Perovskite Single-Crystal Solar Cells: Going Forward

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ABSTRACT – Most efficient perovskite solar cells are based on polycrystalline thin films; however, substantial structural disorder and defective grain boundaries place a limit on their performance. Perovskite single crystals are free of grain boundaries, leading to significantly low defect densities and thus hold promise for high-efficiency photovoltaics. However, the surfaces of perovskite single crystals present a major performance bottleneck because they possess a higher density of traps than the bulk. Hence, it is crucial to understand and control the surface trap population to fully exploit perovskite single crystals. This perspective highlights the importance of surface-trap management in unleashing the potential of perovskite single-crystal photovoltaics and discusses strategies to take this technology beyond the proof-of-concept stage.

TOC GRAPHICS

MAIN TEXT

Can perovskite single-crystal photovoltaics outperform their polycrystalline counterparts? For conventional semiconductors (such as Si, Ge, and GaAs), the answer is very straightforward: single-crystal semiconductors perform better than polycrystalline thin films in photovoltaics, as crystals have significantly lower defect densities.¹ However, the situation (so far) is different for perovskites: the best performances to date have been achieved with polycrystalline thin films. Interest in single-crystal perovskite solar cells (SC-PSCs) lags far behind that in polycrystalline perovskite solar cells (Pc-PSCs). Pc-PSCs have received most of the attention partly due to the relative ease of their fabrication; they have also enjoyed a rapid increase in performance over the past seven years. However, the efficiency of Pc-PSCs, as expected, has now plateaued due to their inherently high density of structural defects [grain boundaries (GBs), point defects, etc.].²⁻⁷

Compared with polycrystalline perovskites, perovskite single crystals have trap densities that are several orders of magnitude lower, leading to a ~100 times longer carrier diffusion length. While single crystals can perform beyond the limits of Pc-PSCs,⁸⁻⁹ their synthesis and device integration are complex; for that reason, scarce attention was paid to SC-PSCs. Indeed, there are only a handful of reports on SC-PSCs, with most of them indicating sub-13% efficiency.¹⁰ Table S1 summarizes device configuration and performance of SC-PSCs reported up to date. The first SC-PSC breaking this barrier was reported in 2017, fabricated using methylammonium lead iodide (MAPbI₃) single crystals and exhibiting a 17.8% efficiency.¹¹ The second quantum leap in SC-PSCs efficiency occurred in 2019, reached 21% through the controlled growth of perovskite single-crystal thin films.¹² Since then, the highest efficiency reported for SC-PSCs was 21.93%, achieved through surface modifications.¹³ This value is not far behind the efficiency of state-of-

the-art Pc-PSCs. However, it is still distant from the theoretical Shockley–Queisser (S-Q) limit of 31.64% for a 1.5-eV bandgap semiconductor.¹⁴⁻¹⁵

One question that naturally arises is this: If perovskite single crystals are superior to polycrystalline films, what is limiting them in the context of solar cells? Although the bulk trap density is exceptionally low, the surface trap density is significantly high on perovskite single crystals,¹⁶⁻¹⁸ leading to performance loss.^{2, 19-21} Another question is what is more viable for advancing PSC technology, lowering the bulk trap density in polycrystalline films or the surface trap density of single crystals?^{6, 19} To address these questions, this perspective discusses how the surface chemistry and physics of perovskite single crystals affect their photovoltaic performance and proposes pathways to diminish their harmful effects, which are standing in the way of the application of these materials beyond the proof-of-concept phase.

Figure 1a summarizes the best efficiencies achieved for single-junction solar cells.²² Naturally, single crystals, because of their low concentration of structural defects, produce the highest photovoltaic efficiencies,²³ while corresponding polycrystalline solar cells generally offer lower efficiencies;²⁴⁻²⁵ however, perovskites do not obey this norm—at least not at the moment.

Grain boundaries (GBs) are dominant energy loss centers in conventional polycrystalline solar cells. Substantial nonradiative recombination at grain boundaries leads to a low short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), and—occasionally—fill factor (FF) in solar cells.²⁶ These grain boundaries can be effectively passivated (e.g., in Si, CdTe, and CIGS polycrystalline solar cells).²³⁻²⁴ Another way to avoid the side effects of GBs is using grain-free, single-crystal materials, as is the case for GaAs, Si, and CdTe. However, single crystals are not available for most emerging

thin-film solar materials (such as CIGS, inorganic CZTSSe, quantum-dot, dye-sensitized, and amorphous Si:H solar cells).

Figure 1b compares the performance of polycrystalline and single-crystal forms of several materials. Performance-limiting deep traps for polycrystalline GaAs cells are dislocations in GBs;²⁴ due to the absence of effective GB passivation techniques, the efficiency of these cells is lower—by nearly 10 absolute power points—than that of GaAs thin film single-crystal solar cells.^{24, 27} It is calculated that GaAs polycrystalline cells require grain sizes on the order of tens of microns to achieve efficiencies of over 20%.²⁴ GaAs thin film single-crystals currently hold a record efficiency of 29.1% among all types of single-junction solar cells, a result achieved by effective surface/interface passivation and precise crystal growth to reduce the density of dislocations.^{22, 27-28}

Multicrystalline (polycrystalline) Si (mc-Si) suffers from intrinsic defects such as dangling bonds, dislocations, and extrinsic metal impurities concentrated at GBs. Consequently, the grain size should be large, at least 10 mm, to achieve high efficiencies.²⁹ Control over crystallization to reduce metal impurities in GBs and to produce large-grain wafers allowed this technology to reach 23.3% efficiency.^{22, 27, 29} In single-crystal Si (c-Si), passivation of surface Si dangling bonds with H atoms enabled the record c-Si efficiency of 26.7%.^{22, 27, 30}

GBs in polycrystalline CdTe lead to the loss of device performance. CdCl₂ heat treatment significantly passivates the GBs; also, segregation of Cl atoms to the edge of p-type CdTe grains converts the surface to n-type CdTe, creating a local p-n-p junction.³¹ This unconventional GB-assisted charge collection in CdTe films has led to a PCE of 22.1%, higher than the PCE of their single-crystal counterparts, 19.7%.^{22, 27, 32}

Figure 1: (a) Highest certified efficiencies for single-junction solar cells. (b) Best-efficiency comparison of polycrystalline and single-crystal solar cells of GaAs, Si, CdTe, and perovskite. The efficiency data for polycrystalline GaAs (certified), single-crystal CdTe (certified) and single-crystals perovskite are taken from the reference denoted by letters p^{24} , q^{32} , r^{13} , respectively. (c) Evolution of best perovskite solar cell efficiency for polycrystalline (certified) and single-crystal (non-certified) thin films over time. The dotted line marks the first reports of a single-crystal perovskite. Certified data were extracted from the NREL Best Research-Cell Efficiency Chart²² unless otherwise stated. (d) The year-wise publication history of perovskite solar cells based on data is obtained from Web of Science. (For polycrystalline solar cells, the results were obtained by searching for "perovskite solar cell," excluding results containing the words "single crystal" and "monocrystalline". For single-crystal solar cells, the results were searched for manually in the literature.)

The adverse effects of deep trap levels are indisputable, as summarized above for conventional photovoltaic semiconductors. Organic-inorganic hybrid perovskites have earned the distinction of being defect-tolerant materials, as the formation of deep levels in their bulk is thermodynamically unfavorable.³³⁻³⁴ Whether GBs in perovskite produce deep trap states remains

a matter of active investigation,³⁵⁻³⁷ but it is clear that archetypical small-grain perovskites have abundant GBs.^{2, 26} Nevertheless, the PCE of Pc-PSCs has reached 25.5% in less than ten years (Figure 1b and c) and has now almost plateaued.

MAPbI₃ single crystals prepared by antisolvent vapor crystallization (AVC) and top-seeded solution-growth crystallization (TSSC) from an acidic solution, both reported in 2015, have exhibited a trap density of $\sim 10^{10} \text{ cm}^{-3}$, lower than that of their polycrystalline counterparts by a factor of 10.^{6, 8-9} These methods require one week to produce millimeter-scale crystals. They hence have not been adapted to photovoltaic device applications. Lateral devices made using bulk materials and wafers sliced from bulk crystals have shown less than 2% efficiency.³⁸⁻³⁹ Inverse temperature crystallization (ITC) of high-quality perovskite single crystals, a process that can be completed within several hours,⁴⁰ has become a popular crystallization technique for fabricating single-crystal optoelectronics, such as photodetectors, lasers, transistors, and photovoltaics.^{10, 41-43} ITC-grown MAPbI₃ single crystals have a low trap density of $1.4 \times 10^{10} \text{ cm}^{-3}$, lower than that of a wide range of decade-old and emerging photovoltaics semiconductors, including GaAs ($n_{\text{traps}} \sim 10^{13} - 10^{15} \text{ cm}^{-3}$)⁴⁴, mc-Si ($n_{\text{traps}} \sim 10^{13} - 10^{15} \text{ cm}^{-3}$)⁴⁵⁻⁴⁶, CdTe/CdS ($n_{\text{traps}} \sim 10^{11} - 10^{13} \text{ cm}^{-3}$),⁴⁷ and CIGS ($n_{\text{traps}} \sim 10^{12} - 10^{13} \text{ cm}^{-3}$)⁴⁸. Only high-quality n-type c-Si, grown and re-annealed at thousands of degrees Celsius, offers comparable or better trap densities ($10^8 < n_{\text{traps}} < 10^{15} \text{ cm}^{-3}$)⁴⁹.

Modified ITC for growing thin single crystals between two hydrophobic conductive substrates has enabled the fabrication of vertical SC-PSCs with efficiencies of up to 21.93% (Figure 1c).^{11, 13, 50} This value is lower than that of polycrystalline counterparts, despite these counterparts having a significantly high trap density. Figure 1d compares the number of publications on Pc-PSCs and SC-PSCs reported to date; whereas the number of Pc-PSC-related papers reaches $\sim 10,000$, there are only 19 SC-PSCs-related publications. This comparison shows

that single-crystal perovskite photovoltaics are in their infancy and that the most intriguing findings are yet to come.

The meager interest in SC-PSCs is due to the absence of suitable methods for synthesizing sufficiently thin single-crystal perovskites, free-standing or firmly attached to a substrate, across large lateral dimensions. A few methods have been employed to control the thickness of perovskite single crystals, such as cavitation-triggered asymmetric crystallization,⁵¹ thin-wafer cutting from a bulk single crystal,³⁹ free-standing wafer growth on the surface of a growth solution,⁵² perovskite single-crystal microarray growth on substrate,⁵³⁻⁵⁴ and space-limited ITC^{11, 50}.

Peng et al. reported the first vertical SC-PSC based on MAPbBr₃ crystals grown by sonication-triggered AVC.⁵¹ This method was not suitable for MAPbI₃ crystals but still demonstrated the potential of perovskite crystals to be used in vertical devices. Rao et al. utilized space-limited ITC to grow 16-μm-thick MAPbBr₃ crystals with lateral dimensions of 6×8 mm² on a substrate and achieved 7.11% PCE. Such thin crystals exhibited a trap density of 2.5×10¹⁰ cm⁻³, comparable to that of ITC-grown bulk crystals.⁵⁵ Because MAPbBr₃ is not a widely used solar material due to its relatively high bandgap and there is a lack of studies on mixed cation/anion SC-PSCs, we will hitherto focus on MAPbI₃-based SC-PSCs.

Chen and Dong et al.¹¹ demonstrated vertical MAPbI₃-based SC-PSCs fabricated using space-limited ITC (Figure 2a). An inverted solar cell configuration [ITO/poly(triarylamine) (PTAA)/MAPbI₃ single crystal/phenyl-C61-butyric acid methyl ester (PCBM)/C₆₀/bathocuproine (BCP)/Copper (Cu)] yielded 17.8% efficiency with a 10-μm-thick crystal (Figure 2b). Surface passivation with methylammonium iodide (MAI) was necessary to heal the surface, which was deficient in MAI due to the high growth temperature used.^{11, 56} We reported a 20-μm-thick MAPbI₃

single crystal carefully grown and stored in an inert environment that surpassed the 20% PCE benchmark (PCE of 21.09%, J_{SC} of 23.46 mA cm^{-2} , V_{OC} of 1.08 V, and FF of 83.5%) (Figure 2c).¹² In a later study, we showed that low-temperature growth improved the V_{OC} from 1.08 to 1.144 V and the PCE to a value of 21.93% (J_{SC} of 23.68 mA cm^{-2} and FF of 81%; see Figure 2d).¹³ J – V hysteresis, which is largely related to vacancy-mediated migration of iodide ions, is a major issue in Pc-PSCs.^{57–59} The hysteresis is expected to be suppressed for a SC-PSC having the same absorber thickness as Pc-PSC due to a lower densities of defects. However, reported SC-PSCs are 20–30 times thicker than conventional Pc-PSCs. Therefore, a small hysteresis is still observed in SC-PSCs due high absolute amount of defects in thick single crystal (Figure 2c, d). To eliminate hysteresis, the thickness should be decreased in parallel to developing new methods to suppress ion migration.

Figure 2: (a) Optical and SEM cross-sectional micrographs of thin MAPbI₃ single crystals of various thicknesses. (b) Device architecture and J – V curves for thin MAPbI₃ SC-PSC of different thicknesses. Reprinted with permission.¹¹ Copyright 2017, Nature Publishing Group. (c) Energy band diagram and J – V curves obtained along different scanning directions of MAPbI₃ SC-PSC fabricated, stored, and measured in a N₂ environment. Reprinted with permission.¹² Copyright 2019, American Chemical Society. (d) Device configuration and SEM cross-sectional micrographs of surface-modified thin MAPbI₃ single crystals formed by low-temperature growth and

corresponding $J-V$ curves obtained along different scanning directions. Reprinted with permission.¹³ Copyright 2020, American Chemical Society.

The diffusion length of perovskite single crystals has been a subject of debate as various methods (SCLC, 1D, and 3D methods) have suggested values ranging from one micron to millimeters. The external quantum efficiency (EQE) of recent studies¹²⁻¹³ was consistently above 80%, indicating a charge carrier diffusion length longer than 20 μm in these materials, reconfirming the excellent charge transport properties of these ITC-grown single crystals.⁶⁰

Although perovskite single crystals have exceptional charge transport properties, their surface dangling bonds, dislocations, and chemical contamination hinder their intrinsic properties. In contrast to the bulk diffusion coefficient (Figure 3a),⁸⁻⁹ the surface recombination velocity (SRV) of perovskite single crystals is higher than that of polycrystalline films by a factor of 6 (Figure 3a). The photoluminescence (PL) lifetime of the MAPbI_3 crystal surface is comparable or inferior to that of the polycrystalline film surface.^{16,31}

Light intensity-dependent impedance spectroscopy (IS) and transient photovoltage (TPV) measurements indicated that surface recombination in single crystals becomes a dominant factor at light intensities near 1-sun illumination (Figure 3b-c), which suggests that surface recombination limits the lifetime at a high light intensity.⁹ The local distortion of the crystal structure, which is enhanced by introducing more structural defects, results in the widening of the bandgap at the surface of perovskite single crystals (Figure 3d).⁶¹⁻⁶² Simultaneously, the fast decaying part of the PL recombination lifetime shows a dramatic contrast between the surface and bulk of the crystal (Figure 3e). PL recombination dynamics indicate that defect-induced nonradiative recombination is more dominant in the perovskite crystal surface than its bulk, as illustrated in Figure 3f. The

nonradiative recombination in the surface is dominantly governed by Pb^0 and PbI_2 defects located excessively on the surface, a detailed discussion will be given later in this article.

Figure 3: (a) Diffusion coefficient (D) and surface recombination velocity (S) of single-crystal and polycrystalline MAPbI₃. Data were taken from ref.¹⁷ (b) Impedance spectra (IS) and (c) transient photovoltaic (TPV) decay curves of MAPbI₃ single-crystal devices under 0.1- and 1-sun illumination. The inset of (b) is the recombination lifetime calculated from IS measurements of the MAPbI₃ single-crystal and the polycrystalline thin-film devices at various voltage biases under 1-sun illumination. The inset of (c) is the charge recombination lifetime calculated from TPV measurements of a MAPbI₃ single-crystal device under various light intensities. Reprinted with permission.⁹ Copyright 2015, AAAS. (d) MAPbI₃ α/s (absorption/scattering), bulk emission ($\lambda_{\text{ex}}=1200 \text{ nm}$), and surface emission ($\lambda_{\text{ex}}=600 \text{ nm}$) profiles. (inset: MAPbI₃ single-crystal image) and (e) MAPbI₃ bulk emission and surface transient photoluminescence (TRPL) dynamics at the same wavelengths. Reprinted with permission.⁶¹ Copyright 2016, Wiley. (f) Schematic representation of PL recombination dynamics into bulk and surface recombination channels. Reprinted with permission.⁶³ Copyright 2016, AAAS.

To understand how detrimental the bulk and surface defects of single crystals are to the photovoltaic efficiency, we conducted SCAPS simulations.⁶⁴ A thin MAPbI₃ single crystal was modeled in three parts: the bulk, the top surface (perovskite/ C_{60} interface), and the bottom surface (PTAA/perovskite interface) (Figure 4a, Figure S1a). We located the surface defects at a depth of

10 nm from the interfaces;⁶⁵⁻⁶⁶ in addition, we added a region that increases the defect density exponentially from the bulk to the surface level of defect density.¹⁸ The additional layer was added because optical measurements suggested that the depth of the surface defects is comparable to the depth of light penetration at the wavelength of surface TRPL measurements, i.e., ~80 nm for 532 nm.^{16, 67} The thickness-dependent performance simulation shows that the device performance is maximized at 2.5 μm (Figure S2). We chose the absorber thickness of 20 μm to make the simulation consistent with the reported highest efficiency SC-PSCs fabricated from ~20 μm -thick perovskite single crystals. We simulated the J - V curves for two situations: (i) a variation in bulk defect density with a constant surface defect density (at 10^{17} cm^{-3}) on both sides (Figure 4b, c) and (ii) a variation in surface defect density on both sides with a constant bulk defect density (at 10^{11} cm^{-3}). The bulk and surface defect densities were chosen in agreement with previously reported data.^{8-9, 16, 40, 61, 65-66, 68}

Varying the bulk defect density from 10^{12} to 10^8 cm^{-3} (Figure S1b) leads to a slight increase in efficiency, while V_{OC} shows no significant change (Figure 4b). Trap-free 20- μm -thick SC-PSCs show a substantial enhancement in performance. Varying the surface defect densities from 10^{17} to 10^{13} (Figure S1c) leads to an improvement in J_{SC} (till 10^{16} traps per cm^{-3}) and V_{OC} (up to 10^{14} cm^{-3} , see Figure 4c). We repeated the same calculations with 2.5- μm MAPbI₃ single crystal and observed a similar trend in performance (Figure S3). The trends in the V_{OC} and performance after reduced surface trap density of SC-PSC are in agreement with the trends of Pc-PSCs.^{3, 5, 69-72}

Figure 4d summarizes the simulations. The calculations clearly indicate that improving the bulk defect density does not imply an apparent increase in device efficiency at high surface defect densities. However, a low density of surface defects helps PSCs reach the performance of defect-free single-crystal solar cells. Reducing the surface defect density is more beneficial than reducing

the bulk defect density; therefore, strategies for improving SC-PSCs should focus on ameliorating the surface of perovskite single crystals.

Figure 4: (a) The device architecture used to simulate thin SC-PSCs. The simulation details for the trap profiles is given in supplementary Figure S1. (b) The J - V curves were obtained by simulation for a varying bulk trap density with the surface trap densities of perovskite/ C_{60} and perovskite/PTAA held constant at 10^{17} cm^{-3} . (c) The J - V curves were obtained by simulation for a varying surface trap density at perovskite/ C_{60} and perovskite/PTAA surfaces while bulk trap density was held constant at $1 \times 10^{11} \text{ cm}^{-3}$. The dashed curve in (c) and (e) is the calculated J - V curve for an ideal 20-μm MAPbI₃ single crystal without surface or bulk traps. (d) Overall summary of the effect of bulk and surface trap densities on device efficiency with the trap densities of the remaining parts in the simulation held constant, as mentioned above. The orange region is the reported range for MAPbI₃ surface defect densities, and the green region is the reported range for MAPbI₃ single-crystal defect densities.

Although the bulk of a single crystal is nearly trap-free, a defect-rich crystal surface is a major bottleneck for further augmenting the PCE of SC-PSCs.^{13, 18, 71} The chemistry of surface

defects depends on the synthesis conditions applied (I-rich, Pb- rich, or moderate).⁷³⁻⁷⁵ The escape of volatile products (e.g., decomposition of organics under thermal stress) leaves behind electronically harmful nonvolatile PbI_2 and metallic Pb^0 (Figure 5a,b).^{56, 76-78}

Managing the single-crystal growth process to avoid surface defect formation is one strategy to suppress trap states in SC-PSCs. A high temperature of $>120\text{ }^\circ\text{C}$ in conventional perovskite thin single-crystal growth leads to a large number of surface trap states due to the escape of MAI (Figure 5b-e).¹³ A solvent-engineering approach using a mixture of propylene carbonate (PC) and γ -butyrolactone (GBL) allowed for the low-temperature ($<90\text{ }^\circ\text{C}$) ITC of MAPbI_3 thin single crystals; as a result, the surface of the crystals was improved (Figure 5c,d), and the corresponding solar cells showed a V_{OC} of 1.15 V and an efficiency of 21.9% (Figure 5e).¹³

Additive-assisted single-crystal growth also allows for the tuning of crystal shape and defect density. Feng et al. used a choline bromide additive to produce cuboid CsPbBr_3 crystals with a low defect density.⁷⁹ Jiao et al. reported a ligand-mediated strategy to control the shape.⁸⁰ We recently demonstrated that surface-anchoring alkylamine ligands suppress defect density, remarkably increasing V_{OC} and PCE.³ The facet-dependent optoelectronic properties derive from anisotropic defect species and densities.⁸¹ These large functional molecules are not incorporated into the perovskite lattice; they instead tune crystallization and surface defects with the aid of functional groups.^{75, 82}

Figure 5: (a) MAPbI₃ photodecomposition and thermal degradation processes leading to irreversible and reversible decomposition to organic volatile gas species leaving nonvolatile PbI₂ and metallic Pb⁰ under illumination or mild heat conditions (~70 °C). Reprinted with permission.⁵⁶ Copyright 2020, Royal Society of Chemistry. (b) XRD 2θ patterns, (c) TRPL and (d) PL mapping comparisons of MAPbI₃ single-crystal films grown at high temperature (High-T, ~130 °C) and low temperature (Low-T, ~90 °C) and (e) the corresponding *J*–*V* curves of the champion devices. The inset of (b) shows a magnified peak for PbI₂. Reprinted with permission.¹³ Copyright 2020, American Chemical Society. (f) XPS and (g) TRPL and measurements of MAPbI₃ single-crystal surface before and after MAI treatment. (h) *J*–*V* curves under different illumination of lateral MAPbI₃ single-crystal solar cells. With and without MAI treatment. Reprinted with permission.⁷⁶ Copyright 2020, Nature Publishing Group.

Another strategy to reduce the surface trap states is the post-treatment of as-grown single crystals. MAI post-treatment reduces the surface trap density of perovskite thin single crystals 2-

to 5-fold.¹¹ Song et al. demonstrated that MAI surface treatment could suppress the formation of metallic Pb⁰, one of the main types of surface traps in perovskite materials (Figure 5f, g), leading to a PCE increase from 4.0% to 11.5% in a lateral solar cell under 1-sun illumination (Figure 5h).⁷⁶ Lei et al. demonstrated that surface restructuring with a supersaturated MAPbI₃/GBL solution is an effective method to restore and clean damaged or rough surfaces with decomposition residues (Figure 6a, b).⁸³ Mechanical polishing to remove as-grown defect-rich surfaces and expose a deeper perovskite lattice as a new surface can also reduce the surface trap density (Figure 6e).¹⁷ Further chemical surface treatment by converting the perovskite surface into a wide-bandgap oxysalt layer reduces the trap state density further by passivating undercoordinated surface lead centers (Figure 6f).^{18, 84}

Hydrophobic substrates facilitate the diffusion of ions and enable the continuous growth of thin perovskite single crystals up to several millimeters using a space-confinement method.¹¹ Therefore, the options for transport layers on which the single crystals grow are limited, and devices are mostly based on a p-i-n device configuration. The highest efficiency Pc-PSCs are made from the n-i-p structure. The best certified efficiencies of the n-i-p and p-i-n devices are 25.5% and 22.75%, respectively.^{22, 85} More efforts are needed to grow perovskite single crystals on different substrates to realize both n-i-p and p-i-n devices and develop strategies to address surface nonradiative recombination. The n-i-p device structure for SC-PSCs should be investigated more, since this architecture is expected to yield a better performance according to the trends observed in Pc-PSCs. Additionally, the defect passivation strategies, such as adding layers of PFN (HTL side) and LiF (ETL side), demonstrated in Pc-PSC studies can also be adapted to single-crystal devices to suppress surface nonradiative recombination (Figure 6g, h).⁶

Figure 6: (a) Top-view SEM and (b) AFM images of a UV–ozone-damaged MAPbI₃ single crystal and the crystal after GBL washing. (c) XRD ω scan measurements and (d) PL comparison showing differences before and after GBL washing. Reprinted with permission.⁸³ Copyright 2020, Nature Publishing Group. (e) Illustration of a MAPbI₃ thin single crystal on a substrate before mechanical polishing, after mechanical polishing, and after oxysalt treatment. (f) Trap density near the C₆₀/MAPbI₃ single-crystal interface before mechanical polishing, after mechanical polishing, and after oxysalt treatment. Reprinted with permission.¹⁸ Copyright 2020, AAAS. Quasi-Fermi-level splitting (QFLS) histogram and TRPL measurements (g) of a PTAA/PFN/ polycrystalline MAPbI₃ film on glass compared to a PTAA/polycrystalline MAPbI₃ film (h) and of a perovskite/LiF/C₆₀ film on glass compared to a C₆₀/polycrystalline MAPbI₃ film. Reprinted with permission.⁶ Copyright 2020, Nature Publishing Group.

Perovskite single crystals offer a platform to investigate their fundamental properties as they have the smallest density of defects and degree of disorder possible due to the lack of GBs. The single crystals also promise high performance devices. As any technology in its early stage of development, solar cells based on perovskite single crystals faced a number of challenges to be solved in future.

All efficient SC-PSCs are made of MAPbI₃, an intrinsically unstable perovskite due to volatilization of methylamine. Although MAPbI₃-based SC-PSCs are stable for 30 days at dark and at low humidity,¹¹ their stability at maximum power point (MPP) conditions remains to be studied. Formamidinium lead iodide (FAPbI₃)-based Pc-PSCs have received significant attention after successful perovskite-polymorph stabilization. FAPbI₃ offers improved stability and an optimal bandgap for solar cells. However, the growth of single crystals involves different crystallization dynamics, and hence methods known for stabilization of FAPbI₃ thin films may not be directly applied for their single crystals. Phase stabilization and utilization of the FA-based single crystals is another pathway to increase the device stability and efficiency of SC-PSCs.

Another issue is that MAPbI₃ undergoes a crystal structure phase transition from tetragonal to cubic phase at ~60 °C.⁸⁶ Solar cells reach this temperature under MPP operation. As a result, MAPbI₃ single-crystal-based devices experience loss of efficiency over long period of testing due to delamination induced by polymorphism-assisted volumetric change⁸⁷. Therefore, compositional engineering is required to improve the stability of SC-PSCs. Mixed cation, e.g., based on FA and/or Cesium (Cs), perovskites⁸⁸⁻⁹⁰ with improved chemical and structural stability under MPP conditions offer a path towards stable SC-PSCs. Reducing the volatile MA content in single crystals will also lead to better surfaces, device performance and interfacial stability.

Free-standing thin perovskite single crystals could address delamination issues, since they will not require substrates to be grown on, and charge selective layers can be directly deposited on both sides of the crystals. However, currently-optimized 20 µm-thick perovskite single are brittle and challenging to handle. Thicker crystals could be more mechanically stable, but they do not have sufficient carrier transport.^{50, 91} the diffusion length of perovskites should be increased to achieve by reducing bulk defect densities, compositional engineering and optimizing synthetic

approaches. For commercialization, the device yield is critical. Due to the detachment of crystals, the device yield of SC-PSCs is currently poor with existing methods of growing on substrates. With the increase of crystal area, the yield drops further. Strategies for the growth of free-standing vertical SC-PSCs can increase the device yield for large area cells.

Lateral solar cells could also address delamination issues. Lateral SC-PSC based on MAPbI₃ single crystals indeed showed a stable MPP operation for over 200 h.⁷⁶ However, lateral SC-PSCs suffer from low efficiencies and can be improved by suppressing surface traps.

Upscaling SC-PSCs is another major challenge. The best performing GaAs and Si single crystals are fabricated by chemical vapor deposition (CVD) on Ge crystals and wafer-slicing of a bulk ingot grown by Czochralski method at 1500 °C, respectively. CVD requires lattice matching of substrate and epilayer, and was attempted on insulating substrates (e.g. SrTiO₃) to form CsPbBr₃ non-continuous thin films;⁹²⁻⁹³ this perovskite has a wide bandgap and is not suitable for photovoltaics.

Space limited ITC was developed to form free-standing perovskite wafers.⁵⁰ In addition, wafer-slicing of ITC-grown large crystals also allows making thin perovskite wafers of over 100 cm² lateral dimensions.⁹¹ However, both these methods offer crystal thicknesses of over 100 μm, 5x higher than perovskite diffusion length leading to low performing devices.

A-micron thick MAPbI₃ single crystal sheets of over 25 cm² dimensions can be epitaxially grown on patterned polymer sheets covering a bulk single-crystal.⁸³ However, their efficiency peaked at 17% for MAPbI₃ for 0.09 cm² active area – significantly lower than the best SC-PSCs – and dropped after thicknesses of 2 μm, indicating short carrier diffusion lengths. The 9 cm² devices

Pb – Sn mixed devices made with this method achieved 10.3%. This promising method can be further improved to achieve large-area efficient SC-PSCs.

In conclusion, we have shown that the efficiency of SC-PSCs is suppressed by their surface properties, and we have highlighted feasible methods for healing their surfaces. The most recent findings on curing the surface defects of perovskite single crystals during the growth process or enhancing the surface properties by post-treatment methods indicate the potential of these materials in further enhancing solar cell performance. To this end, new crystal growth and post-treatment methods exclusive to single crystals should be elaborated. The interlayers utilized to suppress nonradiative recombination should also be considered in parallel. Another key challenge is upscaling single-crystal growth to meet industrial standards. More efforts to improve the surface properties of perovskite crystals, combined with their already superior optoelectronic properties, can help SC-PSCs surpass their polycrystalline counterparts. While surpassing conventional polycrystalline PSCs is not the end goal for SC-PSCs, it is the authors' perspective that any material that relies on charge carrier diffusion, will eventually equilibrate in its highest quality.

ASSOCIATED CONTENT

The Supporting Information is available free of charge. Includes the details of the theoretical calculations.

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QUOTES

- Perovskite single crystals are free of grain boundaries, leading to significantly low defect densities and thus hold promise for high-efficiency photovoltaics.
- Naturally, single crystals, because of their low concentration of structural defects, produce the highest photovoltaic efficiencies, while corresponding polycrystalline solar cells generally offer lower efficiencies; however, perovskites do not obey this norm—at least not at the moment
- The surface recombination velocity (SRV) of perovskite single crystals is higher than that of polycrystalline films by a factor of 6.
- Reducing the surface defect density is more beneficial than reducing the bulk defect density; therefore, strategies for improving SC-PSCs should focus on ameliorating the surface of perovskite single crystals.

REFERENCES

1. Luque, A.; Hegedus, S., *Handbook of photovoltaic science and engineering*. John Wiley & Sons: 2011.
2. Luo, D.; Su, R.; Zhang, W.; Gong, Q.; Zhu, R., Minimizing non-radiative recombination losses in perovskite solar cells. *Nature Reviews Materials* **2020**, 5 (1), 44-60.
3. Zheng, X.; Hou, Y.; Bao, C.; Yin, J.; Yuan, F.; Huang, Z.; Song, K.; Liu, J.; Troughton, J.; Gasparini, N.; Zhou, C.; Lin, Y.; Xue, D.-J.; Chen, B.; Johnston, A. K.; Wei, N.; Hedhili, M. N.; Wei, M.; Alsalloum, A. Y.; Maity, P.; Turedi, B.; Yang, C.; Baran, D.; Anthopoulos, T. D.; Han, Y.; Lu, Z.-H.; Mohammed, O. F.; Gao, F.; Sargent, E. H.; Bakr, O. M., Managing grains and interfaces via ligand anchoring enables 22.3%-efficiency inverted perovskite solar cells. *Nature Energy* **2020**, 5 (2), 131-140.
4. Aydin, E.; De Bastiani, M.; De Wolf, S., Defect and contact passivation for perovskite solar cells. *Advanced Materials* **2019**, 31 (25), 1900428.
5. Zheng, X.; Troughton, J.; Gasparini, N.; Lin, Y.; Wei, M.; Hou, Y.; Liu, J.; Song, K.; Chen, Z.; Yang, C.; Turedi, B.; Alsalloum, A. Y.; Pan, J.; Chen, J.; Zhumekenov, A. A.; Anthopoulos, T. D.; Han, Y.; Baran, D.; Mohammed, O. F.; Sargent, E. H.; Bakr, O. M., Quantum Dots Supply Bulk-and Surface-Passivation Agents for Efficient and Stable Perovskite Solar Cells. *Joule* **2019**, 3 (8), 1963–1976.
6. Stolterfoht, M.; Wolff, C. M.; Márquez, J. A.; Zhang, S.; Hages, C. J.; Rothhardt, D.; Albrecht, S.; Burn, P. L.; Meredith, P.; Unold, T.; Neher, D., Visualization and suppression of interfacial recombination for high-efficiency large-area pin perovskite solar cells. *Nature Energy* **2018**, 3 (10), 847-854.
7. Akin, S.; Arora, N.; Zakeeruddin, S. M.; Graetzel, M.; Friend, R. H.; Dar, M. I., New Strategies for Defect Passivation in High-Efficiency Perovskite Solar Cells. *Advanced Energy Materials* **2020**, 10 (13), 1903090.
8. Shi, D.; Adinolfi, V.; Comin, R.; Yuan, M.; Alarousu, E.; Buin, A.; Chen, Y.; Hoogland, S.; Rothenberger, A.; Katsiev, K.; Losovyj, Y.; Zhang, X.; Dowben, P. A.; Mohammed, O. F.;

- Sargent, E. H.; Bakr, O. M., Low trap-state density and long carrier diffusion in organolead trihalide perovskite single crystals. *Science* **2015**, 347 (6221), 519-522.
9. Dong, Q.; Fang, Y.; Shao, Y.; Mulligan, P.; Qiu, J.; Cao, L.; Huang, J., Electron-hole diffusion lengths >175 μm in solution-grown $\text{CH}_3\text{NH}_3\text{PbI}_3$ single crystals. *Science* **2015**, 347 (6225), 967-970.
 10. Wang, K.; Wu, C.; Hou, Y.; Yang, D.; Priya, S., Monocrystalline perovskite wafers/thin films for photovoltaic and transistor applications. *Journal of Materials Chemistry A* **2019**, 7 (43), 24661-24690.
 11. Chen, Z.; Dong, Q.; Liu, Y.; Bao, C.; Fang, Y.; Lin, Y.; Tang, S.; Wang, Q.; Xiao, X.; Bai, Y.; Deng, Y.; Huang, J., Thin single crystal perovskite solar cells to harvest below-bandgap light absorption. *Nat. Commun.* **2017**, 8 (1), 1890.
 12. Chen, Z.; Turedi, B.; Alsalloum, A.; Yang, C.; Zheng, X.; Gereige, I.; AlSaggaf, A.; Mohammed, O. F.; Bakr, O. M., Single-Crystal MAPbI₃ Perovskite Solar Cells Exceeding 21% Power Conversion Efficiency. *ACS Energy Letters* **2019**, 4 (6), 1258-1259.
 13. Alsalloum, A. Y.; Turedi, B.; Zheng, X.; Mitra, S.; Zhumekenov, A. A.; Lee, K.; Maity, P.; Gereige, I.; AlSaggaf, A.; Roqan, I. S.; Mohammed, O. F.; Bakr, O. M., Low Temperature Crystallization Enables 21.9% Efficient Single-Crystal MAPbI₃ Inverted Perovskite Solar Cells. *ACS Energy Letters* **2020**, 5 (2), 657–662.
 14. Ma, C.; Park, N.-G., A Realistic Methodology for 30% Efficient Perovskite Solar Cells. *Chem* **2020**, 6 (6), 1254-1264.
 15. Zheng, X.; Alsalloum, A. Y.; Hou, Y.; Sargent, E. H.; Bakr, O. M., All-Perovskite Tandem Solar Cells: A Roadmap to Uniting High Efficiency with High Stability. *Accounts of Materials Research* **2020**, 1 (1), 63–76.
 16. Nayak, P. K.; Moore, D. T.; Wenger, B.; Nayak, S.; Haghighirad, A. A.; Fineberg, A.; Noel, N. K.; Reid, O. G.; Rumbles, G.; Kukura, P.; Vincent, K. A.; Snaith, H. J., Mechanism for rapid growth of organic–inorganic halide perovskite crystals. *Nature Communications* **2016**, 7 (1), 13303.
 17. Yang, Y.; Yang, M.; Moore, David T.; Yan, Y.; Miller, Elisa M.; Zhu, K.; Beard, Matthew C., Top and bottom surfaces limit carrier lifetime in lead iodide perovskite films. *Nature Energy* **2017**, 2 (2), 16207.
 18. Ni, Z.; Bao, C.; Liu, Y.; Jiang, Q.; Wu, W.-Q.; Chen, S.; Dai, X.; Chen, B.; Hartweg, B.; Yu, Z.; Holman, Z.; Huang, J., Resolving spatial and energetic distributions of trap states in metal halide perovskite solar cells. *Science* **2020**, 367 (6484), 1352-1358.
 19. Wolff, C. M.; Caprioglio, P.; Stolterfoht, M.; Neher, D., Nonradiative Recombination in Perovskite Solar Cells: The Role of Interfaces. *Advanced Materials* **2019**, 31, 1902762.
 20. Wetzelaer, G. J. A.; Scheepers, M.; Sempere, A. M.; Momblona, C.; Ávila, J.; Bolink, H. J., Trap-assisted non-radiative recombination in organic–inorganic perovskite solar cells. *Advanced Materials* **2015**, 27 (11), 1837-1841.
 21. Stranks, S. D., Nonradiative losses in metal halide perovskites. *ACS Energy Letters* **2017**, 2 (7), 1515-1525.
 22. NREL Best Research-Cell Efficiencies. **2021**, <https://www.nrel.gov/pv/cell-efficiency.html>.
 23. Polman, A.; Knight, M.; Garnett, E. C.; Ehrler, B.; Sinke, W. C., Photovoltaic materials: Present efficiencies and future challenges. *Science* **2016**, 352 (6283), aad4424.
 24. Kurtz, S. R.; McConnell, R. In *Requirements for a 20%-efficient polycrystalline GaAs solar cell*, AIP Conference Proceedings, American Institute of Physics: 1997; pp 191-205.

25. Queisser, H. J.; Haller, E. E., Defects in Semiconductors: Some Fatal, Some Vital. *Science* **1998**, *281* (5379), 945-950.
26. Ono, L. K.; Liu, S. F.; Qi, Y., Reducing Detrimental Defects for High-Performance Metal Halide Perovskite Solar Cells. *Angewandte Chemie (International Ed. in English)* **2020**, *59* (17), 6676.
27. Green, M. A.; Dunlop, E. D.; Hohl-Ebinger, J.; Yoshita, M.; Kopidakis, N.; Ho-Baillie, A. W., Solar cell efficiency tables (version 55). *Progress in Photovoltaics: Research and Applications* **2019**, *28*, 3-15.
28. Schnitzer, I.; Yablonovitch, E.; Caneau, C.; Gmitter, T., Ultrahigh spontaneous emission quantum efficiency, 99.7% internally and 72% externally, from AlGaAs/GaAs/AlGaAs double heterostructures. *Applied physics letters* **1993**, *62* (2), 131-133.
29. Schindler, F.; Fell, A.; Müller, R.; Benick, J.; Richter, A.; Feldmann, F.; Krenckel, P.; Riepe, S.; Schubert, M. C.; Glunz, S. W., Towards the efficiency limits of multicrystalline silicon solar cells. *Solar Energy Materials and Solar Cells* **2018**, *185*, 198-204.
30. Yoshikawa, K.; Kawasaki, H.; Yoshida, W.; Irie, T.; Konishi, K.; Nakano, K.; Uto, T.; Adachi, D.; Kanematsu, M.; Uzu, H.; Yamamoto, K., Silicon heterojunction solar cell with interdigitated back contacts for a photoconversion efficiency over 26%. *Nature Energy* **2017**, *2* (5), 17032.
31. Yan, Y.; Yin, W.-J.; Wu, Y.; Shi, T.; Paudel, N. R.; Li, C.; Poplawsky, J.; Wang, Z.; Moseley, J.; Guthrey, H.; Moutinho, H.; Pennycook, S. J.; Al-Jassim, M. M., Physics of grain boundaries in polycrystalline photovoltaic semiconductors. *Journal of Applied Physics* **2015**, *117* (11), 112807.
32. Becker, J. J.; Boccard, M.; Campbell, C. M.; Zhao, Y.; Lassise, M.; Holman, Z. C.; Zhang, Y.-H., Loss analysis of monocrystalline CdTe solar cells with 20% active-area efficiency. *IEEE journal of photovoltaics* **2017**, *7* (3), 900-905.
33. Ball, J. M.; Petrozza, A., Defects in perovskite-halides and their effects in solar cells. *Nature Energy* **2016**, *1* (11), 1-13.
34. Shan, W.; Saidi, W. A., Segregation of native defects to the grain boundaries in methylammonium lead iodide perovskite. *The journal of physical chemistry letters* **2017**, *8* (23), 5935-5942.
35. Long, R.; Liu, J.; Prezhdo, O. V., Unravelling the effects of grain boundary and chemical doping on electron-hole recombination in CH₃NH₃PbI₃ perovskite by time-domain atomistic simulation. *Journal of the American Chemical Society* **2016**, *138* (11), 3884-3890.
36. de Quilettes, D. W.; Vorpahl, S. M.; Stranks, S. D.; Nagaoka, H.; Eperon, G. E.; Ziffer, M. E.; Snaith, H. J.; Ginger, D. S., Impact of microstructure on local carrier lifetime in perovskite solar cells. *Science* **2015**, *348* (6235), 683-686.
37. Jankowska, J.; Long, R.; Prezhdo, O. V., Quantum dynamics of photogenerated charge carriers in hybrid perovskites: Dopants, grain boundaries, electric order, and other realistic aspects. *ACS Energy Letters* **2017**, *2* (7), 1588-1597.
38. Dong, Q.; Song, J.; Fang, Y.; Shao, Y.; Ducharme, S.; Huang, J., Lateral-structure single-crystal hybrid perovskite solar cells via piezoelectric poling. *Advanced Materials* **2016**, *28* (14), 2816-2821.
39. Schlipf, J.; Askar, A. M.; Pantle, F.; Wiltshire, B. D.; Sura, A.; Schneider, P.; Huber, L.; Shankar, K.; Müller-Buschbaum, P., Top-down approaches towards single crystal perovskite solar cells. *Scientific reports* **2018**, *8* (1), 1-8.

40. Saidaminov, M. I.; Abdelhady, A. L.; Murali, B.; Alarousu, E.; Burlakov, V. M.; Peng, W.; Dursun, I.; Wang, L.; He, Y.; Maculan, G.; Goriely, A.; Wu, T.; Mohammed, O. F.; Bakr, O. M., High-quality bulk hybrid perovskite single crystals within minutes by inverse temperature crystallization. *Nature communications* **2015**, *6*, 7586.
41. Liu, Y.; Yang, Z.; Liu, S., Recent Progress in Single-Crystalline Perovskite Research Including Crystal Preparation, Property Evaluation, and Applications. *Advanced Science* **2018**, *5* (1), 1700471.
42. He, Y.; Petryk, M.; Liu, Z.; Chica, D. G.; Hadar, I.; Leak, C.; Ke, W.; Spanopoulos, I.; Lin, W.; Chung, D. Y.; Wessels, B. W.; He, Z.; Kanatzidis, M. G., CsPbBr₃ perovskite detectors with 1.4% energy resolution for high-energy γ -rays. *Nature Photonics* **2020**, *15*, 36–42.
43. Li, X.; He, Y.; Kepenekian, M.; Guo, P.; Ke, W.; Even, J.; Katan, C.; Stoumpos, C. C.; Schaller, R. D.; Kanatzidis, M. G., Three-dimensional Lead Iodide Perovskitoid Hybrids with High X-ray Photoresponse. *Journal of the American Chemical Society* **2020**, *142* (14), 6625–6637.
44. Haughn, C.; Schmieder, K.; Zide, J.; Barnett, A.; Ebert, C.; Opila, R.; Doty, M., Quantification of trap state densities in GaAs heterostructures grown at varying rates using intensity-dependent time resolved photoluminescence. *Applied Physics Letters* **2013**, *102* (18), 182108.
45. Tan, J.; Cuevas, A.; MacDonald, D.; Trupke, T.; Bardos, R.; Roth, K., On the electronic improvement of multi-crystalline silicon via gettering and hydrogenation. *Progress in Photovoltaics: Research and Applications* **2008**, *16* (2), 129–134.
46. Macdonald, D.; Cuevas, A., Trapping of minority carriers in multicrystalline silicon. *Applied Physics Letters* **1999**, *74* (12), 1710–1712.
47. Balcioglu, A.; Ahrenkiel, R.; Hasoon, F., Deep-level impurities in CdTe/CdS thin-film solar cells. *Journal of Applied Physics* **2000**, *88* (12), 7175–7178.
48. Kerr, L.; Li, S. S.; Johnston, S.; Anderson, T.; Crisalle, O.; Kim, W.; Abushama, J.; Noufi, R., Investigation of defect properties in Cu (In, Ga) Se₂ solar cells by deep-level transient spectroscopy. *Solid-State Electronics* **2004**, *48* (9), 1579–1586.
49. Haynes, J.; Hornbeck, J., Trapping of minority carriers in silicon. II. n-type silicon. *Physical Review* **1955**, *100* (2), 606.
50. Liu, Y.; Zhang, Y.; Yang, Z.; Yang, D.; Ren, X.; Pang, L.; Liu, S., Thinness-and shape-controlled growth for ultrathin single-crystalline perovskite wafers for mass production of superior photoelectronic devices. *Advanced Materials* **2016**, *28* (41), 9204–9209.
51. Peng, W.; Wang, L.; Murali, B.; Ho, K. T.; Bera, A.; Cho, N.; Kang, C. F.; Burlakov, V. M.; Pan, J.; Sinatra, L.; Ma, C.; Xu, W.; Shi, D.; Alarousu, E.; Goriely, A.; He, J. H.; Mohammed, O. F.; Wu, T.; Bakr, O. M., Solution-Grown Monocrystalline Hybrid Perovskite Films for Hole-Transporter-Free Solar Cells. *Adv Mater* **2016**, *28* (17), 3383–90.
52. Zhumekenov, A. A.; Burlakov, V. M.; Saidaminov, M. I.; Alofi, A.; Haque, M. A.; Turedi, B.; Davaasuren, B.; Dursun, I.; Cho, N.; El-Zohry, A. M.; De Bastiani, M.; Giugni, A.; Torre, B.; Di Fabrizio, E.; Mohammed, O. F.; Rothenberger, A.; Wu, T.; Goriely, A.; Bakr, O. M., The role of surface tension in the crystallization of metal halide perovskites. *ACS Energy Letters* **2017**, *2* (8), 1782–1788.
53. Cho, N.; Li, F.; Turedi, B.; Sinatra, L.; Sarmah, S. P.; Parida, M. R.; Saidaminov, M. I.; Murali, B.; Burlakov, V. M.; Goriely, A.; Mohammed, O. F.; Wu, T.; Bakr, O. M., Pure crystal orientation and anisotropic charge transport in large-area hybrid perovskite films. *Nature communications* **2016**, *7* (1), 1–11.

54. Lee, L.; Baek, J.; Park, K. S.; Lee, Y.-E.; Shrestha, N. K.; Sung, M. M., Wafer-scale single-crystal perovskite patterned thin films based on geometrically-confined lateral crystal growth. *Nature communications* **2017**, 8 (1), 1-8.
55. Rao, H.-S.; Chen, B.-X.; Wang, X.-D.; Kuang, D.-B.; Su, C.-Y., A micron-scale laminar MAPbBr₃ single crystal for an efficient and stable perovskite solar cell. *Chemical Communications* **2017**, 53 (37), 5163-5166.
56. Juarez-Perez, E. J.; Ono, L. K.; Maeda, M.; Jiang, Y.; Hawash, Z.; Qi, Y., Photodecomposition and thermal decomposition in methylammonium halide lead perovskites and inferred design principles to increase photovoltaic device stability. *Journal of Materials Chemistry A* **2018**, 6 (20), 9604-9612.
57. Snaith, H. J.; Abate, A.; Ball, J. M.; Eperon, G. E.; Leijtens, T.; Noel, N. K.; Stranks, S. D.; Wang, J. T.-W.; Wojciechowski, K.; Zhang, W., Anomalous hysteresis in perovskite solar cells. *The journal of physical chemistry letters* **2014**, 5 (9), 1511-1515.
58. Chen, B.; Yang, M.; Priya, S.; Zhu, K., Origin of J-V hysteresis in perovskite solar cells. *The journal of physical chemistry letters* **2016**, 7 (5), 905-917.
59. Haruyama, J.; Sodeyama, K.; Han, L.; Tateyama, Y., First-principles study of ion diffusion in perovskite solar cell sensitizers. *Journal of the American Chemical Society* **2015**, 137 (32), 10048-10051.
60. Ma, D.; Mai, L.; Saliba, M.; Sargent, E. H.; Kamat, P. V., Energy Selects: Perovskite Photovoltaics and Storage Batteries. *ACS Energy Letters* **2019**, 4 (6), 1455-1457.
61. Wu, B.; Nguyen, H. T.; Ku, Z.; Han, G.; Giovanni, D.; Mathews, N.; Fan, H. J.; Sum, T. C., Discerning the surface and bulk recombination kinetics of organic-inorganic halide perovskite single crystals. *Advanced Energy Materials* **2016**, 6 (14), 1600551.
62. Grancini, G.; D'Innocenzo, V.; Dohner, E. R.; Martino, N.; Kandada, A. S.; Mosconi, E.; De Angelis, F.; Karunadasa, H. I.; Hoke, E. T.; Petrozza, A., CH₃NH₃PbI₃ perovskite single crystals: surface photophysics and their interaction with the environment. *Chemical science* **2015**, 6 (12), 7305-7310.
63. Fang, H.-H.; Adjokatse, S.; Wei, H.; Yang, J.; Blake, G. R.; Huang, J.; Even, J.; Loi, M. A., Ultrahigh sensitivity of methylammonium lead tribromide perovskite single crystals to environmental gases. *Science Advances* **2016**, 2 (7), e1600534.
64. Burgelman, M.; Nollet, P.; Degraeve, S., Modelling polycrystalline semiconductor solar cells. *Thin solid films* **2000**, 361, 527-532.
65. Yadav, P.; Pandey, K.; Bhatt, P.; Raval, D.; Tripathi, B.; Pandey, M. K.; Kumar, M., Exploring the performance limiting parameters of perovskite solar cell through experimental analysis and device simulation. *Solar Energy* **2015**, 122, 773-782.
66. Minemoto, T.; Murata, M., Device modeling of perovskite solar cells based on structural similarity with thin film inorganic semiconductor solar cells. *Journal of applied physics* **2014**, 116 (5), 054505.
67. De Wolf, S.; Holovsky, J.; Moon, S.-J.; Löper, P.; Niesen, B.; Ledinsky, M.; Haug, F.-J.; Yum, J.-H.; Ballif, C., Organometallic halide perovskites: sharp optical absorption edge and its relation to photovoltaic performance. *The journal of physical chemistry letters* **2014**, 5 (6), 1035-1039.
68. Adinolfi, V.; Yuan, M.; Comin, R.; Thibau, E. S.; Shi, D.; Saidaminov, M. I.; Kanjanaboos, P.; Kopilovic, D.; Hoogland, S.; Lu, Z. H.; Bakr, O. M.; Sargent, E. H., The In-Gap Electronic State Spectrum of Methylammonium Lead Iodide Single-Crystal Perovskites. *Advanced materials* **2016**, 28 (17), 3406-3410.

69. Jiang, Q.; Zhao, Y.; Zhang, X.; Yang, X.; Chen, Y.; Chu, Z.; Ye, Q.; Li, X.; Yin, Z.; You, J., Surface passivation of perovskite film for efficient solar cells. *Nature Photonics* **2019**, *13* (7), 460-466.
70. Tan, H.; Jain, A.; Voznyy, O.; Lan, X.; De Arquer, F. P. G.; Fan, J. Z.; Quintero-Bermudez, R.; Yuan, M.; Zhang, B.; Zhao, Y.; Fan, F.; Li, P.; Quan, L. N.; Zhao, Y.; Lu, Z.-H.; Yang, Z.; Hoogland, S.; Sargent, E. H., Efficient and stable solution-processed planar perovskite solar cells via contact passivation. *Science* **2017**, *355* (6326), 722-726.
71. Zheng, X.; Chen, B.; Dai, J.; Fang, Y.; Bai, Y.; Lin, Y.; Wei, H.; Zeng, X.; Xiao, C.; Huang, J., Defect passivation in hybrid perovskite solar cells using quaternary ammonium halide anions and cations. *Nature Energy* **2017**, *2* (7), 17102.
72. Abdi-Jalebi, M.; Andaji-Garmaroudi, Z.; Cacovich, S.; Stavrakas, C.; Philippe, B.; Richter, J. M.; Alsari, M.; Booker, E. P.; Hutter, E. M.; Pearson, A. J.; Lilliu, S.; Savenije, T. J.; Rensmo, H.; Divitini, G.; Ducati, C.; Friend, R. H.; Stranks, S. D., Maximizing and stabilizing luminescence from halide perovskites with potassium passivation. *Nature* **2018**, *555* (7697), 497-501.
73. Yin, W.-J.; Shi, T.; Yan, Y., Unusual defect physics in CH₃NH₃PbI₃ perovskite solar cell absorber. *Applied Physics Letters* **2014**, *104* (6), 063903.
74. Zheng, X.; Yuan, S.; Liu, J.; Yin, J.; Yuan, F.; Shen, W.-S.; Yao, K.; Wei, M.; Zhou, C.; Song, K.; Zhang, B.-B.; Lin, Y.; Hedhili, M. N.; Wehbe, N.; Han, Y.; Sun, H.-T.; Lu, Z.-H.; Anthopoulos, T. D.; Mohammed, O. F.; Sargent, E. H.; Liao, L.-S.; Bakr, O. M., Chlorine Vacancy Passivation in Mixed Halide Perovskite Quantum Dots by Organic Pseudohalides Enables Efficient Rec. 2020 Blue Light-Emitting Diodes. *ACS Energy Letters* **2020**, *5* (3), 793-798.
75. Xue, J.; Wang, R.; Yang, Y., The surface of halide perovskites from nano to bulk. *Nature Reviews Materials* **2020**, *5*, 809-827.
76. Song, Y.; Bi, W.; Wang, A.; Liu, X.; Kang, Y.; Dong, Q., Efficient lateral-structure perovskite single crystal solar cells with high operational stability. *Nature Communications* **2020**, *11* (1), 1-8.
77. Wang, L.; Zhou, H.; Hu, J.; Huang, B.; Sun, M.; Dong, B.; Zheng, G.; Huang, Y.; Chen, Y.; Li, L.; Xu, Z.; Li, N.; Liu, Z.; Chen, Q.; Sun, L.-D.; Yan, C.-H., A Eu³⁺-Eu²⁺ ion redox shuttle imparts operational durability to Pb-I perovskite solar cells. *Science* **2019**, *363* (6424), 265-270.
78. Shi, L.; Bucknall, M. P.; Young, T. L.; Zhang, M.; Hu, L.; Bing, J.; Lee, D. S.; Kim, J.; Wu, T.; Takamure, N.; McKenzie, D. R.; Huang, S.; Green, M. A.; Ho-Baillie, A. W. Y., Gas chromatography-mass spectrometry analyses of encapsulated stable perovskite solar cells. *Science* **2020**, *368* (6497), eaba2412.
79. Feng, Y.; Pan, L.; Wei, H.; Liu, Y.; Ni, Z.; Zhao, J.; Rudd, P. N.; Cao, L. R.; Huang, J., Low defects density CsPbBr₃ single crystals grown by an additive assisted method for gamma-ray detection. *Journal of Materials Chemistry C* **2020**, *8* (33), 11360-11368.
80. Jao, M.-H.; Lu, C.-F.; Tai, P.-Y.; Su, W.-F., Precise Facet Engineering of Perovskite Single Crystals by Ligand-Mediated Strategy. *Crystal Growth & Design* **2017**, *17* (11), 5945-5952.
81. Kim, D.; Yun, J.-H.; Lyu, M.; Kim, J.; Lim, S.; Yun, J. S.; Wang, L.; Seidel, J., Probing Facet-Dependent Surface Defects in MAPbI₃ Perovskite Single Crystals. *The Journal of Physical Chemistry C* **2019**, *123* (23), 14144-14151.

82. Wang, R.; Xue, J.; Wang, K.-L.; Wang, Z.-K.; Luo, Y.; Fenning, D.; Xu, G.; Nuryyeva, S.; Huang, T.; Zhao, Y.; Yang, J. L.; Zhu, J.; Wang, M.; Tan, S.; Yavuz, I.; Houk, K. N.; Yang, Y., Constructive molecular configurations for surface-defect passivation of perovskite photovoltaics. *Science* **2019**, *366* (6472), 1509-1513.
83. Lei, Y.; Chen, Y.; Zhang, R.; Li, Y.; Yan, Q.; Lee, S.; Yu, Y.; Tsai, H.; Choi, W.; Wang, K.; Luo, Y.; Gu, Y.; Zheng, X.; Wang, C.; Wang, C.; Hu, H.; Li, Y.; Qi, B.; Lin, M.; Zhang, Z.; Dayeh, S. A.; Pharr, M.; Fenning, D. P.; Lo, Y.-H.; Luo, J.; Yang, K.; Yoo, J.; Nie, W.; Xu, S., A fabrication process for flexible single-crystal perovskite devices. *Nature* **2020**, *583* (7818), 790-795.
84. Yang, S.; Chen, S.; Mosconi, E.; Fang, Y.; Xiao, X.; Wang, C.; Zhou, Y.; Yu, Z.; Zhao, J.; Gao, Y.; Angelis, F. D.; Huang, J., Stabilizing halide perovskite surfaces for solar cell operation with wide-bandgap lead oxysalts. *Science* **2019**, *365* (6452), 473-478.
85. Li, F.; Deng, X.; Qi, F.; Li, Z.; Liu, D.; Shen, D.; Qin, M.; Wu, S.; Lin, F.; Jang, S.-H.; Zhang, J.; Lu, X.; Lei, D.; Lee, C.-S.; Zhu, Z.; Jen, A. K.-Y., Regulating Surface Termination for Efficient Inverted Perovskite Solar Cells with Greater Than 23% Efficiency. *Journal of the American Chemical Society* **2020**, *142* (47), 20134–20142.
86. Luan, M.; Song, J.; Wei, X.; Chen, F.; Liu, J., Controllable growth of bulk cubic-phase CH₃NH₃PbI₃ single crystal with exciting room-temperature stability. *CrystEngComm* **2016**, *18* (28), 5257-5261.
87. Moloney, E. G.; Yeddu, V.; Saidaminov, M. I., Strain Engineering in Halide Perovskites. *ACS Materials Letters* **2020**, *2* (11), 1495-1508.
88. Saliba, M.; Matsui, T.; Seo, J.-Y.; Domanski, K.; Correa-Baena, J.-P.; Nazeeruddin, M. K.; Zakeeruddin, S. M.; Tress, W.; Abate, A.; Hagfeldt, A.; Grätzel, M., Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency. *Energy & environmental science* **2016**, *9* (6), 1989-1997.
89. Saliba, M., Polyelemental, multicomponent perovskite semiconductor libraries through combinatorial screening. *Advanced Energy Materials* **2019**, *9* (25), 1803754.
90. Wang, Y.; Dar, M. I.; Ono, L. K.; Zhang, T.; Kan, M.; Li, Y.; Zhang, L.; Wang, X.; Yang, Y.; Gao, X.; Qi, Y.; Grätzel, M.; Zhao, Y., Thermodynamically stabilized β -CsPbI₃-based perovskite solar cells with efficiencies > 18%. *Science* **2019**, *365* (6453), 591-595.
91. Liu, Y.; Ren, X.; Zhang, J.; Yang, Z.; Yang, D.; Yu, F.; Sun, J.; Zhao, C.; Yao, Z.; Wang, B.; Wei, Q.; Xiao, F.; Fan, H.; Deng, H.; Deng, L.; Liu, S. F., 120 mm single-crystalline perovskite and wafers: towards viable applications. *Science China Chemistry* **2017**, *60* (10), 1367-1376.
92. Chen, J.; Morrow, D. J.; Fu, Y.; Zheng, W.; Zhao, Y.; Dang, L.; Stolt, M. J.; Kohler, D. D.; Wang, X.; Czech, K. J.; Hautzinger, M. P.; Shen, S.; Guo, L.; Pan, A.; Wright, J. C.; Jin, S., Single-crystal thin films of cesium lead bromide perovskite epitaxially grown on metal oxide perovskite (SrTiO₃). *Journal of the American Chemical Society* **2017**, *139* (38), 13525-13532.
93. Chen, J.; Fu, Y.; Samad, L.; Dang, L.; Zhao, Y.; Shen, S.; Guo, L.; Jin, S., Vapor-phase epitaxial growth of aligned nanowire networks of cesium lead halide perovskites (CsPbX₃, X= Cl, Br, I). *Nano letters* **2017**, *17* (1), 460-466.