

REVIEW

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Cite this: *Energy Environ. Sci.*,
2024, 17, 1781

Recent progress in monolithic two-terminal perovskite-based triple-junction solar cells

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Multi-junction solar cells are the most famous approach to overcome the power conversion efficiency (PCE) limit of single-junction solar cells. Metal halide perovskite absorber materials offer low-cost fabrication and tunable bandgap that make them suitable candidates for multi-junction applications. Perovskite-based dual-junction solar cells have already shown impressive PCE improvement in recent years. As a next step, triple-junction structures can allow for further PCE increase; however, research on triple-junction solar cells with perovskite materials is still at an early stage. In this review, we present the status of three monolithic perovskite-based triple-junction technologies available: perovskite/perovskite/silicon, perovskite/perovskite/perovskite, and perovskite/perovskite/organic solar cells. First, an overview of the potential of these solar cell types based on simulation is given. Further, a summary of scientific and experimental challenges in the field as well as strategies to achieve suitable absorber materials and contact layers that can be implemented in these structures are presented. Finally, global cell characterization of triple-junction solar cells together with a guideline on correct measurement of this type of solar cells are discussed.

Received 25th August 2023,
Accepted 4th December 2023

DOI: 10.1039/d3ee02822d

rsc.li/ees

Broader context

Tackling climate change requires transformation of global energy from conventional fossil fuels toward cleaner sources. This is achievable through electrification of energy demand as well as increasing the share of renewable sources for electricity production. Among all the renewable energy sources, photovoltaics (PV) plays a crucial role. Even though the electricity share of the PV is only 4.5%, its world installed capacity has reached 1 TWdc and is further growing. Entering the terawatt scale raises the need for reducing the cost of PV technology. Therefore, increasing the efficiency of the PV module is more important than ever. To do so, multi-junction solar cells have proven to be the most attractive option, yet development of efficient and low-cost subcells is necessary. In this regard, metal halide perovskite is one of the most promising candidates with perovskite/silicon holding the dual-junction record efficiency. Improving this efficiency further is possible by increasing the number of junctions to three as it has been demonstrated by III-V semiconductor materials. Realizing the triple-junction solar cell with perovskite material comes with several challenges and requirements which we have outlined in this review.

1. Introduction

The most famous approach to overcome the efficiency limit of single-junction solar cells and achieve efficient usage of the solar spectrum is the use of multi-junction solar cells. In this approach, solar cells with different bandgaps are stacked on top of each other in a bandgap descending order with the highest

bandgap solar cell facing the sun. This way, the top solar cell absorbs the high energy photons up to its bandgap and the lower energy photons are transmitted to reach the underlying subcells with lower bandgaps. This reduces the thermalization losses and leads to better harvesting of the solar spectrum. Fig. 1a shows this principle for the case of triple-junction solar cells.

According to simulation by Philipps *et al.*, the highest theoretical PCE that can be achieved in a detailed balance limit (Auger recombination is not taken into account) by a dual-junction solar cell is 45.9% under Air Mass 1.5 global (AM 1.5g) spectrum.¹ This PCE limit can be exceeded by increasing the number of junctions in a solar cell. However, as shown in Fig. 1b the incremental increase becomes lower towards more junctions. Furthermore, the additional junctions introduce new

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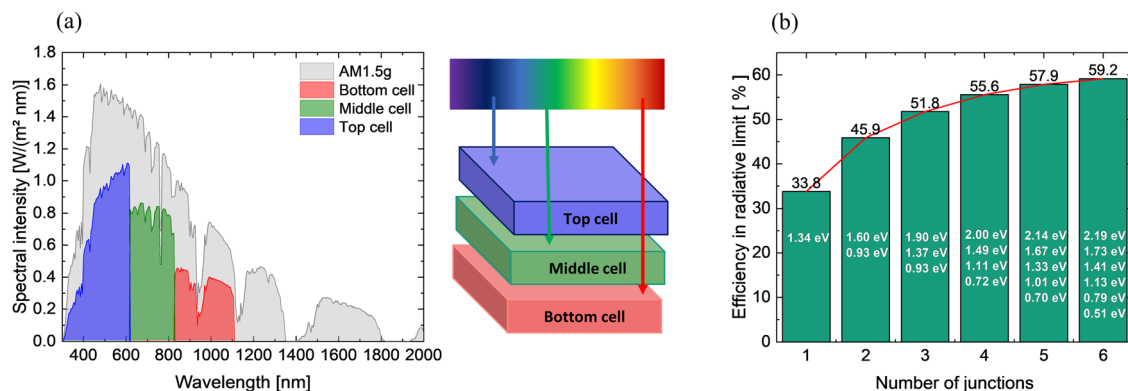


Fig. 1 (a) Use of the solar spectrum by a triple-junction solar cell consisting of a silicon bottom cell, a 1.50 eV middle cell (e.g. GaInAsP), and a 2.00 eV top cell (e.g. AlGaInP). The transmission and thermalisation losses are reduced compared to single-junction and dual-junction solar cells. (b) Theoretical efficiency of multi-junction solar cells in the radiative limit as a function of the number of junctions. The optimum bandgap combination is given for the maximum PCE under the AM 1.5g spectrum. The gain in efficiency becomes lower by increasing the number of junctions. Data taken from ref. 1.

challenges in terms of processing, choice of materials and interaction between the layers. Thus, triple-junction solar cells are a reasonable approach to achieve a good balance between efficiency potential, processing, and device complexity.

So far, highly efficient triple-junction solar cells are made of III–V semiconductor materials and are commercially available for concentrator photovoltaic and space application. Triple-junction solar cells using III–V materials reached 39.5% efficiency for a gallium indium phosphide (GaInP) top cell, gallium indium arsenide (GaInAs)/gallium arsenide phosphide (GaAsP) quantum well middle cell, and GaInAs bottom cell under the AM 1.5g spectrum.² This exceeded the previous record of a sextuple-junction solar cell and made the triple-junction solar cell the most efficient non-concentrated terrestrial PV technology to date. Cells made from III–V compound semiconductor absorbers are highly efficient thanks to the low defect density that can be achieved in the single-crystalline materials and due to the direct

nature of their bandgap. However, they require expensive deposition techniques such as metalorganic or hydride vapor phase epitaxy (MOVPE, HVPE) or molecular beam epitaxy (MBE) to achieve the required high crystal quality. The high production costs prevent these technologies from entering the terrestrial photovoltaic markets and consequently limit them to concentrator photovoltaic and space application where the high efficiency is the decisive factor. Several works have been done to couple III–V materials on a silicon bottom cell to reduce the cost and to benefit from the fact that the photovoltaic (PV) market is dominated by crystalline silicon. For the first time in 2013 Derendorf *et al.* reported successful integration of GaInP/GaAs/silicon in a triple-junction structure using wafer bonding.³ A record efficiency of 35.9% was achieved in 2021 for this type of solar cell.⁴ Technologically, wafer bonding is not favorable as it is an expensive serial process and requires an extra chemical-mechanical polishing (CMP) step.⁵ However, direct growth of III–V materials



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on silicon is also challenging due to lattice mismatch between the two materials and to date the efficiency of triple-junction solar cells by directly growing the III–V material on silicon is limited to 25.9%.⁶ A cheaper and yet promising alternative to III–V materials are metal halide perovskites. These materials have exceptional properties such as high absorption coefficient, long carrier diffusion length, direct bandgap, and high mobility of charge carriers.^{7–9} In addition, low cost, and simple fabrication methods as well as the ease of bandgap tuning make them ideal to be used in a multi-junction structure. Two-terminal perovskite-based dual-junction solar cells have shown significant efficiency improvement over the recent years with certified PCE of 28.0% for perovskite/perovskite,¹⁰ 24.2% for perovskite/copper indium gallium selenide (CIGS)¹¹ and 24.5% for perovskite/organic solar cells.¹² Perovskite silicon dual-junction solar cells have reached 33.9% PCE¹³ which is higher than the efficiency of III–V based dual-junction solar cells and proves their great potential for the multi-junction concept.

Compared to the intense research on dual-junction perovskite-based solar cells, the research on its triple-junction structure is still at an early stage. Depending on the choice of the bottom cell, three types of triple-junction solar cells based on perovskite materials have been reported to date: (I) perovskite/perovskite/perovskite (known as all-perovskite), (II) perovskite/perovskite/silicon and (III) perovskite/perovskite/organic solar cells. The highest PCE reported is 23.3% for all-perovskite,¹⁴ 22.2% for perovskite/perovskite/silicon,¹⁵ and 19.4% for the perovskite/perovskite/organic¹⁶ triple-junction solar cells. Among them only the 23.3% PCE reported for all-perovskite triple-junction solar cell is certified. Fig. 2 summarizes the evolution of triple-junction solar cells that have silicon and/or perovskite solar cells in their structure.

In order to maximize the PCE of a triple-junction solar cell, appropriate bandgaps of the subcells should be combined. If there is no constraint in the bandgap of the bottom cell, the ideal combination of bandgaps that results in the maximum efficiency in a triple-junction solar cell are 0.93 eV, 1.37 eV, and 1.90 eV for bottom cell, middle cell, and top cell, respectively.¹ A bottom cell with such a low bandgap is demonstrated with III–V materials.² Perovskite solar cells with a bandgap around 1.20 eV^{14,24,25} and organic solar cells around 1.30 eV¹⁶ have been employed as bottom cells in triple-junction applications. Fig. 3 shows the theoretical PCE that can be achieved by a triple-junction solar cell with respect to the choice of the bottom cell. In addition, the optimum bandgap pairs for middle and top cells to maximize PCE in each structure is given in Table 1. Among these three types, perovskite/perovskite/silicon reaches a comparably high theoretical efficiency limit of 49% (neglecting Auger recombination), *i.e.*, assuming a bottom cell absorber material with a direct bandgap of 1.10 eV. Moreover, high maturity of the silicon technology and its longevity make it most appealing for future market application.

It is important to note that the optimum bandgaps discussed are based on the theoretical efficiency limit, which does not necessarily give the maximum practical efficiency. In fact, Hörantner and Leijtens *et al.* assessed the practical potential of perovskite/perovskite/silicon triple-junction solar cells by combining optical and electrical simulation and reported an ideal

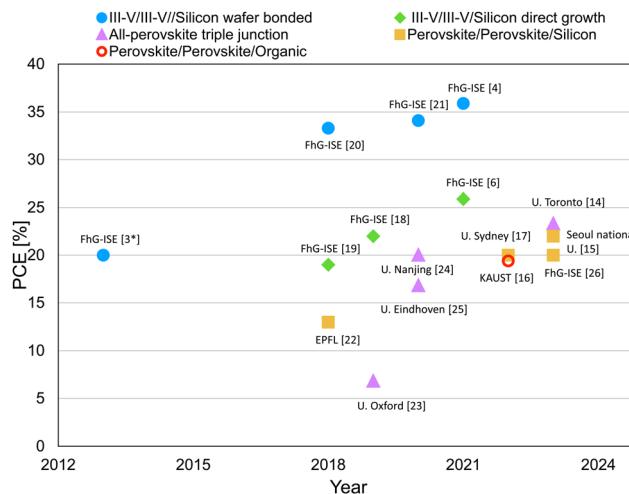
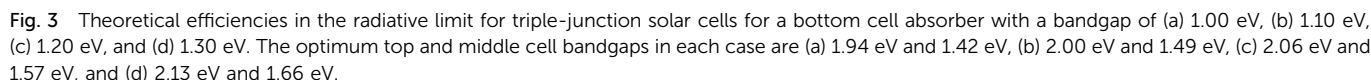


Fig. 2 PCE evolution of two-terminal triple-junction solar cells with silicon and/or perovskite in their structure. Data taken from ref. 3, 4, 6 and 14–26. The record efficiency achieved for III–V/III–V/silicon solar cells are 35.9% and 25.9% using wafer bonding and direct growth respectively. The highest efficiency reported for all-perovskite triple-junction solar cell is 23.3%, for perovskite/perovskite/silicon is 22.2% (not certified) and for perovskite/perovskite/organic is 19.4% (not certified). All data are reported from measurement at AM 1.5g spectrum except for the first wafer bonded III–V/III–V/silicon which was measured at Air Mass 1.5 direct (AM 1.5d) spectrum *.

combination of 1.44 eV and 1.95 eV for middle cell and top cell on a silicon bottom cell.²⁷ In this simulation, optical and electrical losses such as parasitic absorption, series and shunt resistance derived from their experimental data are considered. Based on their simulation a 38.8% efficient perovskite/perovskite/silicon triple-junction solar cell can be achieved by optimizing charge extraction and recombination layers, while only 34.6% efficiency is feasible if absorbers with bandgaps limited to 1.50 eV and 2.00 eV are used. In a similar approach their simulation shows a 36.6% efficient all-perovskite triple-junction solar cell with a bandgap combinations of 2.04 eV, 1.58 eV, and 1.22 eV (Fig. 4).²⁷ This change in optimum bandgap combinations based on more realistic assumption has also been previously reported on multi-junction solar cells of up to five junctions by taking non-radiative recombination of subcells into account.²⁸ This indicates that the optimum combination of bandgaps is affected by properties of all layers and different loss mechanisms and should be determined according to each structure and choice of interlayer materials.

Another important criterion in a series-connected multi-junction solar cell is current matching. In this type of solar cells, the current is limited by the subcell that generates the lowest current. Therefore, to maximize the current output of the solar cell, the current generated in each subcell should be the same.²⁹ Achieving current matching in such a complex system is not trivial. In addition to bandgap adaptation, optimizing the thickness of absorber layers, reducing reflection losses as well as minimizing parasitic absorption of contact layers (*e.g.*, thinning all the layers except for the absorber layers) is crucial. Even with the above mentioned considerations, the current matched device under standard test condition may not



Bottom cell (eV)	Middle cell (eV)	Top cell (eV)
1.00	1.42	1.94
1.10	1.49	2.00
1.20	1.57	2.06
1.30	1.66	2.13

So far, this introduction covered the potential of triple-junction solar cells based on simulation. Realization of such photovoltaic devices with maximum possible output in real lab conditions demands consideration of practical factors and limitations. Beyond optimization of individual layers, the processing sequence and layer interactions of the whole multilayer stack strongly influence the final device performance. Thus, a thorough analysis and comparison of the approaches taken for realizing the proof of

2. Perovskite-based triple-junction solar cells: categories and status

A monolithically integrated multi-junction solar cell consists of many layers processed sequentially on top of each other with different deposition methods. Process compatibility of each layer with its underlying layer is therefore of great importance.

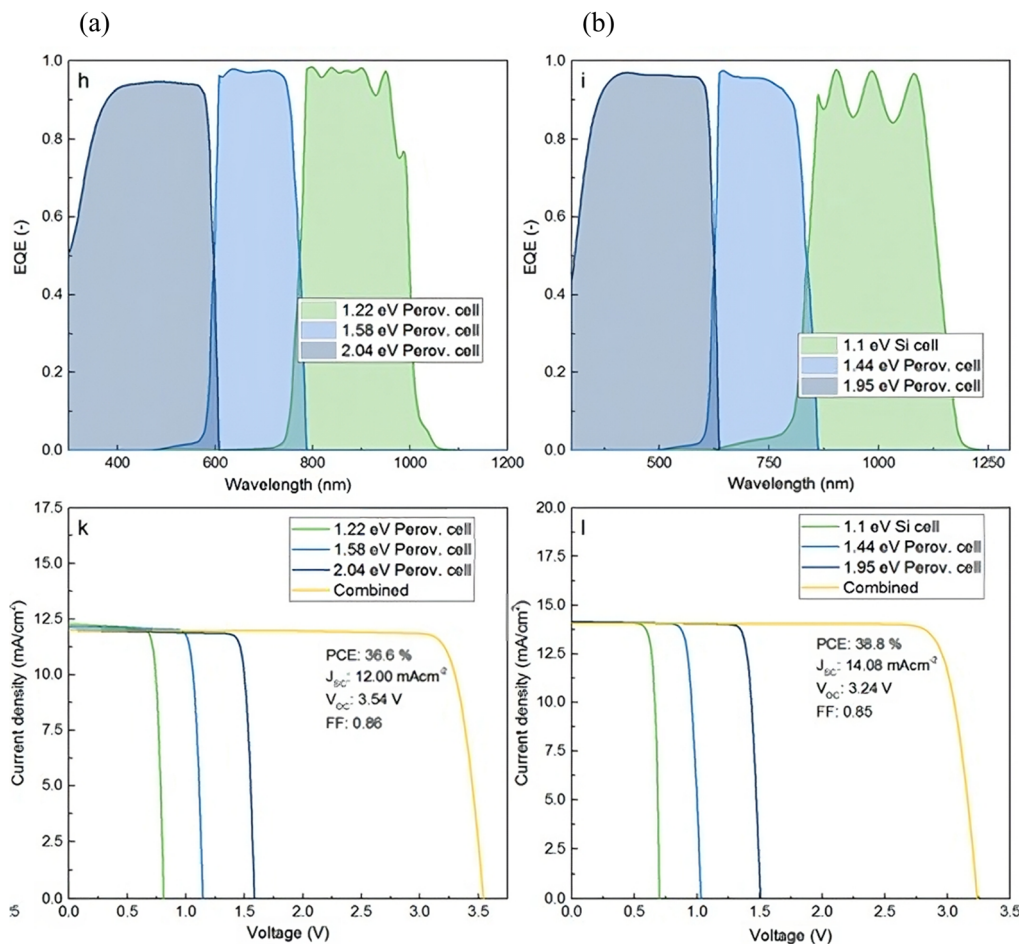


Fig. 4 Simulated external quantum efficiency (EQE) and current density–voltage (jV) curves for maximum practical PCE (a) 36.6% for an all-perovskite triple-junction solar cell with perovskite's bandgaps of 1.22 eV, 1.58 eV, and 2.04 eV for the subcells and (b) 38.8% for a perovskite/perovskite/silicon triple-junction solar cell with bandgaps of 1.44 eV and 1.95 eV for perovskite subcells. Reproduced with permission from ref. 27, Copyright © 2017, American Chemical Society.

For example, solvent orthogonality, possible processing damage as well as thermal budget of the bottom layers should be considered when processing subsequent layers. Moreover, addition of each subcell increases the number of layers, which consequently introduces new challenges.

Multi-junction solar cells can be divided into superstrate or substrate configuration (Fig. 5) depending on the type of bottom solar cell technology. In case of thin film bottom solar cells, such as in all-perovskite and perovskite/perovskite/organic solar cells, the superstrate configuration is used; solar cells are deposited on a glass (or foil) which is flipped and facing the sun in the final device. In case of wafer-based bottom solar cells, such as in perovskite/perovskite/silicon, the substrate configuration is used; the bottom cell wafer itself acts as the substrate and subsequent layers are processed on top. Consequently, the processing order of the absorbers is different. In the superstrate configuration, perovskites are processed in bandgap descending order and highest restrictions concerning process compatibility apply for the low bandgap perovskite absorber. In the substrate configuration, perovskite middle and top cells are processed successively on top of the bottom solar cell wafer. Highest

restrictions concerning compatibility, such as annealing temperature and possible solution damage to the underlying layers apply for the processing of high-bandgap perovskite top cell. One example is high-temperature annealed nickel oxide (NiO_x), that cannot be implemented as charge transport layer on top of another perovskite subcell. In addition, the first processed subcell (high bandgap in the superstrate and low bandgap in substrate configuration) must sustain several harsh conditions involved in the deposition of the top layers such as annealing steps, sputtering, *etc.* More discussion on fabrication of respective perovskite layers is presented in Section 3 and 4.

Moreover, perovskite solar cells can be classified by their order of deposition of the electron (n) and hole (p) transport and the perovskite absorber (i) layers into n-i-p (electron transport layer (ETL) deposited first) and p-i-n (hole transport layer (HTL) deposited first) device architectures. The work on perovskite/silicon tandem solar cells started on n-i-p architecture.³³ However, the research focus changed toward the p-i-n structure due to an optically more favorable front contact, ease of fabrication and upscaling.

Similarly, the very first report on all-perovskite triple-junction solar cells in 2019 by McMeekin *et al.* had an n-i-p

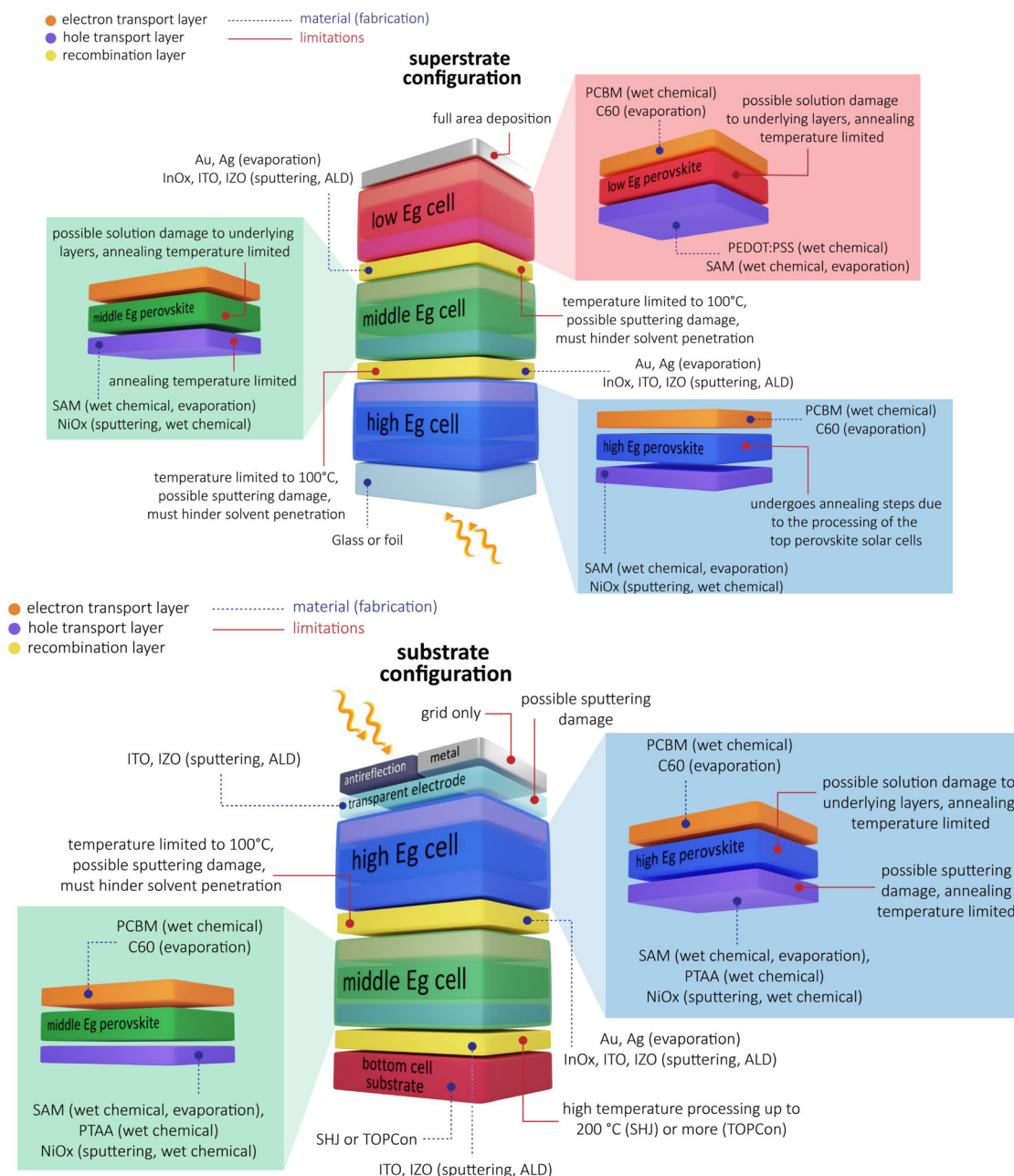


Fig. 5 Schematic illustration of monofacial perovskite-based triple-junction solar cells with (top) superstrate configuration and (bottom) substrate configuration. Perovskite subcells are in p–i–n architecture. Some of the common materials for each layer together with their deposition techniques are shown. The processing of substrate configuration starts with bottom cell (lowest bandgap subcell) while for superstrate configuration the top cell (the highest bandgap subcell) is processed first. The main limitations of the processes are highlighted.

configuration implementing $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.70}\text{I}_{0.30})_3$ (1.94 eV), MAPbI_3 (1.55 eV) and $\text{MAPb}_{0.75}\text{Sn}_{0.25}\text{I}_3$ (1.34 eV) perovskite absorbers.²³ This work remains the only perovskite-based triple-junction solar cell with n–i–p architecture. Another exceptional approach regarding solar cell fabrication was that all the layers except for the silver electrode were solution-processed; even the indium tin oxide (ITO) recombination layer which is usually deposited *via* sputtering was replaced by spin coated ITO nanoparticles. Their strategy to overcome solvent compatibility issue was to change the conventional mixture of dimethylformamide/dimethyl

sulfoxide (DMF/DMSO) as perovskite solvent to a new acetonitrile/methylamine (ACN/MA) solvent system for both low bandgap and middle bandgap perovskites. However, the change in solvent system yielded a reduced PCE. The triple-junction solar cell reached a PCE of 6.7% with an open-circuit voltage (V_{OC}) of 2.70 V. The limited PCE mainly arose from low short-circuit current density (j_{SC}) of 8.3 mA cm^{-2} limited by the low bandgap bottom cell, as well as a low fill factor (FF) of 43.0%. Other possible factors limiting the performance of this structure could be high parasitic absorption, especially in the 60 nm thick



either NiO_x alone or double hole transport layers with NiO_x in their structure^{14,16,17} (Fig. 6).

Recently, Wang *et al.* published the first certified perovskite-based triple-junction solar cell.¹⁴ In this work, an all-perovskite triple-junction solar cell was made using $\text{Rb}_{0.15}\text{Cs}_{0.85}\text{PbI}_{1.75}\text{Br}_{1.25}$ (2.00 eV), $\text{Cs}_{0.05}\text{FA}_{0.90}\text{MA}_{0.05}\text{Pb}(\text{I}_{0.90}\text{Br}_{0.10})_3$ (1.60 eV), and $\text{Cs}_{0.05}\text{FA}_{0.70}\text{MA}_{0.25}\text{Pb}_{0.50}\text{Sn}_{0.50}\text{I}_3$ with 5% SnF_2 (1.22 eV) perovskite absorbers. This cell showed a certified PCE of 23.3%, a j_{SC} of 9.6 mA cm^{-2} , a V_{OC} of 3.20 V and a FF of 76.2%. The encapsulated sample maintained 80% of its initial efficiency after 450 h of measurement in an ambient atmosphere. The main factor leading to this 23.3% efficient triple-junction cell was development of a rubidium (Rb), cesium (Cs) all-inorganic high bandgap perovskite absorber with improved stability. Details on this high bandgap perovskite are summarized in Section 4.3. Here, also a double HTL layer of $\text{NiO}_x/\text{Me-4PACz}$ was employed for both top and middle subcells. The high V_{OC} of 3.2 V partially originated from the high-quality of the perovskite/charge transport layer interface. Me-4PACz has been shown to have a lossless interface with perovskite.³⁷ In addition, in this work the perovskite/PCBM interface was passivated with phenethylammonium iodide and ethane-1,2-diammonium iodide (PEAI-EDAI_2) to reduce the recombination loss at this interface. Moreover, to better protect the underlying layers, polyethyleneimine ethoxylated (PEIE) was spin coated on PCBM layer, prior to deposition of SnO_x similar to the approach that has been previously reported by Palmstrom *et al.*³⁸ As recombination layer between the top and middle cell, 20 nm of sputtered ITO was used whereas 1 nm evaporated Au served as the recombination layer between the middle and bottom cells. This work is the only perovskite-based triple-junction solar cell with certified efficiency.

The proof of concept for a perovskite/perovskite/silicon triple-junction solar cell was reported 1 year earlier than the all-perovskite triple-junction in 2018 by Werner *et al.* using a both-side textured silicon heterojunction (SHJ) bottom cell.²² In this work, perovskite solar cells had a p-i-n configuration. For deposition of perovskite layers on textured surfaces, a hybrid two-step deposition method was used, which the same group reported earlier for a both-side textured perovskite/silicon tandem solar cell.³⁹ This hybrid method is a combination of co-evaporation of a scaffold of the inorganic precursors lead iodide (PbI₂) and cesium bromide (CsBr) and subsequent spin coating of the organic precursors formamidinium iodide (FAI) and formamidinium bromide (FABr) from solution. Adaptation of the FAI/FABr ratio in the second step allows for control of the bandgap. The final perovskites had the general formula of Cs_xFA_{1-x}Pb(I_yBr_{1-y})₃ with non-specified values for x and y but bandgaps of 1.53 eV and 1.80 eV for middle and top cell absorbers, respectively. In this work, 150 nm indium zinc oxide (IZO) was used as a recombination layer between the two perovskite subcells. The champion cell exhibited 14.0% PCE with a FF of 68.0%, a V_{OC} of 2.69 V and a j_{SC} of 7.7 mA cm⁻². The current of the final device was limited by the j_{SC} of the middle cell. In order to estimate the ideal bandgap and thickness ranges for their material stack configuration, they performed optical simulations which showed that when the

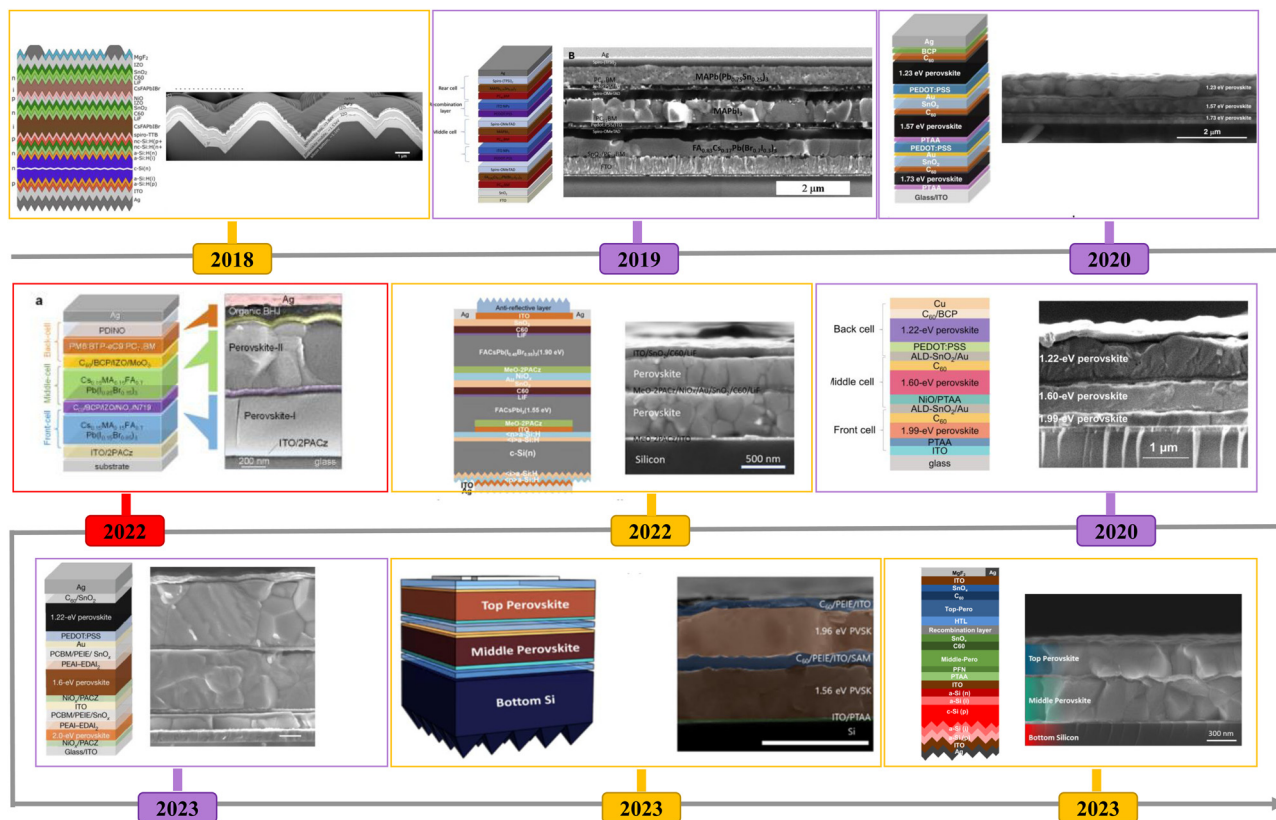


Fig. 6 Structure evolution and cross sectional SEM images of perovskite-based triple-junction solar cells. Reproduced with permission from ref. 14–17, 22–26. Copyright © 2018, American Chemical Society. Copyright © 2019 Published by Elsevier Inc. Copyright © 2020, Wang *et al.*, Published by Springer Nature, Copyright © 2020, American Chemical Society, Copyright © 2022, American Chemical Society, Copyright © 2022, American Chemical Society, Copyright © 2023, Wang *et al.* under exclusive licence to Springer Nature Limited, Copyright © 2023, American Chemical Society, Copyright © 2023 Heydarian *et al.*, Published by American Chemical Society.

bandgap of the top cell is kept at 1.80 eV, the middle cell bandgap should be lowered to ~ 1.40 eV to achieve current matching at a j_{SC} of ~ 12.2 mA cm $^{-2}$ for a flat silicon bottom cell and a $j_{SC} > 13.0$ mA cm $^{-2}$ for a both-side textured bottom cell.

In 2022, Zheng *et al.* achieved 20.1% PCE for a perovskite/perovskite/silicon triple-junction solar cell.¹⁷ In contrast to the previous work, they employed solution-based spin coated perovskite absorbers on a SHJ bottom cell with flat front side and textured rear surface. Their champion device was based on a FA_{0.9}CS_{0.1}PbI₃ (1.55 eV) middle cell absorber and FA_{0.80}CS_{0.20}Pb(I_{0.45}Br_{0.55})₃ (1.90 eV) top cell absorber and reached 20.1% PCE, 86.0% FF and 8.5 mA cm $^{-2}$ j_{SC} with a V_{OC} of 2.74 V. The cell showed acceptable stability measured for more than 40 s at maximum power point. In this work, 1 nm of Au was used as recombination layer between the perovskite subcells. The top perovskite absorber layer had a higher bandgap compared to the previous publication. This bandgap combinations for perovskite middle and top cells are closer to the optimum values suggested by simulations. As an antireflection layer, textured polydimethylsiloxane (PDMS) was used at the front side of the device. Overall, current matching was still not achieved in this work and the perovskite middle cell limited the j_{SC} of the device.

Very recently, Choi *et al.* reported on a 22.2% perovskite/perovskite/silicon triple-junction solar cell¹⁵ on a flat front side

and textured rear side SHJ. Perovskite middle and top cells in this work were Cs_{0.10}FA_{0.85}MA_{0.05}PbI₃ (1.56 eV) and MAPb(I_{0.50}Br_{0.35}Cl_{0.15})₃ (1.96 eV), respectively. To avoid the solvent damage while processing the perovskite top cell, they followed a similar approach as the first all-perovskite triple-junction solar cell by McMeekin *et al.*²³ They employed ACN/MA solvent system instead of DMF/DMSO for the top perovskite which was removed immediately after spin coating and prevented solvent penetration to the underlying layers. By taking advantage of this optimization, the perovskite top cell was fabricated without the ALD SnO_x protection layer. Similar to the record all-perovskite triple-junction work,¹⁴ here PEIE was spin coated on top of C₆₀. In addition, they employed a high-quality high bandgap perovskite achieved *via* additive engineering by adding urea into their perovskite precursor solution. With these two optimizations, the best performing cell showed 22.2% PCE, 78.6% FF and 10.2 mA cm $^{-2}$ j_{SC} with a V_{OC} of 2.78 V. The cell showed satisfactory stability for 600 s measured at maximum power point in ambient atmosphere at room temperature. The j_{SC} of the final device was limited by the middle cell.

Our team recently fabricated perovskite/perovskite/silicon triple-junction solar cell with 20.0% PCE. A SHJ cell with flat front and textured rear side was employed as the bottom cell and perovskite middle and top cells were in p–i–n configuration



similar to the previous works. Perovskite composition for the middle cell was $\text{Cs}_{0.05}(\text{FA}_{0.90}\text{MA}_{0.10})_{0.95}\text{Pb}(\text{I}_{0.95}\text{Br}_{0.05})_3$ with a bandgap of 1.56 eV while the top perovskite absorber was a $\text{Cs}_{0.05}(\text{FA}_{0.55}\text{MA}_{0.45})_{0.95}\text{Pb}(\text{I}_{0.55}\text{Br}_{0.45})_3$ perovskite with 1.83 eV bandgap. The champion cell exhibited 20.1% PCE with a FF of 78.1%, a j_{SC} of 8.9 mA cm^{-2} and V_{OC} of 2.87 eV. The open-circuit voltage was higher than the previously reported values for this structure. This has been achieved through optimizing the interconnection layers between the perovskite subcells with minimum voltage loss by replacing the Au/PTAA interlayer with ITO/2PACz as well as adapting the deposition technique for perovskite top cell to prevent solvent penetration to the middle cell. With regards to the latter, standard antisolvent deposition technique was replaced by an adapted gas quenching method. The solar cell showed acceptable stability for 360 s measured at fixed voltage close to the maximum power point voltage. In addition, for the first time the jV measurement of triple-junction perovskite-based solar cells were performed under a spectrum-adjusted solar simulator. More details on the measurement procedure are discussed in Section 6.2. Similar to the other reported perovskite/perovskite/silicon solar cells, the j_{SC} of this device was limited by the middle cell.²⁶

The only two-terminal perovskite/perovskite/organic triple-junction solar cell was developed by Isikgor and coworkers in 2022 with a p-i-n architecture achieving a V_{OC} of more than 3.00 V. $\text{Cs}_{0.15}\text{MA}_{0.15}\text{FA}_{0.70}\text{Pb}(\text{I}_{0.15}\text{Br}_{0.85})_3$ (2.05 eV) and $\text{Cs}_{0.15}\text{MA}_{0.15}\text{FA}_{0.70}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ (1.62 eV) were used as perovskite absorbers.¹⁶ A ternary organic bulk heterojunction (BHJ) PM6:BTP-eC9:PC₇₁BM with 1.33 eV bandgap served as bottom cell. The champion perovskite/perovskite/organic triple-junction solar cell delivered a PCE of 19.4% with a V_{OC} of 3.03 V, a j_{SC} of 9.1 mA cm^{-2} , and a FF of 70.4%. The cell showed satisfactory stability measured for 600 s at maximum power point in N_2 environment. The limitation of their device stemmed mostly from the performance of the high bandgap perovskite top cell. Even though the V_{OC} of this triple-junction solar cell is impressive through passivation of the top cell's perovskite/ C_{60} interface with phenformin hydrochloride, it still can be improved by reducing the 0.78 V V_{OC} deficit of the high bandgap perovskite.

The device structures and photovoltaic parameters V_{OC} , j_{SC} , FF and, PCE of the discussed perovskite-based triple-junction solar cells are summarized in Table 2.

3. Suitable perovskite absorbers for middle cell application

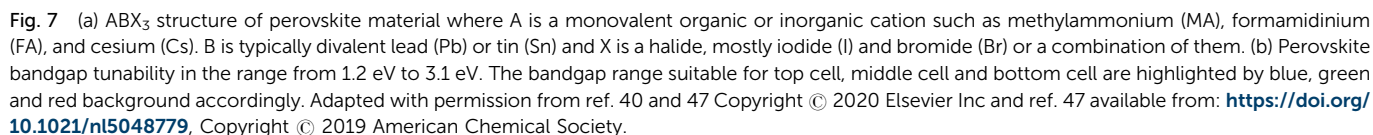
As mentioned in Section 1, in a triple-junction solar cell the optimum bandgap for the middle cell is in the range of 1.40–1.65 eV, depending on the choice of the bottom cell. This range overlays well with the current absorbers used in high-efficient single-junction devices; therefore, development of the middle cell perovskite can strongly benefit from previous research in the field.

Perovskite has a general formula ABX_3 where A is a monovalent organic or inorganic cation such as methylammonium

Table 2 Current density–voltage (jV) performances and device structures of perovskite-based triple-junction solar cells in literature. The values are not certified except for the record all-perovskite solar cell¹⁴

Year	2018	2019	2020	2020	2022	2022	2023	2023	2023
Triple junction type	Perov/pero/silicon	Perov/pero/pero	Perov/pero/pero	Perov/pero/pero	Perov/pero/pero	Perov/pero/organic	Perov/pero/pero	Perov/pero/silicon	Perov/pero/silicon
Structure	Substrate Texture SHJ/spiro TTB/1.53 eV perov/LiF/ C_{60} / SnO_2 /ITO/ NiO_x / 1.8 eV perov/LiF/ C_{60} / SnO_2 /ITO/ MgF_2	Superstrate Glass/FTO/ SnO_x / PCBM/1.94 eV perov/spiro- OMeTAD/PED- OT:PSS/ITO/ PCBM/1.55 eV perov/spiro- OMeTAD/PED- OT:PSS/ITO/ PCBM/1.34 eV perov/spiro (TSF)/ Ag	Superstrate Glass/ITO/PTAA/ SnO_x /Au/PED- OT:PSS/PTAA/ 1.57 eV perov/ C_{60} / SnO_x /Au/PED- OT:PSS/1.23 eV perov/ C_{60} /BCP/Ag	Superstrate Glass/ITO/PTAA/ 1.73 eV perov/ C_{60} / SnO_x /Au/ NiO_x / PTAA/1.6 eV perov/ C_{60} / SnO_x /Au/ PEDOT:PSS/1.22 eV perov/ C_{60} /BCP/ Cu	Substrate SHJ/ITO/ $\text{MeO}2$ - PACz/1.55 eV perov/LiF/ C_{60} / SnO_2 /Au/ NiO_x / $\text{MeO}2$ -PACz/1.9 eV perov/LiF/ C_{60} / SnO_x /ITO/PDMS	Superstrate Glass/ITO/2PACz/ 2.05 eV perov/ Phen-HCl- C_{60} / BCP/ITO/ NiO_x / N719/1.62 eV perov/ C_{60} /BCP/ ITO/ MoO_3 /1.33 eV organic/ PDINO/Ag	Superstrate Glass/ITO/ NiO_x / Me-4PACz/ 2.0 eV perov/PEAI- EDAI ₂ / PCBM/PEIE/ SnO_x /ITO/ NiO_x /Me-4PACz/1.6 eV perov/PEAI-EDAI ₂ /PCBM/ PEIE/ SnO_x /Au/PEDOT:PSS/ 1.22 eV perov/ C_{60} / SnO_x /Ag	Substrate SHJ/ITO/PTAA/ PFN/1.56 eV perov/ C_{60} / SnO_x / ITO/2PACz/1.83 eV perov/ C_{60} / SnO_x /ITO/Ag/ MgF_2	Substrate
Config	p-i-n	n-i-p	p-i-n	p-i-n	p-i-n	p-i-n	p-i-n	p-i-n	p-i-n
Scan direction	Reverse	Forward	Reverse	Forward	Reverse	Forward	Reverse	Forward	Reverse
PCE (%)	14.0	12.1	6.7	NA	16.8	16.4	16.4	20.1	20.1
FF (%)	68.0	58.7	43.0	NA	82.0	81.0	81.1	78.6	78.1
j_{SC} (mA cm^{-2})	7.7	7.7	8.3	NA	7.3	7.3	7.3	10.2	8.9
V_{OC} (V)	2.69	2.69	2.70	NA	2.79	2.77	2.77	2.78	2.87
Area (cm^2)	1.420	0.092	0.092	NA	0.068	0.049	0.049	NA	1.000
Ref.	22	23	25	17	24	16	14	15	26





Primarily, the perovskite's bandgap is determined by the B- and X-site ions forming a $[\text{BX}_6]$ octahedral framework. The valence band maximum (VBM) consists of B-s and X-p orbital coupling, while CBM consists mainly of B-p orbital contribution.⁴⁴ The A-site cation has ionic character and its electronic states do not contribute to the VBM or CBM.⁴⁵ Nonetheless, the A cation can influence the $[\text{BX}_6]$ framework sterically or electrostatically. In this way, expansion or tilting of the lattice structure can lead to changes in the bandgap.⁴⁶ Depending on the B-site cation used (Pb or Sn), smaller cations on the A-site ($\text{Cs} < \text{MA} < \text{FA}$) can either increase or reduce the bandgap.⁴⁶ Most commonly, A- and X-sites are tuned at the same time to adjust the bandgap and ensure phase stability of the final composition.

3.1 Middle perovskite subcell in current triple-junction solar cells

The record PCE of p-i-n perovskite single-junction solar cells is 24.7% using a tri-cation double halide absorber with a $\text{Cs}_{0.05}(\text{FA}_{0.95}\text{MA}_{0.05})_{0.95}\text{Pb}(\text{I}_{0.95}\text{Br}_{0.05})_3$ composition and a 1.55 eV bandgap.⁵¹ Currently the perovskite middle cells in reported triple-junction solar cells have bandgaps in the range of 1.55 eV to 1.62 eV. Table 3 summarizes compositions and bandgaps of

As mentioned before, so far, the reported perovskite/perovskite/silicon triple-junction solar cells suffer from current mismatch in a way that the middle cell is limiting the overall current of the device and highest current is being generated in the silicon bottom cell. For improved current matching, reducing the bandgap of the middle cell perovskite absorber is required. In the following sections, we discuss the two most promising perovskite candidates with bandgap lower than 1.50 eV.

3.2 Strategies for stable FAPbI₃ perovskite with bandgap of 1.47 eV

Compared to MAPbI₃, implementing FA on the A-site allows to form a nearly cubic structure, a reduced bandgap (1.47 eV), and improved thermal stability.^{52,53} Moreover, its bandgap is ideal to be used as middle cell absorber in a triple-junction structure with a 1.12 eV bottom cell. The work on FAPbI₃ solar cell has mostly been in the n-i-p architecture which holds the record single-junction perovskite solar cell with a PCE of 25.8%.⁵⁴ Despite the relatively fewer works on the FAPbI₃ based p-i-n solar cells, recently an impressive PCE of 24.1%⁵⁵ has been reported, which is promising for multi-junction solar cell's application.

The major challenge of FAPbI₃ perovskite lies in its limited structural stability. Due to disordered FA-I ion interaction, the asymmetrical FA cation takes an off-centered position, which results in the formation of a trigonal instead of a cubic structure. Experimentally, a 1D yellow non-perovskite polymorph (yellow δ -phase) is formed for usual low-temperature annealing around ~ 100 °C. Annealing at 160 °C allows to form the desired cubic phase (black α -phase),⁵⁶ which could harm temperature-sensitive underlying layers. Moreover, exposure to ambient environment, particularly high humidity, can trigger the phase transition from black α - to yellow δ -phase.⁵⁶

Fig. 8 shows the PCE evolution of FAPbI₃ perovskites for n-i-p and p-i-n structures.

Table 3 *j*V performance, perovskite composition, bandgap, absorber layer thickness, and device structure of perovskite single-junction solar cells with middle perovskite absorber used in perovskite-based triple-junction solar cells in literature. Single-junction solar cell values for the first perovskite/perovskite/silicon solar cell are not available (due to the fully textured design and respective optimization of processes on textured silicon bottom solar cells)²²

Year	2019	2020	2020	2022	2022	2023	2023	2023
Composition	MAPbI ₃	FAPbI ₃	FA _{0.66} MA _{0.34} PbI _{2.85} Br _{0.15}	Cs _{0.1} FA _{0.9} PbI ₃	Cs _{0.15} MA _{0.15} FA _{0.70} PbI _{2.85} Br _{0.15}	Cs _{0.05} FA _{0.95} PbI ₃	Cs _{0.1} FA _{0.85} MA _{0.05} PbI ₃	Cs _{0.05} (FA _{0.9} MA _{0.1}) _{0.95} PbI _{2.95} Br _{0.05}
Bandgap (eV)	1.57	1.57	1.57	1.55	1.62	1.60	1.56	1.56
Structure	Glass/FTO/SnO ₂ /perovskite/PCBM/perovskite/Ag/spiro-OMeTAD/Ag	Glass/ITO/PTAA/perovskite/C60/BCP/Al	Glass/ITO/PTAA/perovskite/C60/BCP/Cu	Glass/ITO/HTL/perovskite/LiF/C60/BCP/Cu	Glass/ITO/NiO _x /perovskite/C60/BCP/Ag	Glass/ITO/NiO _x /Me-4PCz/perovskite/PEAI-EDAI ₂ /PCBM/PEIE/SnO ₂ /Ag	Glass/ITO/PTAA/PFN-Br/perovskite/C60/PEIE/Ag	Glass/ITO/PTAA/PFN-Br/perovskite/C60/SnO _x /Ag/MgF ₂
Molarity (M)	1.03 : 1	1.03 : 1	1.03 : 1	1.03 : 1	1.03 : 1	1.03 : 1	1.03 : 1	1.03 : 1
Thickness (nm)	530	450	280	NA	NA	780	NA	450
PCE (%)	15.3	16.5	19.4	18.1	21.0	21.1	20.1	15.6
FF (%)	70.0	76.0	80.2	78.0	79.4	77.3	80.3	77.2
<i>J</i> _{sc} (mA cm ⁻²)	20.8	21.0	22.4	23.3	22.4	22.5	24.5	19.8
<i>V</i> _{oc} (V)	1.06	1.03	1.08	1.01	1.18	1.20	1.04	1.02
Top cell in	Pero/pero/pero	Pero/pero/pero	Pero/pero/pero	Pero/pero/silicon	Pero/pero/organic	Pero/pero/pero	Pero/pero/silicon	Pero/pero/silicon
Ref.	23	25	24	17	16	14	15	26

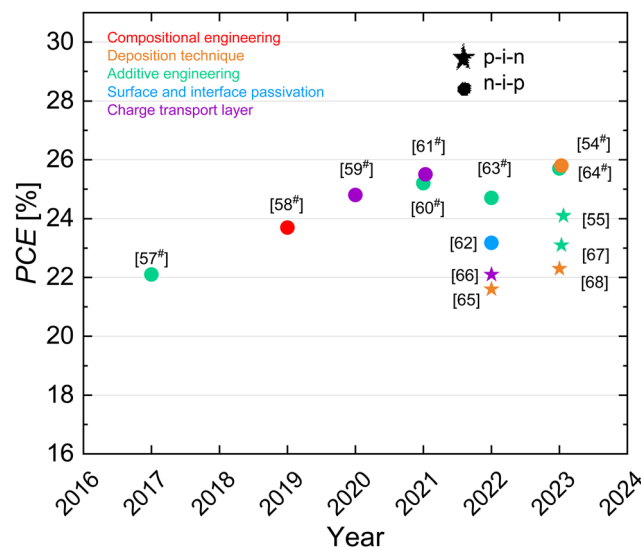


Fig. 8 PCE evolution of FAPbI₃ solar cells in p-i-n and n-i-p configuration discussed in this review for different strategies that resulted in efficient solar cells and improved stability (red: compositional engineering, orange: deposition technique, green: additive engineering, blue: surface and interface passivation and purple: charge transport layer). Data for n-i-p configuration are taken from ref. 54 and 57–64 and for p-i-n configuration from ref. 55 and 65–68. Certified values are marked with #.

In order to improve the stability of FAPbI₃ and achieve the black perovskite phase at low annealing temperature several strategies have been reported in the literature, which we briefly summarize below:

(1) Compositional engineering: the most famous approach to stabilize the black α -phase is alloying a small concentration of cations and anions with smaller ionic radius such as MA, Cs and Br to the composition. For example, Lee *et al.* showed that by adding a small amount of CsI to FAPbI₃, a black perovskite phase can be formed even prior to the annealing step.⁶⁹ This approach however has the drawback of increasing the bandgap of perovskite. Min *et al.* reported stable α -FAPbI₃ by incorporation of small amount of methylenediammonium dichloride (MDACl₂) into perovskite lattice. The film annealed for 10 minutes at 150 °C, showed almost identical bandgap compared to the control film, and the corresponding solar cell delivered 23.7% certified efficiency. This perovskite solar cell retained 90% of its PCE for 20 h in air under 150 °C with no encapsulation.⁵⁸ Moreover, non-stoichiometric modified precursors have shown several advantages in film quality of different perovskite compositions. For FAPbI₃ perovskite, excess FAI resulted in formation of the black film at low annealing temperature of 60 °C⁷⁰ or even without annealing at room temperature.⁷¹ Zhang *et al.* systematically studied the effect of excess PbI₂ in FAPbI₃ precursor solution and found that it reduced charge trap densities and prolonged charge carrier lifetimes.⁶⁶ Previous studies have confirmed the impact of excess PbI₂ in passivating the grain boundaries of perovskite.⁷²

(2) Deposition technique: the fabrication method employed to deposit the perovskite layer is known to influence film crystallization. Instead of common one-step spin coating

deposition, a two-step sequential deposition is found to form stable α -phase FAPbI₃ at low annealing temperature of 80 °C.⁷³ In this technique, PbI₂ is first deposited and then FAI solution is processed on top. It is crucial to obtain a highly porous thin film of PbI₂ in first place to form stable phase-pure α -FAPbI₃.⁷⁴ Xu *et al.* showed that by using DMF/N-methyl-2-pyrrolidone (NMP) solvent mixture for PbI₂, a porous morphology can be achieved. In addition, they introduced a dynamic spin coating method in which a pure α -phase FAPbI₃ film formed even prior to the annealing step.⁷⁴ Huang *et al.* used a mixture of isopropanol/hexafluorobenzene solvent for the organic salt of the second step and achieved a very high efficiency of 25.8% which retained 94% of its efficiency for more than 1000 h of MPP tracking.⁵⁴ Vacuum deposition is an alternative method to conventional solution processing. Borchert *et al.* showed that by co-evaporation of FAI and PbI₂, homogeneous and pinhole-free FAPbI₃ film can be formed. They demonstrated that in contrast to the standard solution processing which requires long annealing steps, here only a very short annealing time of 1 minute at 170 °C was needed to convert δ -phase of FAPbI₃ to the desired α -phase.⁷⁵

(3) Additive engineering is reported to enhance phase stability of FAPbI₃ by improving perovskite crystallization and defect passivation. For example, adding methylammonium chloride (MACl) into the perovskite precursor solution has been reported in both inverted⁶⁷ and regular^{54,63,76} architectures. Park *et al.* reported a 25.7% PCE by adding propylammonium chloride (PACl) as a secondary additive to the FAPbI₃ with MACl additive.⁶⁴ Jeong *et al.* added 2% formamidinium formate (FAHCOO) which is a pseudo-halide additive into the precursor solution and reported a certified PCE of 25.2% for a FAPbI₃ perovskite solar cell with improved operational stability over 450 h with no encapsulation.⁶⁰ Jiang *et al.* incorporated methylamine formate (MAFa) ionic liquid into FAPbI₃ perovskite which resulted in crystallinity and morphology improvement and increase of charge carrier lifetime. As a result, record PCE of 24.1% for inverted architecture was achieved. In addition, this strategy led to prolong stability against moisture with only 10% loss of PCE after storing the sample for 1000 h in ambient without encapsulation.⁵⁵ Furthermore, adding CsPbBr₃⁶³ and MAPbBr₃⁵⁷ into FAPbI₃ solution are reported to reduce the deep level defects concentration and increase the performance.

(4) Interfacial and surface passivation: interfacial treatment by formation of thin two-dimensional perovskite capping layers, between the 3D perovskite and the subsequent charge transport layer can protect FAPbI₃ from moisture penetration and stabilize its α -phase. Wang *et al.* demonstrated that post treatment of the perovskite surface with cyclopropylcarbamide hydrochloride (CPAH) resulted in formation of a hydrophobic 2D layer of (CPA)₂PbI₂Cl₂ on top of the perovskite surface which significantly improved the stability of the solar cells against humidity. CPAH treated samples retained 74% of the initial PCE after 150 h storage in ambient environment.⁷⁷ In a similar approach Kareem *et al.* treated FAPbI₃ surface with a 2-(4-fluorophenyl) ethyl ammonium iodide (FPEAI). The PCE of the not-passivated device maintained only 46% of its initial

PCE, while the device with FPEAI showed 80% of its efficiency during more than 1000 h measurement due to the formation of 2D/3D heterostructure.⁶²

(5) Charge transport layer: the charge transport layer plays an important role on phase stability of FAPbI₃ films. Roß *et al.* studied the effect of the HTL on phase stability of co-evaporated FAPbI₃ in p-i-n configuration and demonstrated that free phosphonic acids groups of the self-assembling molecule MeO-2PACz significantly improved the stability of the black FAPbI₃ perovskite phase.⁷¹ Zhang *et al.* also compared the effect of different commonly used HTL materials in p-i-n configuration: PEDOT:PSS, PTAA, NiO_x, and MeO-2PACz in FAPbI₃ solar cells. Similarly, they reported that devices with MeO-2PACz showed higher PCE and much longer stability as 92% of the PCE was retained after 800 h storage at room temperature and high humidity with no encapsulation.⁶⁶ Min *et al.* reported a 25.5% FAPbI₃ solar cell which was achieved by chemical passivation of perovskite/ETL interface in an n-i-p configuration. By coating a Cl-containing perovskite on a Cl-bonded SnO_x, a FASnCl_x interlayer was formed between the perovskite and the underlying ETL. The successful passivation not only resulted in improved charge extraction and reduced non-radiative recombination but also led to better long term stability (90% of the initial PCE was retained after 500 h of MPP tracking) of the device with no encapsulation.⁶¹ A study by Jeong *et al.* compared Spiro-OMeTAD, Spiro-mF and Spiro-oF as HTLs and showed that the fluorination of Spiro-OMeTAD helps to achieve high-efficient FAPbI₃ cells with improved stability (Fig. 9).⁵⁹

More detailed reviews on FAPbI₃-based perovskites as well as strategies to overcome the challenges associated with them are presented in recent review articles.^{53,56,78,79}

3.3 Strategies for stable Pb-Sn perovskite with bandgaps below 1.47 eV

Further lowering the bandgap of perovskite is possible by complete or partial substitution of Pb with Sn in B-site cation, which directly alters the conduction band.^{44,80,81} Sn-containing perovskites with mixture of halides in the composition (Br/I) cover a broad bandgap range from 1.2 eV to 2.0 eV.⁸² The reduction of bandgap however does not follow a linear trend when substituting Pb with Sn;^{80,81} studies have shown that in mixed Sn-Pb perovskites the bandgap continuously reduces by increasing Sn content and reaches its minimum at approximately 80% Sn content and then widens afterwards. Thus, MAPb_{0.20}Sn_{0.80}I₃ shows a lower bandgap of 1.19 eV compared to MASnI₃ with 1.28 eV bandgap.⁸⁰ Sn-based perovskite solar cells were first explored in 2012⁸³ and significant progress has been made ever since; in 2023 the PCE of Sn-containing perovskite increased to 23.7% using a Cs_{0.2}FA_{0.8}Pb_{0.5}Sn_{0.5}I₃ (1.29 eV) absorber.⁸⁴ Fig. 10 shows the PCE evolution of Pb-Sn perovskites along with their corresponding compositions and bandgaps.

Sn-containing perovskite absorbers have been widely used as low bandgap bottom cell in all-perovskites dual-junction and recently triple-junction devices. The community therefore has focused on perovskites with low bandgap ~ 1.20 eV; less research is available on Sn-based perovskites with bandgaps



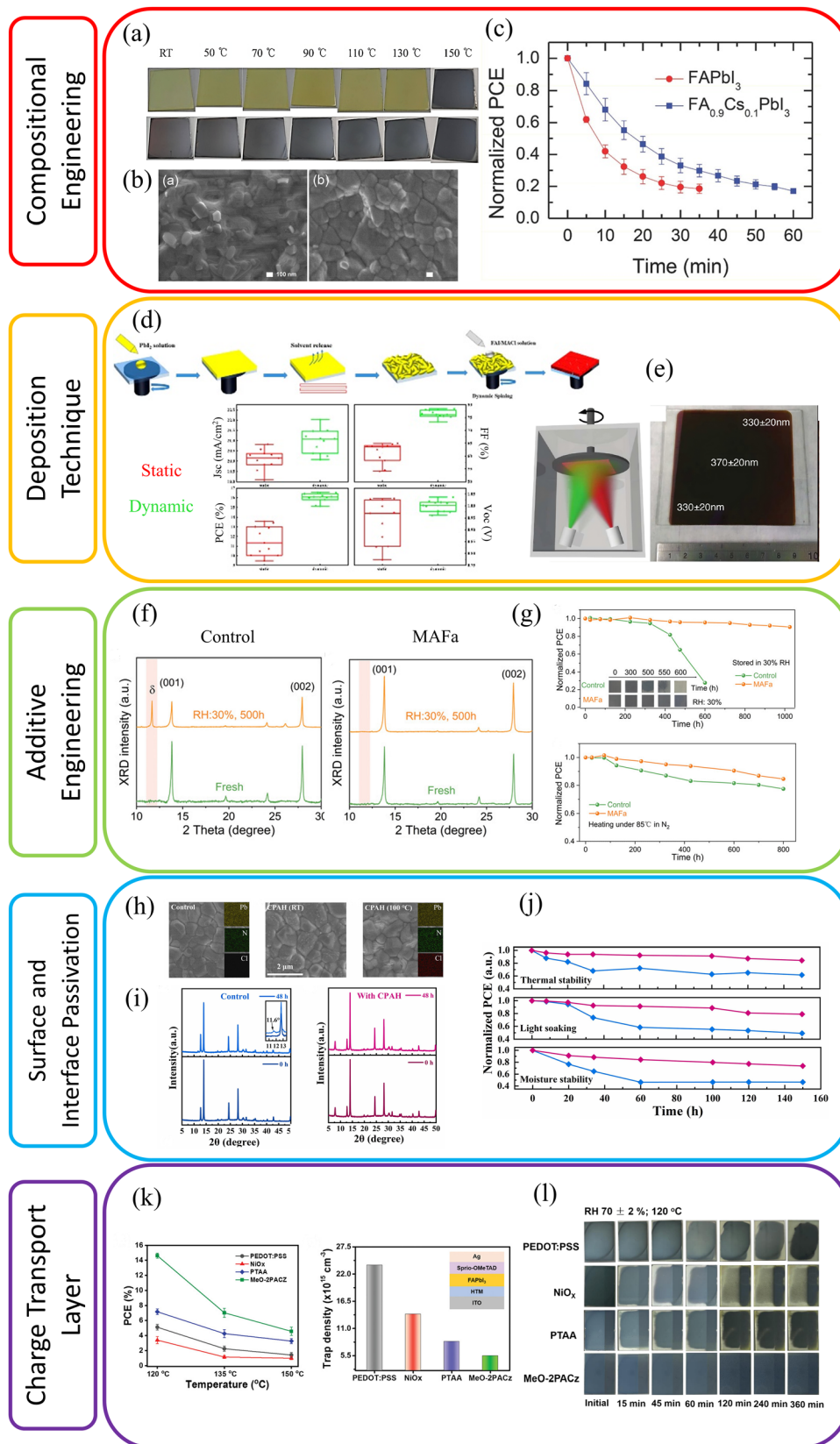


Fig. 9 General approaches reported in literature to improve performance and stability of FAPbI₃ perovskite solar cells. (a) FAPbI₃ and FA_{0.9}Cs_{0.1}PbI₃ films with different annealing temperatures, (b) Top view SEM images of FAPbI₃ and FA_{0.9}Cs_{0.1}PbI₃ and (c) normalized PCE of their respective solar cells without encapsulation measured over time in ambient. Cs incorporation resulted in formation of black perovskite even at room temperature. FA_{0.9}Cs_{0.1}PbI₃ has improved film quality and stability compared to pure FAPbI₃. Reproduced with permission from ref. 69. Copyright © 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (d) Schematic illustration of perovskite processing of FAPbI₃ solar cells processed with 2-step deposition method using dynamic

spin coating for the organic salt and statistical photovoltaic parameters (j_{sc} , PCE, FF and V_{oc}) of FAPbI₃ solar cells comparing static and dynamic spin coating for organic salt deposition. Reproduced with permission from ref. 74. Copyright © 2022, Rights managed by AIP Publishing. (e) Schematic illustration of evaporation method for processing of FAPbI₃ and respective FAPbI₃ film processed on large area with this method. Black FAPbI₃ is formed after 1 minute annealing at 170 °C. Reproduced with permission from ref. 75 Copyright © 2017, American Chemical Society. (f) XRD measurement of fresh and aged FAPbI₃ films with and without MAFA additive and (g) operational and thermal stability of FAPbI₃ solar cells with and without MAFA additive. Adding MAFA into perovskite precursor leads to excellent phase stability for 500 h and the corresponding solar cell exhibited improved operational stability. Reproduced with permission from ref. 55. Copyright © 2023 Wiley-VCH GmbH. (h) Top view SEM images of FAPbI₃ films with and without passivation with CPAH, (i) XRD measurement of fresh and aged FAPbI₃ films with and without CPAH treatment and (j) operational and thermal stability of FAPbI₃ solar cells with and without passivation. Passivating the perovskite surface with CPAH resulted in phase stability for 48 h and the corresponding solar cell exhibited improved operational stability. Reproduced with permission from ref. 77. Copyright © 2021 Elsevier Ltd. All rights reserved. (k) PCE of FAPbI₃ solar cell in p-i-n configuration using different HTLs and varied annealing temperature along with the trap density calculated for perovskite films on different HTLs and (l) perovskite films with different HTLs kept under 70% RH and 120 °C condition. Solar cell with MeO-2PACz as HTL indicated highest PCE and lowest trap density. The FAPbI₃ perovskite deposited on MeO-2PACz was more stable compared to other HTLs. Reproduced with permission from ref. 66. Copyright © 2022 Wiley-VCH GmbH.

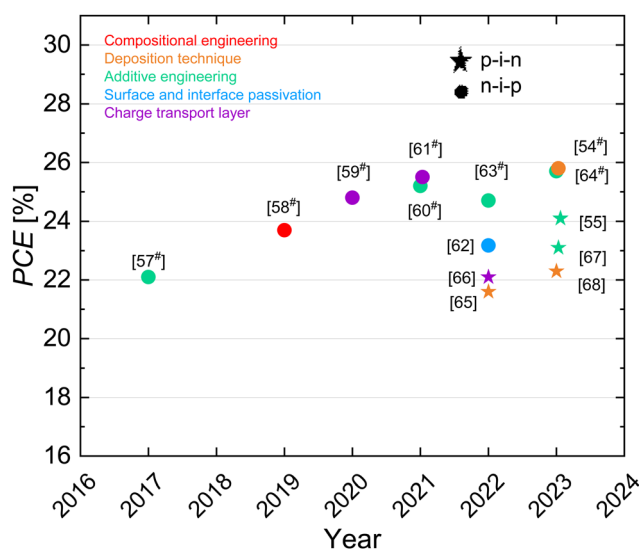


Fig. 10 Composition, bandgap and PCE evolution of Sn-containing perovskites discussed in this review for different strategies that resulted in efficient solar cells and improved stability (red: compositional engineering, orange: deposition technique, green: additive engineering, blue: surface and interface passivation and purple: charge transport layer). Data are taken from ref. 84–92. Certified values are marked with #.

In general, there are two major challenges associated with Sn-containing perovskite. First, Sn^{2+} can easily be oxidized to Sn^{4+} in the presence of small amounts of oxygen leading to defect formation that reduces carrier lifetime.⁹³ Second, due to non-uniform nucleation and fast crystallization of Sn-containing perovskite, fabrication of high-quality, homogeneous, compact, and pinhole-free film is more challenging compared to pure Pb perovskite.^{91,94} Such non-ideal perovskite films with defects and large number of

grain boundaries in turn accelerate the oxidation of Sn^{2+} . Klug *et al.* reported that the photoluminescence intensity of perovskite film decreased by orders of magnitude when replacing only 1% of the Pb with Sn in the composition, which proves the challenges on the way of bringing Sn-based perovskite to the level of pure Pb perovskite.⁹⁵

Some strategies reported in literature to overcome these challenges are:

(1) Compositional engineering: perovskite composition and solution preparation have a crucial impact on the quality of the perovskite film in general and consequently the device performance. This is particularly critical in the case of Sn-based perovskites since they are prone to defects as discussed before. Usually, the perovskite solution is prepared by dissolving the precursor powders in an appropriate solvent. Liao *et al.* introduced a new precursor system by preparing FASnI_3 and MAPbI_3 precursor solutions separately and mixed them subsequently at different molar ratios. The fabricated $(\text{FASnI}_3)_{0.6}(\text{MAPbI}_3)_{0.4}$ perovskite films showed dense grains with no visible pinholes.⁹⁶ Li *et al.* demonstrated that incorporation of Br in mixed Pb–Sn perovskite improves perovskite film quality and effectively passivates the grain boundaries. Optimizing Br concentration to 6% led to 19.0% PCE.⁸⁹ In another approach incorporation of Cs into $\text{FA}_{0.8}\text{MA}_{0.2}\text{Sn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ perovskite improved the operational stability and for the optimum Cs content of 2.5%, PCE of 18.2% was reported.⁹⁷

(2) Deposition technique: as discussed in the previous section, fabrication method can have a huge impact on morphology of the formed perovskite film. Abdollahi Nejand *et al.* introduced processing of Sn-containing perovskite films *via* the vacuum-assisted growth control (VAGC). In this method, instead of using an antisolvent, a vacuum chamber is used to remove the solvents from the film. As a result of process optimization, homogeneous pinhole-free perovskite layers with large grains were achieved.⁹⁴ Werner *et al.* employed the gas quenching method, in which a flow of nitrogen is used to remove the solvent from the film. Sn-containing perovskite films processed with N₂ quenching also showed uniform, pinhole-free morphology.⁹¹ The improvement in morphology was shown to reduce defects at the grain boundaries and is a crucial factor to improve the performance and stability of Sn-containing perovskites.⁹⁸

(3) Additive engineering: introducing inorganic Sn halide additives SnX_2 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) into the precursor solution has

(5) Charge transport layer: the charge transport layer plays an important role for the stability of Sn-containing perovskite solar cells. PEDOT:PSS is the most widely used HTL in p-i-n configuration for Pb-Sn perovskite solar cells. However, stability of solar cells employing this HTL is a concern due to its hygroscopic and acidic nature. Ghimire *et al.* employed a PEDOT:PSS/PTAA bilayer in their Pb-Sn perovskite which resulted in improved morphology and larger grain size. Moreover, due to hydrophobic nature of PTAA, devices incorporating this bilayer as the HTL, exhibited significantly improved stability when compared to those using PEDOT:PSS.¹⁰⁵ Kapil *et al.* achieved 23.3% efficiency by employing a 2PACz/methyl phosphonic acid (MPA) bilayer as HTL in Pb-Sn perovskite. Perovskite films with 2PACz/MPA showed much slower oxidation rate.⁹⁰ Pitaro *et al.* compared

(1) Compositional engineering: the composition of HBG perovskites is an important factor influencing device performance

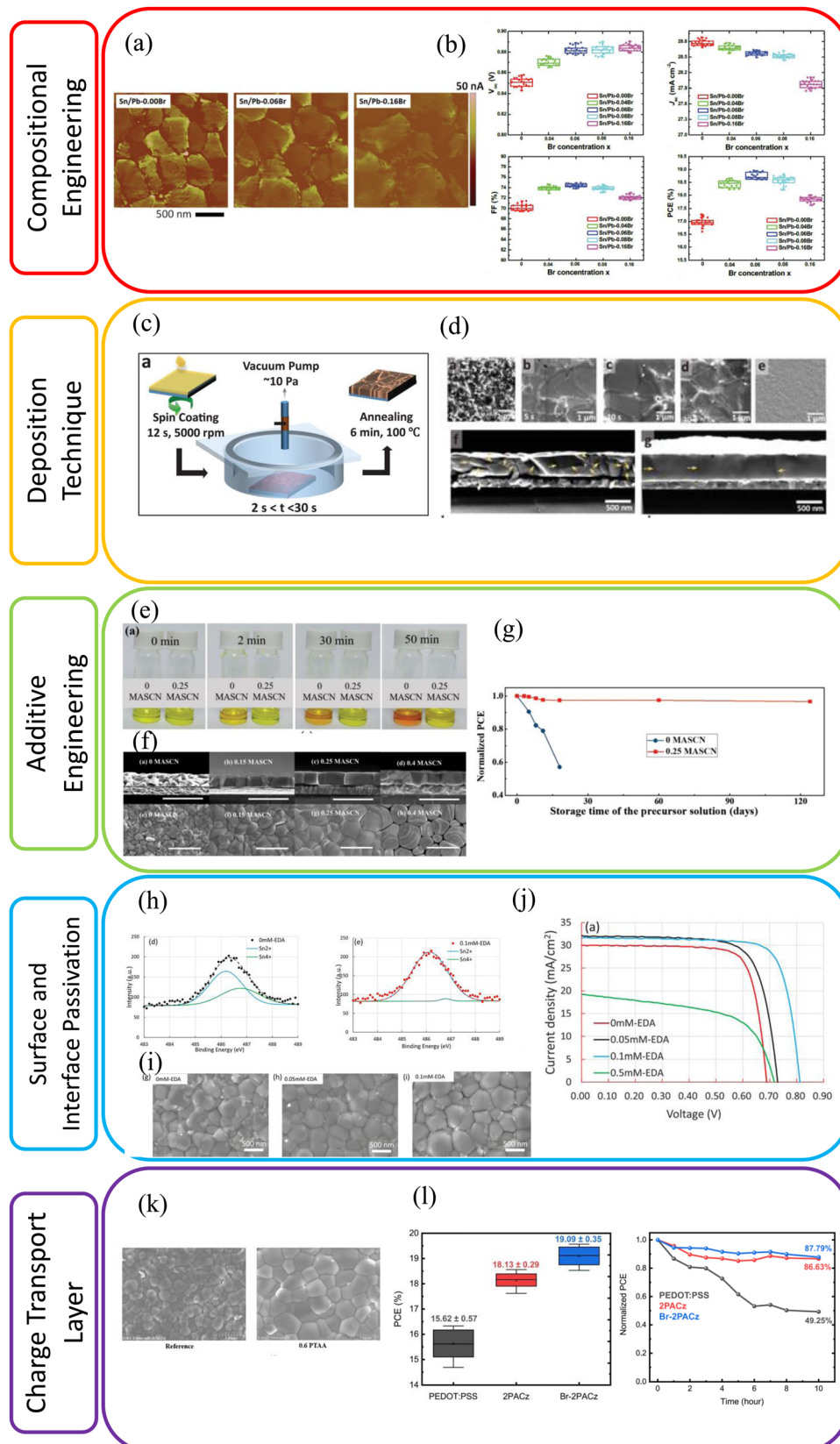


Fig. 11 General approaches reported in literature to improve performance and stability of Pb–Sn perovskite solar cells. (a) AFM images of Pb–Sn perovskite and (b) statistical photovoltaic parameters (J_{SC} , V_{OC} , FF, and PCE) of Pb–Sn perovskite with different Br concentrations. Br incorporation resulted in larger grain size, and the highest PCE is achieved for solar cells with 6% Br concentration. Reproduced with permission from ref. 89 Copyright © 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Schematic illustration of deposition of Pb–Sn perovskite with VAGC and (d) top view and



cross sectional SEM images of perovskite films processed with antisolvent and VAGC methods. Perovskite processed with VAGC had larger grains compared to the film processed with antisolvent. Reproduced from ref. 94 Copyright © 2019 Abdollahi Nejand *et al.* Published by WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim under the Creative Commons CC BY. (e) Aging Pb–Sn perovskite precursor solution with and without MASCN additive. (f) Top view and cross sectional SEM images of perovskite films with different concentrations of MASCN and (g) normalized PCE of the solar cells with and without MASCN additive as a function of precursor solution aging time. Pb–Sn precursor solution with additive showed no oxidation after 50 minutes exposure to air. Enlarged grain size is achieved for the films with additive in the precursor. Reproduced with permission from ref. 101 Copyright © 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (h) XPS measurement of untreated and EDA coated Pb–Sn perovskite films, (i) top view SEM images of perovskite surface and (j) jV characteristic of solar cells with no passivation and passivated with different concentration of EDA. Non-treated perovskite contains higher concentration of Sn^{4+} compared to the treated surface. Better film quality is achieved with EDA treatment. 0.1 mM was found to be optimum EDA concentration resulting in maximum PCE. Reproduced with permission from ref. 103. Copyright © 2021 Wiley-VCH GmbH. (k) Top view SEM images of Pb–Sn perovskite deposited on PEDOT:PSS and PEDOT:PSS/PTAA bilayer. Hydrophobic nature of PTAA compared to PEDOT:PSS resulted in larger grain size formation. Reproduced with permission from ref. 105. Copyright © 2022 Wiley-VCH GmbH. (l) Statistical PCE and stability of Pb–Sn perovskite with PEDOT:PSS, 2PACz and Br-2PACz as HTL. Devices with Br-2PACz exhibited higher PCE and stability. Reproduced from ref. 106. Copyright 2023 © Royal Society of Chemistry under Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

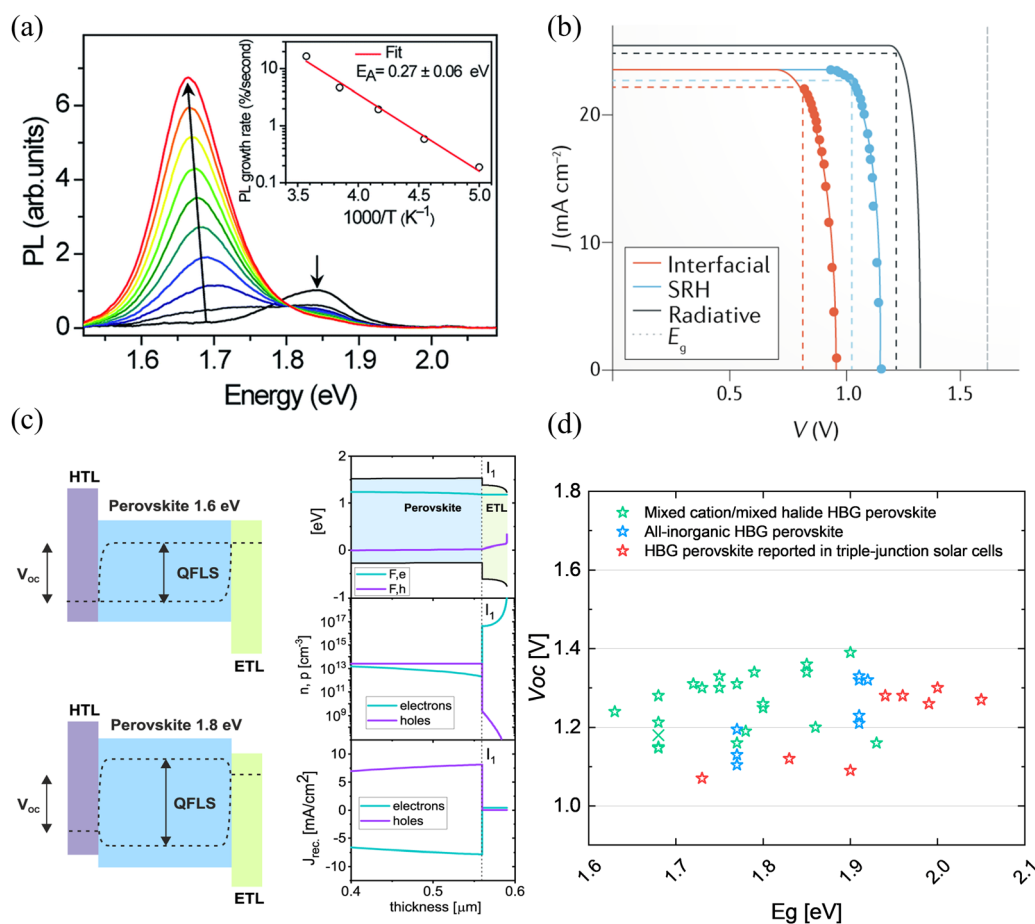


Fig. 12 Origin of V_{OC} limitation in HBG perovskite solar cells. (a) Phase segregation of mixed halide high bandgap perovskite. Reproduced from ref. 112 Copyright © 2015, The Royal Society of Chemistry used under a Creative Commons Attribution CC BY 3.0. (b) V_{OC} loss of a solar cell due to non-radiative recombination loss. Reproduced from ref. 115. Copyright © 2020, Springer Nature Limited. (c) Band diagram of perovskite and its charge transport layers showing a band misalignment for 1.8 eV perovskite due to the fact that the HTL and ETL were optimized for 1.6 eV perovskite. Reproduced from ref. 114 Copyright © 2023, Caprioglio *et al.* under a Creative Commons Attribution CC BY and (d) V_{OC} of some of the high bandgap perovskite solar cells discussed in this review as a function of the reported bandgaps. The discrepancy between V_{OC} and bandgap increases for high bandgap perovskite solar cells.

and stability as each composition may induce a different electronic and crystal structure. Therefore, perovskites with same bandgap and different compositions do not necessarily exhibit similar trap states in their films. Bush *et al.* studied a wide range of double

cation (FA/Cs)/double halide (Br/I) perovskite compositions and found that increasing the bandgap should not only be relied on Br content. Increasing the Cs content allows to reduce the Br content (to a certain extent) while maintaining similar bandgap and

(3) Additive engineering: additive engineering is another strategy to improve the perovskite's quality as well as passivating the trap states at bulk and grain boundaries. Yu *et al.* added lead thiocyanate $\text{Pb}(\text{SCN})_2$ to their HBG perovskite precursors and achieved much larger grain size compared to their reference perovskite.¹²² Kim *et al.* improved the morphology and crystallinity of the HBG perovskite by adding $\text{Pb}(\text{SCN})_2$ and phenethylammonium iodide (PEAI) to the perovskite precursor.¹²³ Chloride-based additives such as MACl have also successfully been implemented in HBG perovskite which resulted in more homogeneous halide distribution and mitigation of phase segregation.^{124–126} Moreover, Thiesbrummel *et al.* added small amount of oleylamine into HBG perovskite which resulted in improvement of V_{OC} .¹²⁷ An *et al.* added phenylethylammonium acetate (PEAAc) additive to a variety of perovskites in the bandgap range of 1.72–1.92 eV. They showed that PEAAc resulted in more homogeneous halide distribution and hence reduced traps.¹²⁸ Urea as an additive has shown impressive improvement in film quality and performance of 1.96 eV perovskite¹⁵ which is discussed further in Section 4.3. It is worth mentioning that the amount of these additives must carefully be tuned with respect to the perovskite composition, bandgap and processing route.¹¹⁹

(4) Interfacial and surface passivation: employing surface and interfacial passivation with materials such as phenylethylammonium iodide (PEAI)¹²⁹ and butylammonium bromide (BABr),¹³⁰ which results in formation of a 2D layer on top of 3D perovskite, is an effective method to enable mitigation of halide segregation

(5) Underlying charge transport layer: proper choice of the charge transport layer can result in enhanced V_{OC} . Up to 2020, PTAA and NiO_x were the most widely used HTL of perovskite solar cells in p-i-n configuration, till a group of carbazole-based self-assembled monolayer (SAM) materials, namely 2PACz, MeO-2PACz and Me-4PACz, were introduced.^{134,135} HBG perovskite devices with SAM exhibited highly improved photostability compared to PTAA.³⁷ Ever since, most of the efficient HBG perovskite solar cells employed SAM in their structure.^{114,124,127,129,136} Recently, He *et al.* developed a new SAM (4-(7*H*-dibenzo[*c,g*]carbazol-7-yl)butyl)phosphonic acid (4PADCB) as HTL of 1.77 eV perovskite and demonstrated the lowest V_{OC} deficit for such HBG perovskite.¹³⁷ Currently the HTLs are not specifically optimized for perovskites with band-gap exceeding 1.80 eV, therefore there could be a mismatch between the HTL and perovskite energy levels which needs to be studied and addressed in future.

Fig. 13 summarizes the approaches that has been successfully employed to enhance the performance and stability of HBG perovskite solar cells.

4.2 Strategies for stable all-inorganic high bandgap perovskites with bandgaps above 1.77 eV

All-inorganic perovskite compositions with general formula of CsPbX_3 are promising to achieve bandgaps above 1.77 eV. They cover a bandgap range of 1.77 eV for CsPbI_3 to 2.30 eV for CsPbBr_3 .⁴⁰ Although the performances of all-inorganic perovskites still lag behind the standard organic inorganic compositions, they feature better photo-¹⁴ as well as thermal stability.¹³⁸ Until now, the focus of research on all-inorganic perovskites has mostly been on the CsPbI_3 composition due to its suitable bandgap for application in dual-junction solar cells. Pure CsPbI_3 typically requires high annealing temperature of above 300 °C to form a black phase.¹³⁸ This becomes challenging in the case of triple-junction solar cells with substrate structure (see Fig. 5) as the high bandgap perovskite is the last solar cell in the deposition order. However, advancement in the field have reduced this high temperature annealing requirement which we explain in this section. In addition, similar to FAPbI_3 composition, CsPbI_3 experiences phase instability under ambient conditions (at room temperature in presence of moisture) which changes its α -phase to a yellow non-perovskite phase.



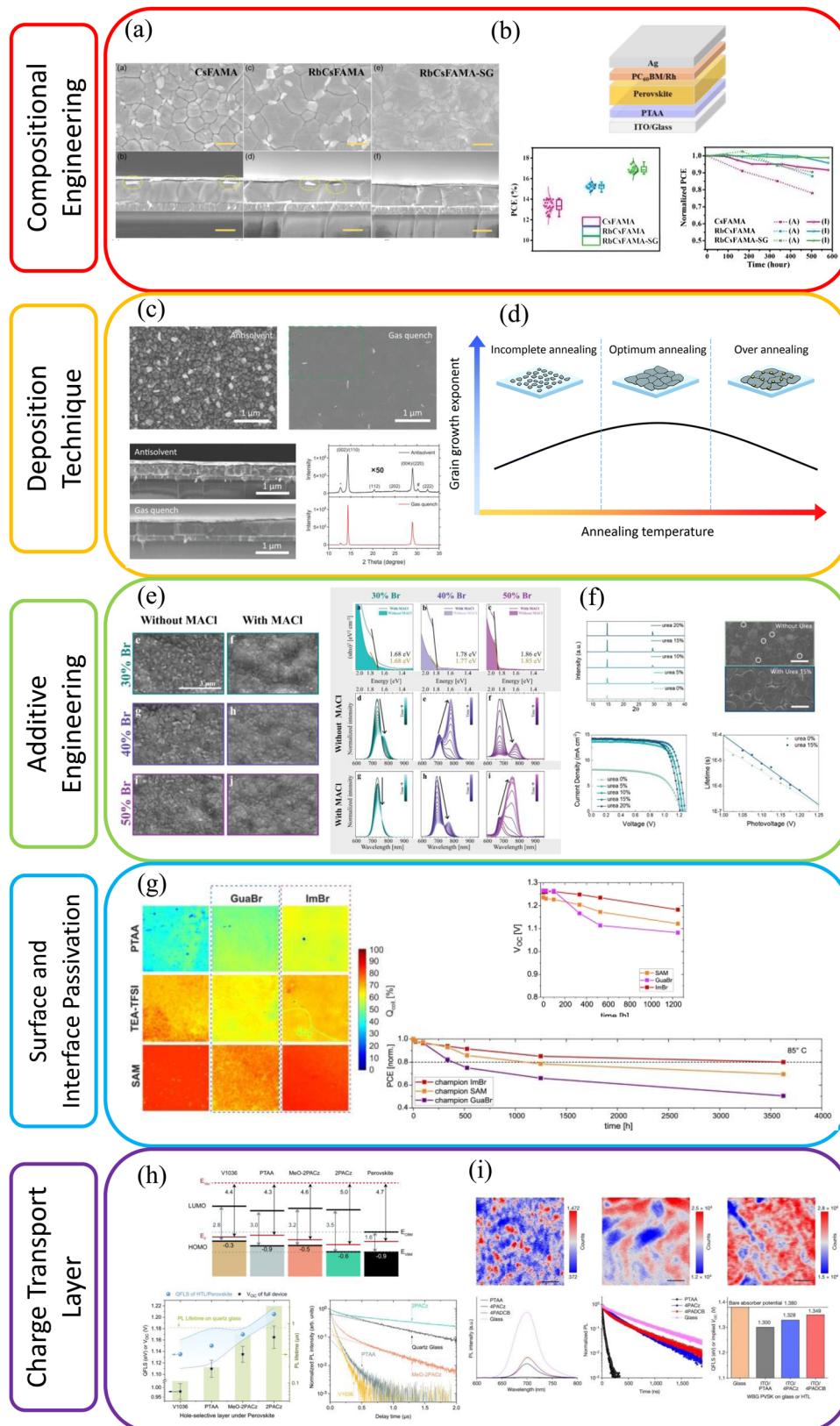


Fig. 13 Approaches reported in literature which successfully suppressed the light-induced phase segregation, non-radiative recombination and energetic band misalignment that improved the V_{OC} and consequently the performance of high bandgap perovskite solar cells. (a) Top view and cross-sectional SEM images of 1.78 eV perovskite films and (b) schematic structure of perovskite solar cell, statistical PCE as well as operational stability over time for perovskite solar cells with and without Rb in the composition. Reproduced with permission from ref. 116. Incorporation of Rb resulted in better film quality, increase in PCE and long term stability. Copyright © 2021 Wiley-VCH GmbH. (c) Top view and cross-sectional SEM images and XRD patterns

(2) Solution preparation and deposition technique: Zhu *et al.* reported that, by aging the perovskite precursor solution up to 3 weeks a pure phase CsPbI₂Br film can be achieved at 100 °C annealing temperature.¹⁴⁵ Liu *et al.* processed CsPbI₂Br at room temperature by replacing the standard solvent of DMF/DMSO with NMP and combining it with vacuum-assisted extraction of the solvent instead of conventional antisolvent

(4) Interfacial and surface passivation: one of the most important methods to improve moisture-resistance of all-inorganic perovskite is passivation of surface and grain boundaries, which protects the perovskite against moisture penetration. Zhang *et al.* passivated CsPbIBr₂ surface with guanidinium iodide (GuaI) and achieved 9.7% PCE.¹⁵² Wang *et al.* improved moisture-resistance of CsPbI₂Br by phenylethyl ammonium chloride (PEACl) treatment.¹⁵³ Similarly, post treatment of CsPbI₃ with phenyltrimethylammonium bromide (PTABr) resulted in surface passivation of perovskite and improved the stability against humidity. After exposing the perovskite films for 30 minutes to humidity of 80 ± 5% and temperature of 35 °C, the control films turned yellow while the treated samples remained in black phase.¹⁵⁴ Very recently Han *et al.*, reported more than 19.0% efficient CsPbI₃ perovskite with sequential treatment of the perovskite's surface with ammonium benzenesulfonate (ABS) and phenylethylammonium iodide (PEAI) materials. Samples could retain around 70% of their PCE after 300 h exposure to ambient environment with no encapsulation.¹⁵⁵

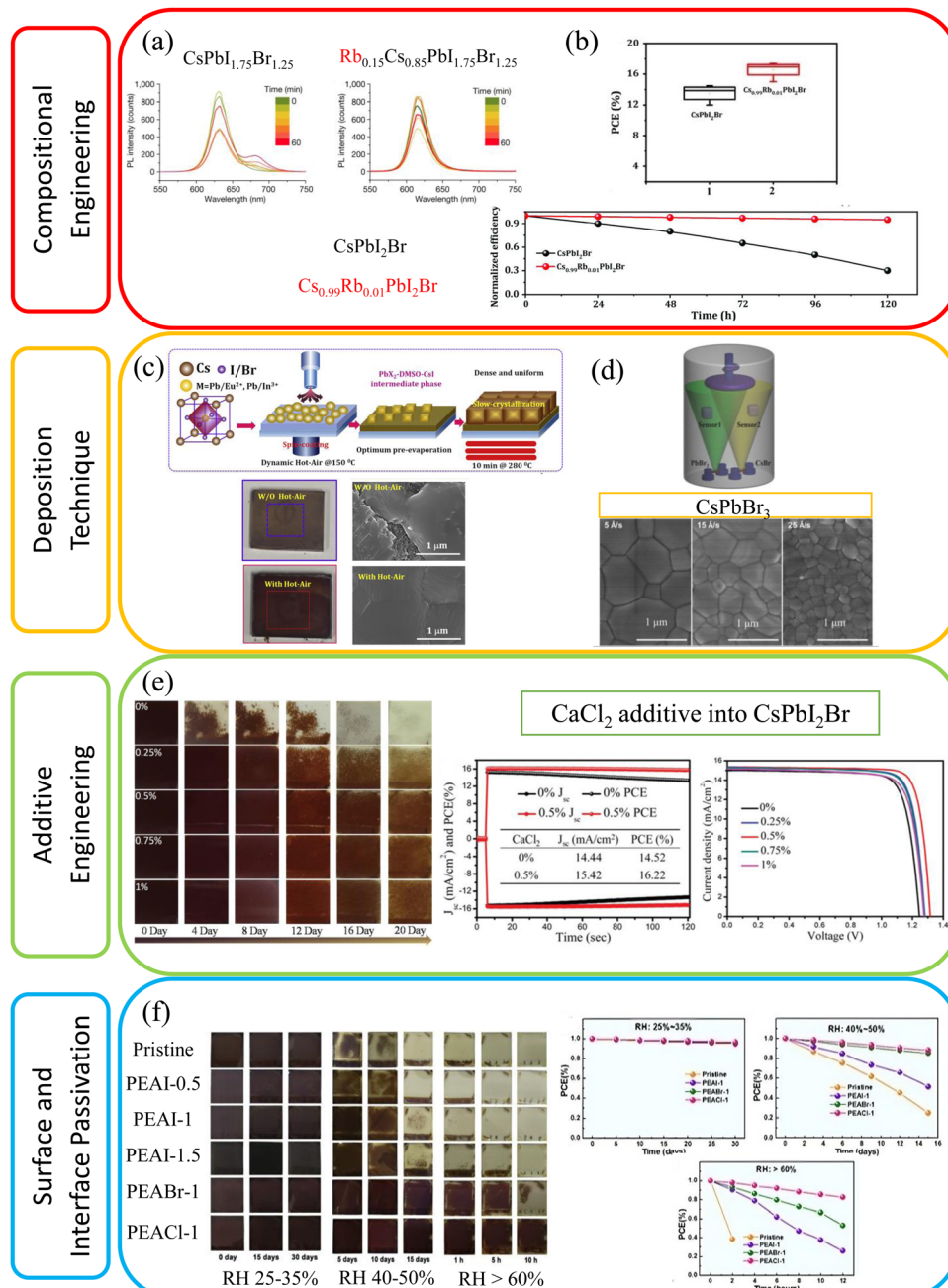


Fig. 14 Approaches reported in literature which successfully improved performance and stability of all-inorganic perovskite. (a) PL measurements of $\text{CsPbI}_{1.75}\text{Br}_{1.25}$ and $\text{Rb}_{0.15}\text{Cs}_{0.85}\text{PbI}_{1.75}\text{Br}_{1.25}$ perovskites. Reproduced with permission from ref. 14. Copyright © 2023, Wang *et al.* under exclusive license to Springer Nature Limited. (b) Statistical PCE, stabilized j_{sc} as well as long term stability of the all-inorganic perovskite solar cells with and without Rb in the composition. Better performance, photostability and long-term stability is achieved by incorporation of Rb. Reproduced with permission from ref. 143. Copyright © 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Schematic illustration of dynamic hot-air assisted deposition technique, optical and top view SEM images of CsPbI_2Br perovskite processed with and without hot air quenching indicating improved film quality for samples prepared by dynamic hot-air assisted method. Reproduced with permission from ref. 147. Copyright © 2020 Elsevier Inc. (d) Schematic illustration of evaporation deposition of CsPbBr_3 and top view SEM images of CsPbBr_3 with different evaporation rates. The best film with large grain size is achieved for 5 Å s⁻¹ evaporation rate. Reproduced with permission from ref. 148. Copyright © 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (e) Images of CsPbI_2Br films with different amount of CaCl_2 additive over time stored at humidity of 40%, together with stabilized j_{sc} and j/V curves of the corresponding solar cells. Samples with high CaCl_2 concentration are more stable under humidity. Highest PCE is achieved for 0.5% CaCl_2 amount. Reproduced with permission from ref. 151. Copyright © 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (f) Images of CsPbI_2Br films with different passivation over time stored at humidity range from 25% to more than 60% as well as long-term stability of their corresponding solar cells. Passivated films showed better stability compared to non-passivated films under humidity. Best stability is achieved for PEACl treatment. Reproduced with permission from ref. 153. Copyright © 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Fig. 14 summarizes the approaches that have been successfully employed to enhance the stability and performance of all-inorganic HBG perovskite solar cells.

More details on strategies toward improving the PCE and stability of this type of solar cells have been well presented in recent review papers.^{139,150,156}

4.3 High bandgap perovskite top cells in current triple-junction solar cells

On a final note, most of the reported triple-junction solar cells implemented a mixed cation mixed halide composition as top cell absorber. Table 4 summarizes compositions and bandgaps of the top perovskite absorbers in current triple-junction solar cells, as well as device structures and jV performances of respective single-junction solar cells. This section is described in more detail compared to the middle cell absorber as greater focus has been dedicated to suitable high bandgap absorbers for top cell application in triple-junction devices and their development so far.

In the first reported all-perovskite triple-junction solar cell, a $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.7}\text{I}_{0.3})_3$ perovskite with 1.94 eV bandgap was used. Steps taken to stabilize the high bandgap perovskite were incorporation of 2% potassium (K^+) in the precursor to help surpassing ion migration as well as utilizing hydroiodic and hydrobromic acids as additive, which enabled achieving apparent grains in micrometer range. In addition their solution was aged for 2 days prior to the processing.²³ As the top cell in the second all-perovskite triple-junction solar cell Wang *et al.* employed a two-step deposition method for fabrication of their $\text{Cs}_{0.1}(\text{FA}_{0.66}\text{MA}_{0.34})_{0.9}\text{PbI}_2\text{Br}$ perovskite (1.73 eV).²⁵ Xiao *et al.* employed $\text{Cs}_{0.2}\text{FA}_{0.8}\text{PbI}_{0.9}\text{Br}_{2.1}$ (1.99 eV) with high bromide content deposited *via* a one-step antisolvent method. To improve the perovskite quality and increase the grain size, they added 5 mol% $\text{Pb}(\text{SCN})_2$ to the perovskite precursor solution.²⁴ For fabrication of fully textured perovskite/perovskite/silicon solar cell, Werner *et al.* used a 1.80 eV double cation double halide perovskite composition achieved *via* sequential co-evaporation of PbI_2 (layer thickness of 180–200 nm) and CsBr continued by spin coating of FABr solution.²² In the perovskite/perovskite/silicon triple-junction solar cell by Zheng *et al.* a 1.90 eV perovskite with $\text{Cs}_{0.20}\text{FA}_{0.80}\text{Pb}(\text{I}_{0.45}\text{Br}_{0.55})_3$ composition was used. No strategy is reported for stabilizing the high bandgap perovskite in this work.¹⁷ The reported perovskite/perovskite/organic triple-junction had a $\text{Cs}_{0.15}\text{MA}_{0.15}\text{FA}_{0.70}\text{Pb}(\text{I}_{0.15}\text{Br}_{0.85})_3$ perovskite with a ~ 2.05 eV bandgap which is the highest bandgap employed in a perovskite-based multi-junction solar cell so far. The perovskite is spin coated from solution with antisolvent method.¹⁶ They passivated the top surface of their perovskite layer with phenformin hydrochloride acid, which was previously shown to suppress phase segregation.¹³¹ For the first time, Wang *et al.* used an all-inorganic high bandgap perovskite with $\text{Rb}_{0.15}\text{Cs}_{0.85}\text{PbI}_{1.75}\text{Br}_{1.25}$ composition that has a 2.0 eV bandgap in the record all-perovskite triple-junction solar cell. The stable all-inorganic perovskite was developed by partially replacing Cs with Rb. Incorporation of Rb resulted in increase in lattice distortion that reduced the ion migration and therefore

Table 4 jV performance, perovskite composition, bandgap, absorber layer thickness and device structure of high bandgap perovskite used in perovskite-based triple-junction solar cells in literature. Single-junction solar cell values for the first perovskite/perovskite/silicon solar cell are not available (due to fully textured design and respective optimization of processes on textured silicon bottom solar cells)²²

Year	2019	2020	2020	2022	2022	2023	2023	2023
Composition	$\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.7}\text{I}_{0.3})_3$	$\text{Cs}_{0.1}(\text{FA}_{0.66}\text{MA}_{0.34})_{0.9}\text{PbI}_2\text{Br}$	$\text{Cs}_{0.2}\text{FA}_{0.8}\text{PbI}_{0.9}\text{Br}_{2.1}$	$\text{Cs}_{0.2}\text{FA}_{0.8}\text{Pb}(\text{I}_{0.45}\text{Br}_{0.55})_3$	$\text{Cs}_{0.15}\text{MA}_{0.15}\text{FA}_{0.70}\text{Pb}(\text{I}_{0.15}\text{Br}_{0.85})_3$	$\text{Rb}_{0.15}\text{Cs}_{0.85}\text{PbI}_{1.75}\text{Br}_{1.25}$	$\text{MAPb}(\text{I}_{0.3}\text{Br}_{0.35}\text{Cl}_{0.15})_3$	$\text{Cs}_{0.05}(\text{FA}_{0.55}\text{MA}_{0.45})_{0.95}\text{Pb}(\text{I}_{0.55}\text{Br}_{0.45})_3$
Bandgap (eV)	1.94	1.73	1.99	1.90	2.05	2.00	1.96	1.83
Structure	Glass/FTO/ SnO_x /PCBM/perovskite/Spiro-OMeTAD/Ag	Glass/ITO/PTAA/perovskite/C60/BCP/Al	Glass/ITO/PTAA/perovskite/C60/BCP/Cu	Glass/ITO/HTL/perovskite/LiF/C60/BCP/Cu	Glass/ITO/2PACz/perovskite/PhenHCl/C60/BCP/Ag	Glass/ITO/ NiO_x /Me-4PACz/perovskite/PEAL-EDAL ₂ /PCBM/PEIE/ SnO_x /Ag	Glass/ITO/Me-4PACz/perovskite/C60/PEIE/Ag	Glass/ITO/2PACz/perovskite/C60/ SnO_x /Ag/MgF ₂
Molarity (M)	0.75	$0.48 (\text{CsI-PbI}_2) + 0.095 (\text{FABr-MABr})$	0.80	1.00	1.10	0.80	0.75	1.20
Thickness (nm)	350	100	280	180–240	100	170	NA	450
PCE (%)	11.6	8.1	10.4	9.1	8.4	13.6	13.9	11.3
FF (%)	76.0	76.0	73.5	71.0	70.4	84.7	76.6	74.6
j_{sc} (mA cm^{-2})	11.9	9.9	11.2	11.7	9.4	12.4	14.16	13.6
V_{oc} (V)	1.28	1.07	1.26	1.09	1.27	1.30	1.28	1.12
Top cell in	Pero/pero/pero	Pero/pero/pero	Pero/pero/pero	Pero/pero/silicon	Pero/pero/organic	Pero/pero/pero	Pero/pero/silicon	Pero/pero/silicon
Ref.	23	25	24	17	16	14	15	26



improved photostability under illumination.¹⁴ In the record perovskite/perovskite/silicon triple-junction solar cell, a triple halide perovskite composition of $\text{MAPb}(\text{I}_{0.50}\text{Br}_{0.35}\text{Cl}_{0.15})_3$ with 1.96 eV bandgap was employed. Urea was added to the perovskite solution to improve crystallinity and achieve a high-quality perovskite film with large grains without pinholes. Consequently, the performance of the high bandgap perovskite cell significantly improved from 6.4% to 13.9%. The main improvement came from increase in (j_{SC}) in the presence of the urea additive, which they attributed to the enhanced thin-film crystallinity and light absorption.¹⁵ We used a $\text{Cs}_{0.05}(\text{FA}_{0.55}\text{MA}_{0.45})_{0.95}\text{Pb}(\text{I}_{0.55}\text{Br}_{0.45})_3$ perovskite composition with 1.83 eV bandgap as top cell absorber of perovskite/perovskite/silicon triple-junction cell. A dynamic gas quenching method was used to prevent solvent damage to the already deposited layers. The perovskite film deposited by the adapted method showed homogeneous and compact morphology with improved crystallinity.²⁶

A comprehensive overview on high bandgap perovskite solar cells can be found in the recent review papers.^{157,158}

5. Recombination layer between the perovskite subcells

In monolithic multi-junction solar cells, the subcells are connected in series through recombination layers. The recombination layer has shown to be one of the key factors influencing the performance of tandem solar cells as its electro-optical properties directly affect all photovoltaic parameters (j_{SC} , V_{OC} and FF) of the device.^{159,160} In a perovskite solar cell, electrons are extracted through an ETL, and holes are extracted through an HTL. In electrically series-connected perovskite subcells without any additional layer, the ETL and HTL of the subcells get in contact. However, there is usually a difference between the work functions of the middle cell's ETL and top cell's HTL.¹⁶¹ Therefore, directly connecting these two layers from different subcells introduce a barrier at this interface^{160,161} and has shown to result in S-shape jV curves and reduced FF of the device.¹⁶² Hence, introducing an additional layer between the subcells with a suitable work function could reduce the mentioned gap and provide recombination sites for the collected charge

carriers at HTL and ETL of different subcells. There are several properties that a recombination layer between perovskite subcells must fulfill (Fig. 15) which can be categorized as follows:

1. Electrical requirements

- As the subcells are electrically connected in monolithic multi-junction solar cells, the recombination layer must have low contact resistance.

- It also requires low lateral conductivity to avoid current diffusion.

2. Optical requirements

- The parasitic absorption of this additional layer should be minimum to transmit the light to the underlying subcell. Given the bandgap combinations of the subcells in the dual-junction solar cell, the recombination layer needs to be transmitting especially in the infra-red (IR) range. This spectrum of interest is broader for the recombination layer between the top and middle cell in triple-junction solar cells and is not limited to IR region.

3. Processing requirements

- To avoid possible damages during the processing of the top layers, the recombination layer must protect the layers underneath.

- The processing of the recombination layer itself needs to be compatible in order not to damage the underlying layers.

Generally, there are two common approaches for the recombination layer between the subcells in perovskite-based multi-junction solar cells. Either employing a transparent conductive oxide (TCO) such as sputtered indium tin oxide (ITO) and indium zinc oxide (IZO) or ultrathin metal layer such as gold (Au) and silver (Ag).

A thick layer of sputtered ITO ($\sim 100\text{--}120\text{ nm}$) has been used as recombination layer between the perovskite subcells in early reports on all-perovskite dual-junction solar cells.^{163,164} In the first proof of concept perovskite/perovskite/silicon triple-junction cell, Werner *et al.* followed a similar approach and employed 150 nm IZO as the recombination layer between the perovskite middle cell and top cell.²² However, the thick TCO layers have several drawbacks such as low sheet resistance which has shown to result in shunting the solar cells.¹⁶⁵ Such thick layers are also optically poor due to high parasitic absorption and possible back reflection.

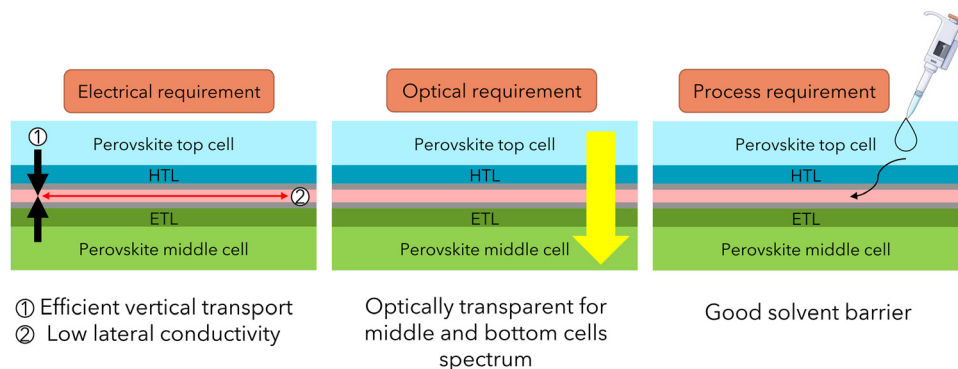


Fig. 15 Schematic of relevant electrical, optical and processing requirements for the monolithic connection of perovskite subcells.



Most of the recent, highly efficient all-perovskite dual-junction solar cells including the current certified record, employed 1 nm evaporated gold (Au) as recombination layer in their structure.^{10,120,166} The advantages of evaporated metal

layer are its damage-free deposition method compared to sputtering as well as its very high conductivity. However, this layer should be kept as thin as possible (~ 1 nm) to minimize parasitic absorption. Later, TCO layers with reduced thickness

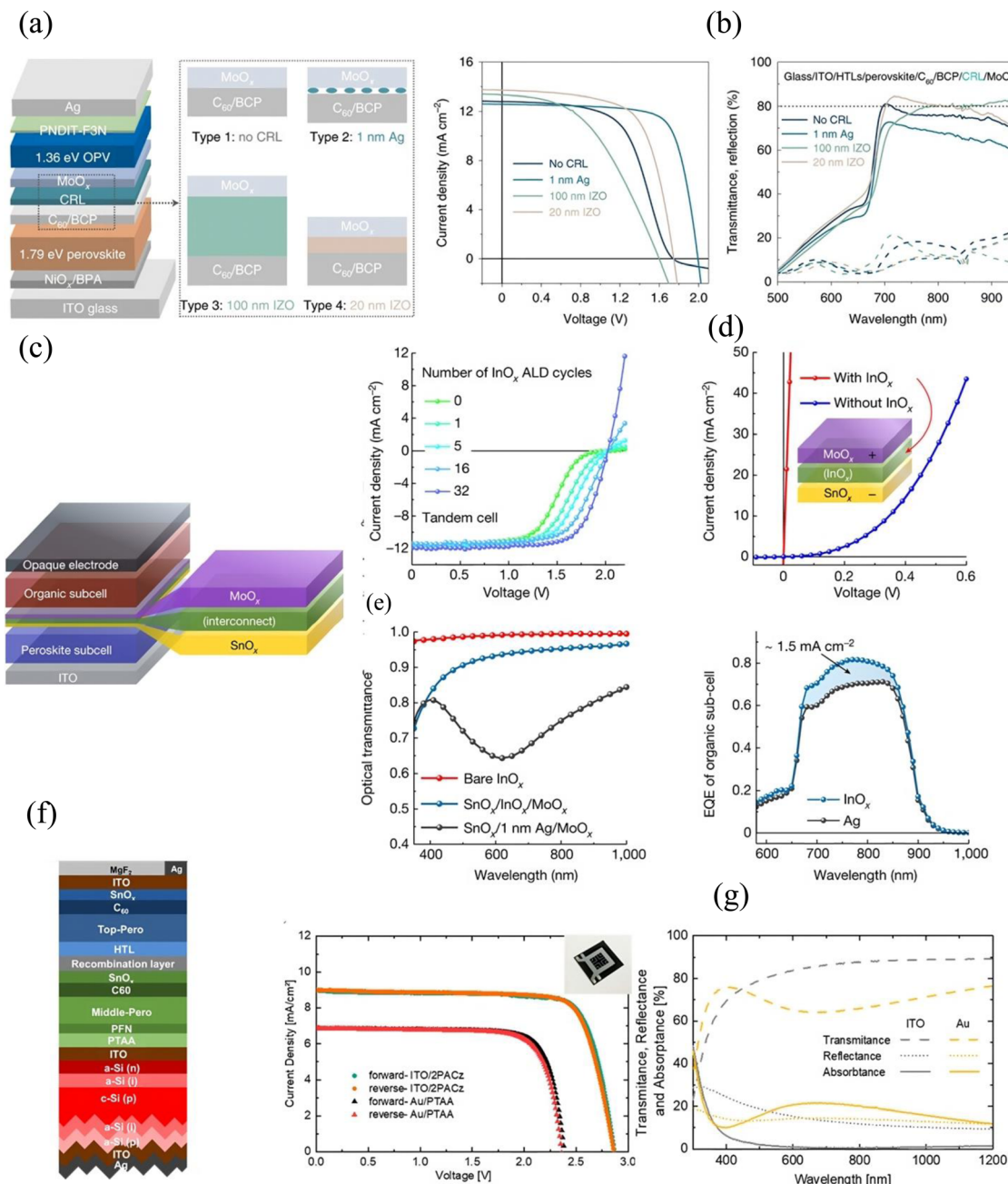


Fig. 16 Replacing metal layer with thin TCO as recombination layer. (a) Schematic structure of perovskite/organic dual-junction solar cell with four types of recombination layers and their corresponding jV curves and (b) comparison of transmittance and reflectance of the tested recombination layers. Reproduced with permission from ref. 162. Copyright © 2022, Springer Nature. (c) Schematic structure of perovskite/organic dual-junction solar cell with different thicknesses of ALD deposited InO_x as recombination layer and their corresponding jV curves. (d) Diode characteristic of (SnO_x)/(InO_x)/(MoO_x). (e) Comparison of transmittance of ~ 1.5 nm of InO_x and 1 nm Ag, and EQE of the organic bottom cell with 1.5 nm of InO_x and 1 nm Ag as recombination layer. Reproduced with permission from ref. 129 Copyright © 2022, Springer Nature. (f) Schematic structure of perovskite/perovskite/silicon triple-junction solar cell with Au/PTAA and ITO/2PACz as interconnection layers and their corresponding jV curves and (g) comparison of transmittance, reflectance and absorbance of the 1 nm of Au with 15 nm of ITO. Reproduced with permission from ref. 26 Copyright © 2023 Heydarian et al., Published by American Chemical Society. Under a Creative Commons Attribution CC-BY-NC-ND 4.0. All examples indicate improved optical properties of the recombination layer upon replacing the metal layer with thin TCO. Improved electrical property is achieved by optimizing the thickness of the TCO layer.



The general method for correct EQE measurement of monolithically series-connected solar cells has been first presented by Burdick and Glatfelter in 1986 for a-Si/Si dual-junction solar cells¹⁷⁸ and was extended for a GaInP/GaInAs/Ge triple-junction solar cell by Meusel *et al.*¹⁷³ The method is used to characterize multi-junction devices independent of their material. In summary, the EQE of each subcell in a two-terminal triple-junction solar cell can be measured individually provided that the subcell of interest limits the overall current. To achieve this, the solar cell is illuminated with spectrally selective bias lights to saturate the other subcells so that they generate larger photocurrents than the subcell under test. The suitable selective bias light depends on the spectral responses of the subcells and can be provided by wavelength specific bias lights such as LEDs or the use of optical filters in combination with broadband light sources.¹⁷⁹ In addition, to determine the EQE correctly, the subcell under test needs to operate at its

For the case of perovskite/perovskite/silicon triple-junction solar cells, we have observed this effect in our lab when

Apart from the common challenges described above, several other factors and measurement conditions are shown to have an impact on the absolute EQE of perovskite solar cells due to their dynamic effects.¹⁸² Mundus *et al.* investigated the non-linearity of various single-junction perovskite solar cells and showed that the j_{SC} has non-linear behavior with respect to the irradiance leading to a dependency of the EQE on bias illumination intensity.^{183,184} Mercaldo *et al.* reported similar effect.¹⁸⁴ Other parameters such as chopper wheel frequency,^{184–188} preconditioning of the cell¹⁸⁷ and applied bias voltage are also reported to affect the absolute EQE.¹⁸⁷ Also, the common approach to measure the EQE with a monochromatic beam smaller than the active area of the solar cell can cause deviations in the signal compared to when illuminating the whole area including all metallization, the edges and spatially different absorber thickness, radiative properties *etc.*¹⁸¹ Therefore, calculating the generated current from measured EQE data obtained for individual subcells is not straightforward. Consequently, determining the current matching situation of the perovskite-based multi-junction solar cells from EQE measurement can result in misinterpretation.¹⁸⁹ An alternative approach based on spectro-metric characterization for precise determination of current matching could in the future be used for perovskite-based triple-junction solar cells.¹⁷² This approach has been successfully applied on perovskite/silicon dual-junction solar cells.¹⁸⁹

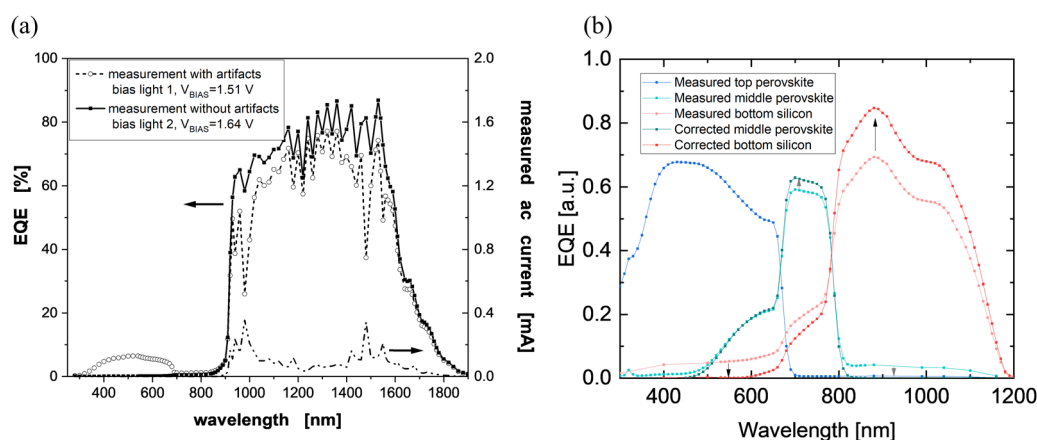


Fig. 17 (a) Measurement artifact at spectral response (SR) range of top cell during EQE measurements of the germanium (Ge) bottom cell of a III–V/III–V/Ge triple-junction solar cell. With permission from ref. 173 Copyright © 2003 John Wiley & Sons, Ltd. (b) EQE curves of a perovskite/perovskite/silicon triple-junction solar cell measured at Fraunhofer ISE CalLab. Artifacts are visible for both middle cell and bottom cell EQEs. The EQE measurements with artifacts and the corrected curves are presented.

Energy Environ. Sci., 2024, 17, 1781–1818 | 1807

achieved for triple-junction solar cells is limited to 22.2%, 23.3%, and 19.4% on a silicon, perovskite, and organic bottom cell, respectively, well below their theoretical potential. We believe that the focus is now changing, and it is only a matter of time until the triple-junction solar cell development undergoes a fast efficiency increase similar to the trend of perovskite/silicon tandem solar cells or even faster as the learnings from single- and dual-junction can be transferred to triple-junction solar cells. In this review we summarized the recent advancements of perovskite-based triple-junction solar cells, their theoretical potential, and their challenges. Based on what has been discussed we identify the main losses and important topics for future work.

Regarding the V_{OC} , according to simulations,²⁷ a practical V_{OC} of 3.54 V for all-perovskite and 3.24 V for perovskite/perovskite/silicon triple-junction solar cells can be achieved, respectively. So far, the maximum V_{OC} values realized for these two types of solar cells are limited to 3.20 V for all-perovskite and 2.87 V for perovskite/perovskite/silicon triple-junction cells. Analyzing the V_{OC} values reported in the subcells of these two configurations, for middle bandgap single-junction cells, the V_{OC} deficit ranges from 0.40 V to 0.54 V, while for high bandgap cells, it is between 0.66 V and 0.81 V. Given the higher V_{OC} deficit in high bandgap perovskite subcells, there is a need for strategies to develop efficient and stable high bandgap perovskite in the optimum range of 1.85–2.15 eV with high voltage output. For this purpose, the high bandgap perovskite needs excellent material quality, which can be achieved by careful compositional engineering, additive engineering, processing control, surface treatment and interfacial passivation. In addition, so far even with the latest progress in the field, which resulted in high bandgap perovskite with satisfactory efficiency, the stability of such perovskite is not fully addressed. In terms of charge transport layer materials, the work function and band alignment of conventional materials with regard to adapted bandgap perovskites have not been fully studied and there has been little adjustment to the respective valence and conduction band levels. More work needs to be done on this topic, as it could bear a big leverage for V_{OC} improvement.

In addition, development of a lossless recombination layer between the middle perovskite and high bandgap perovskite with proper barrier function is a relatively new research field but critical for process compatibility and high voltage output.

In terms of j_{SC} , a practical maximum j_{SC} of 12.0 mA cm⁻² and 14.1 mA cm⁻² can be achieved for all-perovskite and perovskite/perovskite/silicon triple-junction solar cells, respectively.²⁷ However, the maximum j_{SC} reported for these two structures are still lower than expected with 9.6 mA cm⁻² for all-perovskite and 10.2 mA cm⁻² for perovskite/perovskite/silicon triple-junction solar cells. There are two main origins for this j_{SC} limitation. Firstly, triple-junction solar cells consist of many interlayers, which introduce parasitic absorption leading to lower j_{SC} of the final device. In order to maximize the j_{SC} , materials with high transparency need to be employed as electrodes, recombination and charge transport layers. In addition, the thickness of all layers except for the absorber layers should be optimized to

introduce minimum parasitic absorption. Secondly, current matching has not been achieved for most of the reported triple-junction solar cells. Even though proper evaluation of current matching condition requires further effort, it is clear that current perovskite/perovskite/silicon solar cells are using non-optimum bandgap combinations and have a current limitation caused by the middle cell. Up to now, bandgaps employed for the middle cell of this structure are in the range of 1.50–1.60 eV. By lowering the bandgap of the perovskite middle cell (employing FAPbI₃ or Sn-containing perovskite), a better current matching could be achieved in the final device.

In addition to what has been mentioned, depending on the technology, further development and adaptation is necessary.

• Perovskite/perovskite/silicon

Since the high bandgap perovskite cell is the last subcell processed in this structure, not only suitable bandgap with good stability is required, but also a deposition technique must be employed with no damage to the underlying layers. This adds to the challenges of high bandgap perovskite development. In this regard, fully evaporated high bandgap perovskite could be the next focus, as apart from the process compatibility, it has several other advantages *e.g.*, in terms of upscaling.

• Perovskite/perovskite/perovskite

Development of a stable low bandgap perovskite in this structure is of great importance. Moreover, since the low bandgap perovskite is processed in the last step, it requires a deposition technique that introduces no damage to the two-underlying perovskite subcells. Therefore, all-perovskite multi-junction solar cells could highly benefit from development of efficient and stable evaporated Sn-based perovskite.

• Perovskite/perovskite/organic

So far, efficient organic solar cells have mostly been realized with a bandgap of 1.30 eV. Employing the organic solar cell as the low bandgap subcell in triple-junction solar cells requires further reduction of its bandgap.

Finally, it is worth mentioning that precise characterization in parallel to the development of triple-junction solar cells is crucial to increase the reliability of the measurements and get better insight into the limitation of this new technology. For comparable *jV* measurements, it is especially important to correctly adjust the spectrum of the solar simulator in a way that all subcells generate the same current as they would do under the reference spectrum. Furthermore, along with PCE enhancement, stability and scalability of perovskite-based solar cells need to be addressed for future commercialization of this technology. With regards to the triple-junction solar cells, so far, the focus has been on improving the efficiency, while the stability of the reported solar cells is less studied.

Author contributions

M. Heydarian and M. Heydarian (conceptualization, data curation, formal analysis, visualization, writing – original draft, writing – review & editing), P. Schygulla (data curation, formal analysis, visualization; writing – review & editing), S. K. Reichmuth (data



curation, formal analysis, visualization, writing – review & editing), A. J. Bett (formal analysis, writing – review & editing), J. Hohl-Ebinger (project administration, supervision), F. Schindler (funding acquisition, project administration, supervision, writing – review & editing), M. Hermle (funding acquisition, project administration, supervision), M. C. Schubert (funding acquisition, project administration, supervision, writing – review & editing), P. S. C. Schulze (conceptualization, formal analysis, writing – review & editing, supervision), J. Borchert (conceptualization, funding acquisition, project administration, supervision, writing – review & editing), S. W. Glunz (conceptualization, funding acquisition, supervision, writing – review & editing).

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

This work was partially supported by the European Union through the Horizon Europe project Triumph under the number 101075725 and the German Federal Ministry for Economic Affairs and Climate Action (BMWK) under contract number 03EE1132A (RIESEN).

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