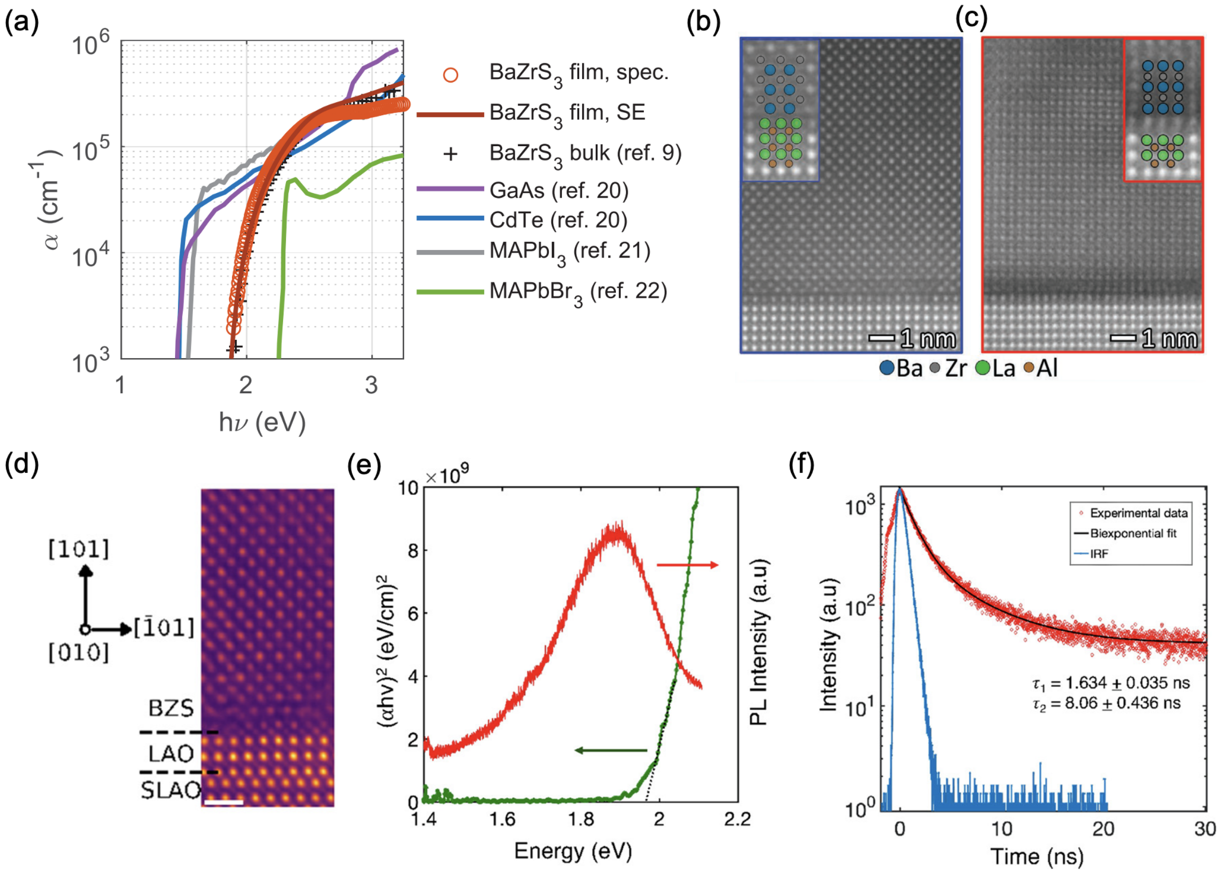

Figure 1: Properties of $BaZrS_3$ chalcogenide perovskite grown by (a–c) molecular beam epitaxy (MBE),[14] and (d–f) pulsed laser deposition (PLD).[13] (a) Optical absorption coefficient of MBE $BaZrS_3$ thin films (measured by spectrophotometry [spec.] and spectroscopic ellipsometry [SE]) compared to bulk powder-pressed samples of $BaZrS_3$, as well as other direct-bandgap materials. High-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) images of the cross-section of $LaAlO_3/BaZrS_3$ grown in modes (b) M1 and (c) M2. Parts (a–c) reproduced with permission from Ref. 14. Copyright 2021 Wiley. (d) HAADF images of $SrLaAlO_4/BaZrS_3$, along with the (e) photoluminescence (PL) spectra and Tauc plot, and (f) PL decay. Parts (d–f) reproduced with permission from Ref. 13. Copyright 2021 American Chemical Society.

of ZTN (1.0 – 2.4 eV). Two major factors influencing the bandgap of ZTN are the cation ratio, Zn/Sn, and the level of oxygen impurities.[22] Additionally, free carrier absorption, known as Burstein-Moss effect, due to the higher carrier concentration of ZTN contributes to an increase in the apparent optical bandgap.[22–26]

In contrast to the wide range of theoretical and materials growth and characterization studies into ZTN over the past decade, to date only two studies have shown photovoltaic

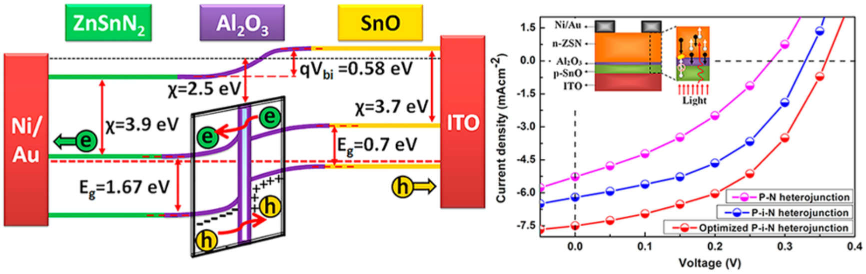

Figure 2: Device structure and light current-voltage characteristics of 1.54% efficient ZTN solar cells adapted from Ref. 27. Copyright 2018 American Chemical Society.

devices based on ZTN light absorbers. In 2007, Javaid and co-workers formed a heterojunction solar cell consisting of n-type ZTN and p-type SnO with the power conversion efficiency of 0.37%.[28] An improved efficiency of 1.54% was achieved by introducing a thin (2 - 3 nm) Al_2O_3 layer between ZTN and SnO by the same group in 2018 (see Figure 2).[27] Given the poor diodic behavior of these devices, a continued search for better junction-forming partners seems necessary to fully realize the potential of ZTN absorbers.

Antimony Chalcogenides

A very high absorption coefficient, bandgap optimal for solar PV, relative Earth abundance of the constituent elements, and lack of competing Sb-Se containing phases, make Sb_2Se_3 an important candidate PV absorber.[29] With the record PCE for this absorber approaching 10%,[30] we discuss three important themes of recent work on the material: defect chemistry, crystal engineering, and device architecture.

Despite steady advances Sb_2Se_3-based device efficiencies,[31] it has taken recent breakthroughs to establish the fundamental characteristics of these materials. There is some discrepancy in the literature over the typical intrinsic carrier type and concentration in bulk Sb_2Se_3. The material is often considered *p*-type, but this is likely due to extrinsic impurities; Hobson et al. have shown the pure, stoichiometric material synthesized at high temperature to be highly insulating,[32] in agreement with theoretical calculations,[33] but can be made *n*-type with the addition of small amounts of Cl.[32] In thin film growth of Sb_2Se_3, care must be taken to suppress the V_{Se} defect, which acts as a deep trap, by ensuring the Se flux is sufficient, although excessive Se can lead to selenization of the CdS window layer, and poor crystallographic orientation of the absorber.[34] The valence band of Sb_2Se_3 consists of a strong contribution from filled Sb 5*s* states at the valence band maximum,[35] offering the possibility of highly mobile holes, or a highly conducting *p*-type material. Intriguingly, the first report of intentionally extrinsically doping Sb_2Se_3 *p*-type (using Sn(II) as the dopant) was reported in the eMRS Fall Symposium F, but at time of writing has not yet been published. Further work on controlling carrier type and concentration benefits to this field.

With a structure consisting of one-dimensional chains, or nanoribbons, carrier mobility in Sb_2Se_3 is highly anisotropic. This means that control of crystal orientation in thin film growth is critical, and a current research topic is crystallographic control during thin film deposition. The substrate is critical for controlling orientation, so the order of deposition, either substrate deposition, where the Sb_2Se_3 absorber is deposited on the metal contact, or superstrate configuration, where Sb_2Se_3 is deposited onto the window material, is of critical importance.[36] Using close spaced sublimation in a substrate configuration, Li et al. achieved the current record efficiency, in part by control of Sb_2Se_3 orientation, which depended strongly on the underlying Mo contact layer thickness.[31] Control of crystal orientation can also be influenced by Se vapour flux, as revealed by Seunghwan Ji at Symposium F, as well as in their recent publication, or by use of a pre-deposited seed layers in a superstrate configuration.[37] As yet there is no clear optimal configuration, and this presents opportunities to influence orientation in Sb_2Se_3 films.

Optimizing the device architecture of a Sb_2Se_3 solar cell requires understanding of the electronic structure and chemistry of each interface. The most common partner for Sb_2Se_3 is CdS, but interdiffusion between Sb_2Se_3 and the CdS window layer is considered by some to be detrimental. Blocking layers of TiO_2 deposited by Atomic Layer Deposition (ALD), or replacement of CdS entirely by TiO_2 have been used to overcome this.[38] Band offsets are another important property which is now being explored in detail. Shiel et al used a novel photoemission method, utilising two photon energies, to probe the band offset and curvature at the Sb_2Se_3-TiO_2 and Sb_2Se_3-CdS interfaces, and suggested that while TiO_2 might act to prevent diffusion, it possesses a less favourable band offset with the absorber, compared with CdS, and therefore an alternative blocking layer may present additional opportunities for efficiency improvement.[39]

Computational Search for Novel Defect-Tolerant Solar Absorbers

Theory and computations have played a pivotal role in advancing our understanding of the defect tolerance features of hybrid perovskites and offered guidelines to search and design perovskite-inspired materials.[4,40] Many computational studies have focused on Earth-abundant PV absorbers, including antimony chalcogenides (e.g., Sb_2Se_3, Sb_2S_3),[32] chalcohalides (e.g., BiOI, SbSeI, $Sn_2SbS_2I_3$),[41] ABZ_2 chalcogenides (e.g., $AgBiS_2$, $NaSbS_2$),[42] binary halides (e.g., InI, BiI_3),[43] and perovskite derivatives (e.g., $Cs_2AgBiCl_6$).[44] A common theme among these classes of materials is the presence of partially-oxidized cations with lone pairs, which is believed to contribute to the defect tolerance of hybrid perovskites.[45] These various classes of materials have been reviewed in detail in recent articles.[30,46] Here, we highlight recent computational studies aimed at discovering defect-tolerant PV absorbers.

Prior computational searches for defect-tolerant PV absorbers have leveraged heuristic guidelines based on bulk properties. While successful in identifying promising material classes, those studies do not explicitly consider the carrier lifetime, which is controlled by non-radiative recombination processes involving defects. Dahliah et al. performed an *ab initio* high-throughput screening of 7000 Cu-based materials taking into account carrier lifetime and defect-mediated recombination.[47] The study uses a modified Shockley and Queisser (SQ) model that accounts for nonradiative lifetimes and concepts presented by Kirchartz et al.[48] and Kim et al.[49] $K_3Cu_3P_2$ and Na_2CuP are identified as potential *p*-type absorbers that are composed of Earth-abundant elements. In a departure from perovskite-inspired materials, these candidates do not feature lone pair cations.

Ternary II-IV-N_2 nitrides have been exhaustively explored as Earth-abundant PV absorbers. However, these nitrides are defect *intolerant* due to significant cation disorder and presence of deep defects.[50] Oba and coworkers theoretically predicted a defect-tolerant ternary nitride YZn_3N_3 with a hexagonal $ScAl_3C_3$ type crystal structure.[51] Thin films grown by reactive cosputtering have a band gap of 1.84 eV, in agreement with theoretical predictions. First-principles defect calculations showed that all native point defects are shallow, except the nitrogen vacancy (V_N introduces a shallow state 0.24 eV below the conduction band minimum). With a band gap $\sim$1.8 eV, YZn_3N_3 is proposed as a top cell absorber in tandem solar cells. While Y is a rare-earth element, the successful theoretical prediction points to the possibility of discovering other defect-tolerant absorbers with Earth-abundant elements. YZn_3N_3 also does not contain an ns^2 lone pair cation, in agreement with previous studies that showed that the presence of ns^2 cation is not sufficient for defect tolerance.[52]

The role of the crystal structure in enabling defect tolerance has been recognized in several studies.[43,52] This has inspired computational efforts to discover defect-tolerant materials with crystal structures that are not perovskites or perovskite-derived, including $BiPS_4$ in a complex orthorhombic structure,[53] and Hg-based spinels.[54] Liang et al. computationally identified HgX_2S_4 (X = In, Sc, Y) spinels as defect-tolerant absorbers due to the presence of cations with delocalized orbitals in the spinel structure.[54] These new reports highlight opportunities to discover non-perovskite absorbers that are defect tolerant and composed of Earth-abundant elements.

Beyond discovery, computations have also synergistically interfaced with experiments to allow the rapid development of emerging Earth-abundant absorbers, including Sb_2Se_3,[32] and $AgBiS_2$.[55] For example, first-principles defect calculations have been instrumental in understanding the complex defect chemistry of Sb_2Se_3.[33] The development of computational methods to calculate carrier capture rates at defect sites has allowed a direct evaluation of conversion efficiency in emerging PV absorbers.[56]

Concluding Remarks

These recent developments show that the Earth-abundant PV field is undergoing many exciting advances, from novel concepts (e.g., effects of cation disorder) to novel materials entering into new phases of development (e.g., advances in low-temperature processing of chalcogenide perovskites). The next few years promise many rich opportunities for discovery and technological progress in this field.

Acknowledgments

Views expressed in this Energy Focus article are those of the authors and not necessarily the views of the ACS. The authors declare no competing financial interest.The authors would like to thank the contributions from the presenters of Symposium F at the 2021 Fall European Materials Research Society (eMRS) conference, as well as to our colleagues and speakers at Symposium R, with whom with had a joint session. We would also like to thank the Symposium sponsors, Oxford PV, ACS Energy Letters, Energy & Fuels, Joule, Matter, as well as support from the eMRS. J. W. C. and B. S. acknowledge the support by Nano-Material Technology Development Program (Green Nano Technology Development Program) through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (No. 2018M3A7B4065662) and NRF grant funded by the Korea Government (MSIT) (No. NRF-2018R1A5A1025594). R. L. Z. H. acknowledges funding from the Royal Academy of Engineering through the Research Fellowship scheme (No.: RF/201718/1701), and the Engineering and Physical Sciences Research Council (EPSRC; No.: EP/V014498/1).

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