Journal of Materials Chemistry A



View Article Online

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REVIEW

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Cite this: J. Mater. Chem. A, 2019, 7, 24150

Received 26th July 2019 Accepted 23rd September 2019

DOI: 10.1039/c9ta08130e

rsc.li/materials-a

Emerging alkali metal ion (Li⁺, Na⁺, K⁺ and Rb⁺) doped perovskite films for efficient solar cells: recent advances and prospects

Chengbo Li,^{ab} Aili Wang,^{ab} Lisha Xie,^{ab} Xiaoyu Deng,^{ab} Kejun Liao,^{ab} Jin-an Yang,^{ab} Tingshuai Li^{ab} and Feng Hao ^b *^{ab}

Metal halide perovskite materials have drawn worldwide attention for application in a variety of optoelectronic devices, especially in the emerging photovoltaic devices. In recent years, remarkable progress has been achieved in the device performance and stability. The optoelectronic properties of metal halide perovskites can be further tuned by ion doping. Herein, a comprehensive review of the incorporation of alkali metal ions (Li⁺, Na⁺, K⁺ and Rb⁺) in emerging perovskite solar cells for a longer carrier lifetime, lower interfacial defect density, faster charge transfer, no hysteresis, higher stability and higher power conversion efficiency is presented. The detailed mechanism behind these beneficial effects has been discussed in terms of electronic properties, film morphology, energy level alignment, carrier recombination dynamics and stability. On the basis of these latest advances and breakthroughs in alkali ion doped perovskite thin films, future research directions and prospects are also discussed, which include further understanding of the underlying photophysical mechanism and extension to other optoelectronic devices where a longer carrier lifetime and lower trap density are needed.

"School of Materials and Energy, University of Electronic Science and Technology of China, Chengdu, 610054, China. E-mail: haofeng@uestc.edu.cn

^bCenter for Applied Chemistry, University of Electronic Science and Technology of China, Chengdu 611731, China

1. Introduction

As the world's population continues to grow, there is a huge gap between energy supply and demand standards. The traditional ways of closing this gap are running out and we need to obtain cheap energy from clean and abundant sources. Using



Chengbo Li received his BS degree from the School of Material Science and Engineering of Southwest University of Science and Technology (SWUST) in 2018. He is currently a master's student in Prof. Feng Hao's group at the School of Materials and Energy of the University of Electronic Science and Technology of China (UESTC). His current research focuses on perovskite materials and solar cells.



Feng Hao received his PhD degree from Tsinghua University in 2012. Then he moved to Northwestern University as a postdoctoral research fellow for four years in the Department of Chemistry. He is now a full professor in the School of Materials and Energy of the University of Electronic Science and Technology of China (UESTC). Currently his research focuses on various photovoltaic mate-

rials and devices including sensitized solar cells and halide perovskite solar cells. Meanwhile, he is also involved in developing many photonic materials such as TCO, functional thin films, and semiconductor compounds. He has published more than 50 international journal papers.

Review

photovoltaic devices is widely recognized as one of the most promising solutions to meet the global energy demand.¹⁻⁷ Organic-inorganic hybrid lead halide perovskites have received extensive attention in the fields of photovoltaics,^{8,9} lasers,¹⁰ photodetectors,¹¹ light-emitting diodes (LEDs)^{10,12,13} and thin film transistors¹⁴ due to their excellent optoelectronic properties, such as suitable optical band gaps, long charge carrier diffusion lengths, and high absorption coefficients.¹⁵⁻¹⁸ Over the past decade, perovskite solar cells (PSCs) have made great progress with a certified record current efficiency of 25.2%.19 The high efficiency of PSCs depends on a high quality light absorbing layer, which is controlled by nucleation and crystal growth of the perovskite layer. However, poor stability against humidity, heat and light of the perovskite layer raise a critical concern for future commercialization.²⁰⁻²² The fracture of the periodic crystal structure occurs in the perovskite film with polycrystalline properties, forming a large number of grain boundaries (GBs) and defects, which served as recombination centers in the charge transport pathway.²³⁻²⁵ Researchers have developed a variety of methods to reduce the defects of the perovskite absorption layer. For example, the introduction of different doping ions or the component adjustment in the precursor solution has been widely investigated in this regard.²⁶⁻³³ Different organic and inorganic additives have been employed to passivate the defect density, such as MACl,³⁴ water,35 guanidinium salt,36 Lewis bases,37-39 N,N-dimethylformamide (DMF)40-43 and so on.

Considering the valence distribution in the lattice of hybrid perovskites and the redox resistance of alkali metals,³ positively charged alkali metal cations (Li⁺, Na⁺, K⁺ and Rb⁺) are considered as ideal dopants. In recent years, the incorporation of these alkali metal cations in perovskite materials has attracted extensive attention.44-47 For example, the incorporation of Cs⁺, Rb⁺ and other cations into the perovskite A site improved not only the power conversion efficiency (PCE) but also the reproducibility and stability of the PSCs. The Cs⁺ doping enables the transformation of the yellow phase (δ -phase) into the perovskite phase. Zhu et al.44 found that partial replacement of FA⁺ with Cs⁺ can improve the stability of humidity due to the shrinkage of the perovskite lattice. Saliba *et al.* added Rb⁺ into (CsFAMA) Pb(I/Br)₃ perovskites with a stabilized PCE of up to 21.6% and remarkable stability at 85 °C for 500 h in a nitrogen atmosphere. The exploration of Rb⁺ prompted us to investigate smaller alkali metal ions (such as K⁺ and Na⁺) for improving the photovoltaic performance of PSCs.⁴⁸⁻⁵⁰ Recently, the addition of K⁺ to the perovskite layer eliminated the hysteresis in the J-V curve of PSCs.⁵¹ The diffusion of sodium ions (Na⁺) can extend the carrier lifetime and reduce the trap density, increasing the efficiency of the device.52 This massive research on alkali metal doping in the perovskite layer greatly improves the performance and stability of PSCs.3,53-55 Thus, a systematical review of the latest advances of alkali metal cation (Li⁺, Na⁺, K⁺ and Rb⁺) doped perovskites is highly necessary. Here we summarize the recent development of alkali metal ion doping in PSCs for a longer carrier lifetime, lower interfacial defect density, faster charge transfer, no hysteresis, and higher stability and PCEs. The detailed mechanism behind these beneficial effects has

been discussed in terms of electronic properties, film morphology, energy level alignment, and carrier recombination dynamics. Some open questions and future perspectives are also given, which include further understanding of the photophysical mechanism, implementation of novel deposition methods, and extension to other optoelectronic devices.

Incorporating position: interstitial or substitution

The basic structure of metal halide hybrid perovskites can be represented by a general formula of ABX₃, wherein the B atom is usually a divalent metal cation (Pb²⁺, Sn²⁺, or Ge²⁺) or mixing cations and X is a halide anion (Cl⁻, Br⁻, or I⁻). The structure consists of an extended framework of corner shared (PbI₆)^{4–} octahedrons in which the A⁺ cation, such as methylammonium cations (CH₃NH₃⁺ and MA⁺), formamidinium cations (HC(NH₂)₂⁺ and FA⁺), or cesium cation (Cs⁺), occupies the central position and is surrounded by 12 nearest neighboring X anions.^{56,57} Therefore, the size of the A⁺ cation is restricted by the space of pores. A tolerance factor (*t*) was proposed in the early 1920s to study the structural stability of perovskites:

$$t = \left(R_{\rm A} + R_{\rm X}\right) \left/ \sqrt{2}R_{\rm B} + R_{\rm X}\right.$$

where R_{A} , R_{B} , and R_{X} are the ionic radius of the A, B, and X ions, respectively. When t > 1, the perovskite tends to form a hexagonal structure. When t < 0.8, it is an orthogonal structure. When 0.8 < t < 1, it is a cubic structure (see Fig. 1(a)).^{58,59} So far, Goldschmidt's tolerance factor t has been widely accepted for studying the ionic radius relationship and predicting the formation of cubic perovskite structures. A large variety of component elements enrich the versatility of perovskite materials. For example, lead toxicity raises serious environmental concerns for the practical application of this technology.⁶⁰ Tin (Sn) analogies of MASnI₃, FASnI₃ and CsSnI₃ were used address the toxicity issues in PSCs with relatively lower PCEs.^{6,31,61,62} MAGeI₃ has also been investigated with good hole and electron conductivity and stability compared with MAPbI₃.63 Transition metal alloys have been studied including Pb/Sn and Pb/Ge hybrid systems, among which MASn_{0.5}Pb_{0.5}I₃ and MAGe_{0.75}-Pb_{0.25}I₃ showed abnormal band gap narrowing and higher theoretical efficiency.⁶⁴ In addition, cationic transmutations have been theoretically calculated with many promising alternatives for photovoltaic applications, such as MAIn_{0.5}Bi_{0.5}I₃,⁶⁵ Cs₂InSbCl₆,⁶⁶ Cs₂InBiCl₆,⁶⁶ etc. Distortion due to the A site cationic substitution can be further used to fine tune the physical properties of perovskites.⁶⁷ It is well known from the tolerance factor that the ionic radius of the A site cation has a critical effect on the crystal structure of the perovskite. A cation with a small ionic radius can shrink the perovskite structure. However, the addition of a small amount of cations (Cs⁺ and Rb⁺) does not cause the collapse of the perovskite crystal structure. Calculations of the tolerance factor from the space size have been used to predict new perovskites as shown in Fig. 1(b). Empirically, perovskites with a t between 0.8 and 1.0 (dotted line) exhibit a photoactive black phase (solid circle)



Fig. 1 (a) Crystal structure of perovskite materials with different tolerance factors. Copyright 2015 American Chemical Society. (b) Calculated Goldschmidt tolerance factors of all perovskite structures. Copyright 2014 Springer Nature Publishing AG. (c) ΔH_{0K} of alkali cation incorporation at an A site (being constant for concentration from 0.5 to 6%) and at an interstitial site. Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (d) The *d*-spacing of various alkali cation containing perovskites was plotted from the peaks of (110) and (200). Copyright 2019 Elsevier B.V. (e) XRD pattern of various alkali cation containing perovskites. M denotes the mixed perovskite of $MA_{0.15}FA_{0.85}Pb(I_{0.85}Br_{0.15})_3$ while Li⁺, Na⁺, K⁺, Rb⁺ and Cs⁺ represent 5% molar alkali cation doped perovskites, respectively. (f) DFT Optimized structures of the 2D K₂PbI₄ perovskite (upper) and 2D/3D K₂PbI₄/MAPbI₃ interface (below). Copyright 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

rather than a non-photoactive phase (open circle). In particular, all cations should be stable up to Rb⁺ and K⁺ using this standard.68 The size of the Rb⁺ cation is very close to this limit, making it a candidate for partially replacing the A-site in the perovskite lattice. However, it was considered that Li⁺, Na⁺, and K⁺ were clearly outside the range of tolerance factors. Empirically, only CsPbI₃ turned black after annealing, RbPbI₃ remained yellow which does not have a photoactive black phase. However, Rb⁺ is particularly attractive due to its inherent oxidative stability. Whether the alkali metal can enter the perovskite crystal lattice is still controversial. On the one hand, some studies showed that Rb⁺ can occupy the A-position of the perovskite crystal lattice, but Li⁺, Na⁺ and K⁺ occupy the interstitials. Grätzel et al.³ first incorporated rubidium cations (Rb⁺) in 2016 with a PCE of 21.6%, maintaining 95% of its initial performance at 85 °C for 500 hours. The amount of cationic substitution also affected the occupancy. Recently, smaller alkali cations such as $\boldsymbol{K}^{\!\!\!\!+}$ and $\boldsymbol{Na}^{\!\!\!\!\!\!+}$ have been introduced into MAPbI3 or MAFAPbI3. Jung et al. indicated that the lattice interplanar spacing grew larger after K⁺ doping and the steric radius of K^+ was much smaller than that of $CH_3NH_3^+$ (K^+ = $0.138 \text{ nm and } CH_3 NH_3^+ = 0.203 \text{ nm}$.⁶⁹ Rb⁺ can be located at the A-site due its similar ion radius, while Li⁺, Na⁺, and K⁺ mainly exist as interstitials, which can be seen from the change of the

lattice. Although the crystal lattice is expanded instead of Rb⁺containing perovskites, the interstitial atoms block the ion migration and thereby inhibit the mutual reaction of halides. Zhao et al.70 investigated the incorporation of extrinsic alkali cations (Rb⁺, K⁺, Na⁺, and Li⁺) into perovskites by density functional theory (DFT), and the size-dependent interstitial occupancy of these cations in the perovskite lattice is demonstrated in Fig. 1(c). Interestingly, the calculations predict that occupation by extrinsic alkali cations in perovskite lattice interstitials can suppress the ion migration, which has been widely recognized as the main reason for the anomalous hysteresis behavior of PSCs.71-73 It was further demonstrated that the incorporation of alkali cations (Rb⁺, K⁺, Na⁺, or Li⁺) into Cs/MA/FA perovskites induced lattice expansion, and extrinsic alkali cations indeed occupied the interstitials more favorably than A site substitution. The smaller alkali cation showed a higher tendency of interstitial occupancy. Accordingly, Rb^{\dagger} partially occupies the A-site while Li⁺, Na⁺, and K⁺ occupy mainly interstitials as evidenced by the lattice variation as shown in Fig. 1(d). Noticeably, the interstitial occupancy is favourable for increasing ion migration barriers in the lattice and thus suppresses ion migration by interacting with halides although the lattice is expanded. Fig. 1(e) shows the X-ray diffraction (XRD) patterns of the perovskite films doped with

various alkali metal cations by Segawaa et al.74 Notable peak shifts can be observed in all diffraction directions of alkali cationic perovskites except for Rb⁺ and Cs⁺. The lattice constants of perovskites with Li⁺, Na⁺ or K⁺ were larger than those of pristine perovskites, and among which the one with Na⁺ showed the largest lattice constants. Perovskites doped with Rb⁺ or Cs⁺ showed similar lattice constants to undoped perovskites. Park et al. also suggested that K⁺ is more energetic in the interstitial site by theoretical studies,75 thus preventing the formation of Frenkel defects which is the origin of the hysteresis of PSCs. A more detailed discussion of the hysteresis behavior by potassium ion passivation will be presented in the following part. On the other hand, some research questioned the actual position of alkali metal ions. For example, Docampo et al. studied the actual position of Cs⁺ and Rb⁺. As the Cs⁺ ion concentration increases, the XRD peak of the original perovskite moves toward a larger diffraction angle, implying a shrinkage of the perovskite crystal lattice. In contrast, as the doping concentration of Rb⁺ ions increases, the peak shifts to a low angle, indicating the expansion of the perovskite crystal lattice. Their experiments demonstrated that Rb⁺ can cause a deficiency of Br in the mixed halide perovskite structure by forming Br-rich side phases.⁷⁶ Gratzel et al. confirmed that Rb⁺ and K⁺ were not incorporated into the A-site of the perovskite crystal lattice.77 The separated Rb-rich phase can be used as a potential material for the perovskite passivation layer. In their another report, they highlighted that there is no evidence that potassium is incorporated into the perovskite lattice using ³⁹K MAS NMR at 21.1 T. The analysis showed that the system formed a commixture of a potassium-rich phase and unreacted KI.78 Sun et al. reported the incorporation of potassium cations (K⁺) into lead halide perovskites through both experiments and theoretical simulations. In order to further explore whether twodimensional K₂PbI₄ is stable in the three-dimensional perovskite, a two-dimensional/three-dimensional perovskite interface model was established and optimized by DFT simulation in Fig. 1(f). A potassium-rich phase was found on the grain boundaries of the K⁺ doped perovskite. It was confirmed that the presence of K⁺ (in the 2D K₂PbI₄ state) on the surface of 3D perovskites is thermodynamically stable, effectively passivating the grain boundaries of the 3D crystal and decreasing the trap state.79 The potassium-rich phase grew in the three-dimensional perovskite grain boundary, which can effectively passivate the grain boundary and reduce the trap state. Similar to Rb⁺, the incorporation of K⁺ can also increase the grain size and crystallinity due to a decrease in crystallization activation energy, resulting in fewer defects, longer carrier lifetime, and better conductivity.51,75,80,81

3. Electronic properties

The addition of a small amount of alkali metal ions (Na⁺, K⁺, and Rb⁺) to the perovskite can inhibit ion migration which is considered to be a major factor affecting the hysteresis behavior of PSCs.⁸² Son *et al.*⁷⁵ developed a general method to eliminate the hysteresis in PSCs by introducing trace amounts of alkali metal ions (\sim 10 µmol) into the perovskite layers. As shown in

Fig. 2(a)(ii)–(iv), it was found that Na⁺, K⁺, and Rb⁺ inhibited J-Vhysteresis. When the ionic radius of the alkali metal ion increases from Li⁺ to K⁺, the hysteresis tends to decrease and disappear at K⁺, and it reappears when the ionic radius is further increased from K⁺ to Cs⁺. By studying the defect density and lattice parameters, it was believed that the addition of K⁺ occupies the octahedral interstitial site $(O_{\rm h})$, thus suppressing the formation of halide Frenkel defects and reducing the defect density and migration of halide ions. Huang et al.52 found that the diffusion of sodium ions (Na⁺) into perovskite can passivate the defects in the perovskite layer, thus improving device performance. Small amounts of alkali metal ions (Na⁺, K⁺, and Rb⁺) were found to be able to act as a suppressor of ion migration in perovskite materials. It is worth noting that the disappearance of hysteresis has nothing to do with the electron transport layer and interface modification. Park et al. believed that the atomic origin of hysteresis is the formation of iodine Frankel defects rather than the migration of iodine vacancies.75 Among all the alkali metals, K⁺ could constrain the formation of Frenkel defects since K⁺ represents a more qualified interstitial than other elements due to its suitable ion radius. Hao et al.83 recently showed that several different types of ion defects can be simultaneously passivated by simple inorganic binary basic halide salts. The effective defect passivation significantly improves the open-circuit voltage (V_{oc}) , improves the steadystate efficiency response, and eliminates the hysteresis phenomenon. In order to accurately locate the positions of K⁺ and Cl⁺, they conducted transmission electron microscopeenergy dispersive spectroscopy (TEM-EDS) and secondary ion mass spectroscopy (SIMS) studies, which strongly proved that KCl existed in the interface functional layer. Segawa et al.51 also found that the addition of K⁺ to the perovskite layer can eliminate the hysteresis in the J-V curve of PSCs. An increased $V_{\rm oc}$ and fill factor (FF) up to 81.9% were observed in the devices with K⁺ doping. Zhong et al.⁸⁴ also reported the elimination of hysteresis in planar PSCs with K⁺ incorporation. Zhao et al.⁷⁰ also concluded that K⁺ doping could maintain high efficiency while effectively reducing hysteresis. The hysteresis behavior is generally recognized to be caused by defects and carrier trapping, as well as the capacitive effect.72,85 Capacitances measured under short-circuit conditions without bias under one sun illumination were reported by Park et al. (Fig. 2(b)).75 The intermediate frequency capacitance is related to the dipole polarization or chemical capacitance in the perovskite layer, which is caused by the electron polarization. The low frequency capacitance is related to the electrode polarization caused by the interfacial phenomenon such as interfacial electric or ionic charge accumulation.⁸⁶⁻⁸⁹ The frequency-dependent capacitance of the device with K⁺ incorporation was significantly lower than that of the control device without K⁺. In the region of 10-100 Hz, the device with KI showed little variation of capacitance with frequency, in accordance with the absence of hysteresis in the *J–V* curve. Furthermore, the incorporation of K⁺ increases charge conductivity and reduces defects. As shown in Fig. 2(c) and (d), the KCsFAMA perovskite film showed a higher conductivity than that of CsFAMA and FAMA films, indicating the faster transport of carriers in the K-containing perovskite



Fig. 2 (a) (i)–(v) J-V curves of perovskite solar cells based on (FAPbl₃)_{0.875}(CsPbBr₃)_{0.125} doped with 10 µmol of Lil, Nal, KI, Rbl and Csl, measured in reverse and forward scans at a scan rate of 130 mV s⁻¹ under AM 1.5G one sun illumination (100 mW cm⁻²). Copyright 2018 American Chemical Society. (b) Capacitance–frequency plots of FTO/TiO₂/(FAPbl₃)_{0.875}(CsPbBr₃)_{0.125}/spiro-MeOTAD/Au. Copyright 2018 American Chemical Society. (c) Dark J-V characteristics of the FAMA, CsFAMA and KCsFAMA perovskite films. (d) Dark J-V characteristics of electron only devices based on FAMA, CsFAMA and KCsFAMA perovskite films. Copyright 2017 the Royal Society of Chemistry.

film. Fig. 2(d) shows the typical dark *J–V* characteristics of electron-only devices with different perovskites using space-charge-limited-current (SCLC) techniques to estimate the trap density.⁴⁵ A reduction in trap density was observed in the K⁺ devices, which was ascribed to the high quality of perovskite films after potassium passivation.⁸⁴

The assessment of the carrier lifetime and the defect density by Segaw *et al.*⁷⁴ revealed that K^+ doping introduced the least number of defects, followed by Rb⁺, Cs⁺, and Na⁺ doping, respectively. In addition to the perovskite/TiO₂ interface, the defects in perovskite films also played a critical role in the hysteresis behavior in the *J*–*V* curves. Consequently, the devices with K^+ doping showed the highest efficiency up to 20% with negligible hysteresis. Boschloo *et al.* also reported a longer fluorescence lifetime with K^+ doping.⁹⁰

The incorporation of alkali cations can also regulate the electronic properties of perovskite films. Jung *et al.*⁶⁹ reported that a significant increase of crystallinity, a red shift of the photoluminescence spectrum and a decrease of surface potential in the perovskite film with K^+ lead to a remarkable improvement of carrier separation and suppression of the charge recombination. More importantly, the addition of K^+ ions prolonged the carrier lifetime of PSCs. The results of charge transfer efficiency (CTE) calculation showed that with the increase of K^+ content, the capacity of electron injection and hole extraction changed significantly. When the K^+ content is 0.2, the perovskite film exhibits excellent ability to separate photogenerated electrons and holes, optimizing the conversion

efficiency to 19.3%.91 Liu et al.23 reported that the addition of small alkali metal ions (Na⁺ and K⁺) significantly improved the quality of perovskite films by increasing the grain size, decreasing the defect state density, passivating the grain boundary and increasing the built-in potential (V_{bi}) . However, Chen et al.92 showed that Na⁺ cation doping can change the conductivity of MAPbI₃ from n-type to p-type. Compared with the original MAPbI₃ perovskite, the hole concentration with NaI doping increased by an order of magnitude and the mobility significantly decreased, indicating that Na⁺ doping can affect the carrier migration characteristics in the perovskite film. Up to now, PSCs have been found to benefit from a variety of alkali metal ion incorporation, as shown in Table 1. Alkali metal cations induced different changes of perovskite films, depending on their concentration and distributions in the perovskite. In Table 1, the device structure was deliberately mentioned due to the differences in energy level alignment and carrier recombination dynamics in conventional and inverted planar devices. Especially, Br⁻-containing perovskites are widely used in K⁺ incorporation systems. Excess halides are immobilized by complexing with potassium to form benign compounds at grain boundaries and surfaces to inhibition migration.

4. Film morphology

The quality of the microscopic morphology of the perovskite film is an important factor affecting the photovoltaic performance. A high-quality perovskite film should have large,

| Perovskite (additive) | Property | PCE/control (%) | PCE/champion (%) | $J_{ m sc} \ ({ m mA~cm}^{-2})$ | $V_{\rm oc}$ (V) | FF (%) | Ref. |
|---|---|--------------------|---------------------|---------------------------------|------------------|--------|------------------------|
| ^b MAPbI ₃ (LiI) | Enhancing perovskite crystallinity | 14.1 | 18.1 | 22.8 | 1.08 | 73.5 | 2017 (⁹³) |
| ^a MAPbI ₃ (LiI) | Enlarging grain size | 17.60 | 18.16 | 21.16 | 1.10 | 78 | $2017 (^{94})$ |
| ^a MAPbI ₃ (LiTFSI) | Enlarging grain size | 11.3 | 15.6 | 23.14 | 1.07 | 63 | $2017 (^{95})$ |
| a MAPbI ₃ (LiI) | | 11.3 | 17.01 | 23.36 | 1.10 | 66 | $2017 (^{95})$ |
| ^{<i>b</i>} MAPbI ₃ (NaCl) | Improving the crystallinity and morphology | 11.40 | 12.77 | 17.59 | 0.96 | 75.62 | 2016 (⁹⁶) |
| ^b MAPbI ₃ (NaI) | Improving the charge carrier lifetime | 13.7 | 14.54 | 20.26 | 0.93 | 78 | 2016 (97) |
| ^b MAPbI ₃ (NaI) | Enlarging perovskite grain | 10.2 | 14.2 | 19.2 | 0.96 | 77 | 2016 (49) |
| ^b MAPbI ₃ (NaI) | Prolonging carrier lifetime | 18.8 | 20.2 | 24.4 | 1.06 | 78.0 | 2017 (52) |
| ^{<i>a</i>} MAPbI ₃ (NaI) | Reducing the trap states | 15.56 | 18.16 | 21.16 | 1.10 | 78 | $2017(^{23})$ |
| ^{<i>a</i>} MAPbI ₃ (NaSCN) | | 12.73 | 15.63 | 20.90 | 1.030 | 72.62 | 2018 (⁹⁸) |
| ^b MAPbI ₃ (KI) | Improving the charge carrier lifetime | 13.7 | 15.31 | 20.95 | 0.94 | 79 | 2016 (97) |
| ^b MAPbI ₃ (KCl) | Improving the crystallinity | 11.40 | 15.08 | 19.42 | 1.04 | 74.67 | 2016 (⁹⁶) |
| ^{<i>a</i>} MAPbI ₃ (KI) | Improving the grain size | 15.56 | 17.81 | 20.88 | 1.10 | 78 | 2017 (23) |
| ${}^{a}FA_{0.85}MA_{0.15}$ PbBr _{0.45} Lo = (KI) | Minimizing the electron transfer barrier | 18.45 | 20.32 | 22.99 | 1.167 | 76 | $2017(^{51})$ |
| a MAPhL _a (KI) | Improving carrier separation properties | 17 30 | 19.27 | 23 33 | 1 111 | 74 | $2017 (^{69})$ |
| a CsPbI ₂ Br (KI) | Facilitating photoexcited charge carrier | 8.2 | 10.0 | 11.6 | 1.18 | 73 | 2017 (⁸⁰) |
| $a(\mathbf{E}\mathbf{A} \mathbf{M}\mathbf{A})$ | Peduced carrier recombination | 19.04 | 20.56 | 22.05 | 1 1 2 2 | 70 | $2017 (^{81})$ |
| $Pb(I_{0.85}Br_{0.15})_3$ (KI) | Reduced carrier recombination | 10.94 | 20.30 | 22.95 | 1.132 | 19 | 2017 () |
| $^{a}Cs_{0.11}MA_{0.15}FA_{0.74}$ PbI ₃ (KI) | Suppressing ion migration | 17.3 | 21.5 | 23.2 | 1.17 | 79 | 2018 (48) |
| a FA _{0.85} MA _{0.15} PbBr _{0.45} | Decreasing defects | 17.60 | 20.55 | 22.92 | 1.154 | 77.7 | $2018 (^{74})$ |
| $a(Cs_{0.06}MA_{0.15}FA_{0.79})$ Pb(I _{0.95} Br _{0.15}) ₂ (KI) | Potassium passivation | 18.2 | 21.6 | 23.06 | 1.18 | 79 | 2018 (⁵⁰) |
| ${}^{a}\text{FA}_{0.85}\text{MA}_{0.15}\text{PbBr}_{0.45}$ | Preventing Frenkel defect formation | 17.14 | 17.55 | 21.47 | 1.128 | 72.5 | 2018 (⁷⁵) |
| a MAPbL Cl (KCl) | Active passivation | 18 12 | 19 44 | 21.82 | 1 1 2 4 | 79.3 | 2018 (⁹⁹) |
| a MAPbL _a (KSCN) | Active publication | 12 73 | 16.59 | 20.45 | 1.124 | 76.20 | $2010(^{98})$ |
| $a_{\rm FA_{0.02}MA_{0.4}-Ph}$ | Passivating the grain boundaries | 17.1 | 20.4 | 23.5 | 1.005 | 75 | $2010(^{79})$ |
| $(I_0 \circ Br_0 = 1)_2$ (KI) | Tubbli uting the grain boundaries | 1.11 | 2011 | 2010 | 1110 | | 2019() |
| $^{a}MA_{o}$ - FA _o - PbI _o (RbI) | Increases phase stability | 17.30 | 21.8 | 22.8 | 1.180 | 81 | $2016 (^{100})$ |
| $a(CsMAFA)Pb(IBr)_{a}(PbI)$ | Decreasing hysteresis | 19.5 | 21.0 | 22.9 | 1 16 | 78 | $2010(^{101})$ |
| $a(Cs_{0.06}MA_{0.15}FA_{0.79})$ Pb(L_s-Br_s-s) (BbI) | Rubidium passivation | 18.1 | 20.6 | 23.11 | 1.14 | 78 | $2019 (^{50})$ |
| a FAPbI ₃ (RbI) | Enhancing moisture stability | 13.56 | 17.16 | 23.93 | 1.07 | 67 | $2017 (^{102})$ |
| ^{<i>a</i>} Conventional planar structure. ^{<i>b</i>} Inverted planar structure. | | | | | | | |

uniform and regular crystals and complete coverage on the bottom layer with few pinholes. The large, regular crystal boundary is conducive to the carrier transport while few pinholes reduce non-radiative recombination and leakage current. Alkali metal doping has been widely adopted to adjust the recrystallization process of the perovskite film. Durstock et al.⁴⁹ first showed that the addition of Na⁺ into the precursors of perovskite can significantly improve the grain structure and the overall morphology of the film. The device incorporating 2 mol% of Na⁺ into the perovskite film showed a high efficiency of 14.2% under AM 1.5G 100 mW cm⁻² conditions. The average grain size of the solvent-annealed perovskite film exhibited a strong dependence on the amount of Na⁺ added to the precursor solution. Perovskite films without horizontal grain boundaries are widely recognized to be beneficial to carrier diffusion and photovoltaic performance. However, Segawa et al.74 reported smaller grains and more cracks in the

perovskites containing Li⁺ or Na⁺ by using a scanning electron microscope (SEM). From the cross-sectional SEM in Fig. 3(a)-(f), it can be observed that the thickness of the perovskite film basically remains the same. Small particles are deposited vertically and along distinct boundaries of the perovskite containing Li⁺ or Na⁺. Interestingly, in K⁺ doped perovskite, the vertical grain boundary is almost negligible (Fig. 3(d)). Meanwhile, the grain boundary of the perovskite containing Rb⁺ is smaller than that of the perovskite containing double cations and Cs^+ (Fig. 3(f)). Due to the vertical migration of the carrier in the perovskite absorber, a high carrier collection efficiency is expected in the perovskite films with fewer grain boundaries. Liu et al.23 compared the variations in film flatness and grain size of perovskite films doped with alkali metal cations (Na⁺ and K⁺). For a clear comparison, an average grain size of \approx 140 nm was observed in the pristine perovskite film, which has been increased to ≈ 220 and 230 nm for films with Na⁺ and K⁺



Fig. 3 SEM images of the PSCs. (a)–(f) Surface and cross-sectional SEM images of perovskite absorbers with different alkali cations (a) M; (b) Li⁺; (c) Na⁺; (d) K⁺; (e) Rb⁺; and (f) Cs⁺, respectively. Copyright 2018 Elsevier B.V. The atom force topology of perovskite films, (g) without or with (h) Nal and (i) KI doping. Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (j) high-angle annular dark field (HAADF) STEM cross-sectional image of the perovskite thin film passivated with K (x = 0.10) and Non-negative Matrix Factorization (NMF) decomposition of the K-passivated sample showing the KBr phase. (k) HAADF STEM cross-sectional image of the perovskite thin film passivated sample showing the Rb–I–Br phase. Copyright 2018 American Chemical Society.

doping, respectively. Meanwhile, lower surface roughness of perovskite films with alkali metal cations ($R_q = 8.99$ nm (Na⁺ doped) and 7.94 nm (K^+ doped)) was observed compared with the control sample ($R_q = 9.91$ nm) by using an atomic force microscope (AFM) as shown in Fig. 3(g)-(i). Passivation of grain boundary defects is further reported to mitigate the ion migration in perovskite films. Huang et al.52 revealed that sodium ions (Na⁺) diffused from the indium tin oxide (ITO) glass substrate to GBs in the process of film preparation and storage, which was expected to promote the improvement of PCE by passivation. Segawa et al.⁵¹ further found that the grains become compact and the sizes grow larger with the addition of K^{+} , and also the horizontal grain boundary is sensitive to the presence of K⁺ in the perovskite layer. Stranks et al.⁴⁸ demonstrated that by modifying the perovskite film and interface with a passivated potassium halide layer, non-radiation loss and photoinduced ion migration can be significantly reduced. They also used scanning transmission electron microscopy and energy dispersive X-ray spectroscopy (STEM-EDX) measurements to study the morphological composition and the local chemical composition of K⁺ and Rb⁺ passivated perovskite films.⁵⁰ As shown in Fig. 3(j)-(k), it was found that the K-rich phase consists mostly of K and Br and is located at the grain

boundary (GB) and interface of the perovskite film in the Kpassivated perovskite films. However, in the Rb-passivated perovskite film, Rb is contained in large micron-sized crystals. Sun *et al.*⁷⁹ reported that a potassium-rich phase can efficiently passivate the grain boundaries on 3D crystal surface and inhibit trap states, which grows in the 3D perovskite crystal grain boundary through both experiments and theoretical simulations. Therefore, understanding of the incorporation position of alkali metal ions will help the control of the perovskite morphology. In doping engineering, Na⁺, K⁺, and Rb⁺ played key roles in the formation of uniform large-grain perovskite films.

5. Energy level alignments

The barrier at the interface of perovskite/ETL or perovskite/HTL will retard the carrier collection rate, thus resulting in the accumulation of electrons or holes at the interfaces. An attractive property of perovskite absorbers is that they can be easily tailored by changing the elemental composition. Therefore, the addition of alkali metal cations is an interesting way to handle the energy level alignment. An efficient PSC requires a long lifetime of photocarriers¹⁰³ and a low optical bandgap to ensure broad light absorption.^{104–106} In this case, the PCE can be

Review

improved by the standard Shockley–Queisser analysis, including reduction of the optical band gap to 1.3-1.4 eV.¹⁰⁷ Giustino *et al.*⁶⁸ showed that there was a large but slowly varying red shift of 0.8–1.1 eV in the family of PbI₃-based perovskites as a function of apical and equatorial metal–halide–metal bond angles as seen in Fig. 4(a). Meanwhile, by properly selecting cations, the band gap can be fine-tuned almost continuously over a very large photon energy range. For example, the band gap of Cs⁺, Rb⁺, K⁺, Na⁺, and Li⁺-doped perovskites increased in turn as shown in Fig. 4(d).⁶⁸ Segawa *et al.*⁷⁴ calculated that the perovskite band gap containing Li⁺, Na⁺ and K⁺ was 1.613 eV, 1.607 eV and 1.609 eV respectively as shown in Fig. 4(b), However, the Rb⁺ (1.627 eV) and Cs⁺ (1.623 eV) incorporation gave rise to an extension of the band gap. The Li⁺, Na⁺ and K⁺ doping lead to a rise of valence band maximum (VBM) and conduction band minimum (CBM) while the incorporation of Cs^+ caused opposite displacement of VBM and CBM. Ion migration has been reported to enable self-doping of perovskite materials and interfacial ions, effectively establishing a built-in field to promote charge transport.^{108–111} It has also been recognized that the ion accumulation at the interface can adjust the band bending near the interface to form an ohmic contact for charge injection.^{112,113} As shown in Fig. 4(c), positive ions (MA⁺ and Li⁺) accumulated at the perovskite/[6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) interface, while perovskite/NiO_x interfaces aggregated negative ions (I⁻). Therefore, the ion built-in field direction was constructed from n pointing to p. This built-in field facilitates the e⁻/h⁺ separation and delivers them to the n and p sides, respectively.⁹³ The Li⁺/I⁻ induced band bending and n/p doping in MAPbI₃ are expected to



Fig. 4 (a)Two-dimensional map of the DFT band gap of the Platonic model of PbI₃-based perovskites as a function of apical and equatorial metal-halide-metal bond angles. Copyright 2014 Macmillan Publishers. (b) Band alignment at the interface of TiO_2 and perovskite. Copyright 2018 Elsevier B.V. (c) The scheme of the PSC working mechanism with Li⁺ and I⁻ accumulation. Copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (d) Calculated band gaps (in eV) of all the PbI₃-based perovskites. The band gaps were obtained after full structural optimization within scalar relativistic DFT. Copyright 2014 Springer Nature Publishing AG.

improve the charge extraction and reduce the interface energy loss. It is reported that Li⁺ can enter the lattice and also concentrate in the surface region, as an n-type donor to generate free electrons to fill the traps, thereby increasing the surface potential and electron injection driving force.⁹⁵

6. Carrier recombination dynamics

Studies have shown that doping of alkali metal cations in perovskite films significantly increases the grain size and lowers the trap state density, which is essential for efficient carrier transport and collection. Abdi-Jalebi *et al.*⁴⁸ used K^+ doping to suppress the halide migration. It was observed that perovskite films with K^+ had a high and stable photoluminescence

quantum efficiency (PLQE) value under continuous illumination, whereas that of pristine films increased slowly with time due to photoinduced halide migration. The added K^+ is proposed to fix the excess halides by forming compounds at the grain boundaries, while excess iodide originated from the potassium iodide to make up for the vacancies of halide. Therefore, halide migration and light-induced ion segregation were suppressed. Fig. 5(a)–(d) show the confocal photoluminescence intensity maps of perovskite films with various K^+ doping (x = 0–0.4). The absolute emission intensity increased continuously with increasing content of K^+ . Fig. 5(e)–(h) further confirm the red shift of microscale photoluminescence (PL) after addition of potassium, consistent with absorption and electroluminescence data. Fig. 5(i) shows the relevant PL decay



Fig. 5 Confocal photoluminescence maps of passivated $(Cs,FA,MA)Pb(I_{0.85}Br_{0.15})_3$ films. (a)–(d) Confocal photoluminescence intensity maps with 405 nm excitation measured in an ambient atmosphere for $(CsFAMA)Pb(I_{0.85}Br_{0.15})_3$ perovskite thin films with x = 0.0 (a), x = 0.10 (b), x = 0.20 (c) and x = 0.40 (d). Centre-of-mass photoluminescence wavelength of the films with x = 0.0 (e), x = 0.10 (f), x = 0.20 (g) and x = 0.40 (h). (i) PL decay curves of various alkali metal cation doped perovskite films. Copyright 2018 Elsevier B.V. (j) Nyquist plots of perovskite solar cells with and without salt additives under AM1.5G 1 sun illumination with a bias of 0.8 V. Copyright 2016 the Royal Society of Chemistry.

curves reported by Segawa et al.74 The results show that the addition of alkali metal cations increases the carrier lifetime except for lithium ions. Meanwhile, the K⁺-containing perovskite presented the longest carrier lifetime, followed by perovskites containing Rb⁺, Cs⁺ and Na⁺. Electrochemical impedance spectroscopy (EIS) can further demonstrate the transport process of charge carriers in perovskite devices. In Fig. 5(j), the Nyquist plot of the perovskite with and without alkali cation doping under AM1.5G 1 sun illumination and with an applied voltage approaching the device $V_{\rm oc}$ is shown.⁹⁶ Defects in the perovskite film are reduced by the addition of KCl and NaCl, resulting in less recombination and better device performance. It was also indicated that the carrier movement within the perovskite film is smoother in the K⁺ and Na⁺ doped devices, resulting in reduced trap and resistance losses. In contrast, devices with LiCl exhibited severe resistance. Liu et al. further reported that alkali metal cation doping can lengthen the carrier lifetime. The result of steady-state PL and dark J-V curves of the hole-only device indicated that the addition of alkali metal cations reduced the trap states of the perovskite film. The average carrier lifetime of the control sample was found to be 16.58 ns, while the average carrier lifetime of Na⁺ and K⁺ doped perovskite films increased to 259.72 ns and 135.16 ns, respectively. These results showed that the alkaline cations can significantly suppress the internal recombination of the perovskite due to the long carrier lifetime.23

7. Stability

Device performance and long-term stability are two mainstream topics for the current PSC research. Generally, mixed-cation perovskites with small amounts of alkali metal ions show excellent stability. Park et al. first reported a perovskite light absorber with organic-inorganic hybrid cations to enhance the photostability and moisture stability. When Cs⁺ is substituted for 10% $HC(NH_2)_2^+$, the photostability and water stability of the perovskite film are significantly improved.114 With the addition of inorganic Cs⁺, the resulting tri-cationic perovskite composition has higher thermal stability and fewer phase impurities, and is less sensitive to processing conditions.³ As aforementioned, RbPbI₃ is outside the tolerance factor range because its ionic radius is less than that of Cs⁺. Grätze et al. added Rb to (CsFAMA)Pb(I/Br)₃ to achieve a stable efficiency of 21.6% and 95% initial performance was maintained for 500 hours under a nitrogen atmosphere at 85 °C.3 Besides the thermal stress, it has also been demonstrated that the $Rb_{0.05}FA_{0.95}PbI_3$ film exhibits excellent stability under high humidity (85%) conditions, while the complete device exhibits 1000 hours of high performance long-term stability in absence of encapsulation.¹⁰² Ko et al. incorporated Rb⁺ in FAPbI₃ to tune the tolerance factor and promote the phase transition from hexagonal yellow to trigonal black FAPbI₃. Gosh et al. investigated the local structures and dynamics of mixed A-cation compositions. An increase in hydrogen bond strength was observed when smaller Rb⁺ was doped into FAPbI₃. This bonding effect locked the octahedral rotation and hindered the movement or tumbling of organic cations in the cages. The results indicate that the

incorporation of Rb⁺ causes a significant decrease in lattice dynamics, a decrease in electronic disorder and an increase in phase stability.115 Negami et al. concluded that even in the case of PbI2-rich, Rb can inhibit the presence of PbI2, and reducing the proportion of Br in the perovskite absorption layer can prevent unnecessary formation of Rb-Br accumulation.116 At 85 °C/85% RH for a stress test, the PCE of the optimized device was more than 20%, and it maintained 92% of the initial PCE after 1000 hours. The discovery of Rb⁺ prompted us to investigate the impact of K⁺ on PSCs. Specifically, Feng et al. found that the incorporation of Rb⁺ and K⁺ at a certain ratio would make the CsPbI₂Br perovskite quite stable, and the synergy between Rb⁺/ K⁺, I⁻ and Br⁻ played a key role.¹¹⁷ More related fundamental studies in this regard are needed. Park et al. reported a compositional engineering approach for cesium lead halide perovskites with K⁺ doping.⁸⁰ A Cs_{0.925}K_{0.075}PbI₂Br planar PSC achieves a maximum PCE of over 10%, exceeding the reference $CsPbI_2Br$ device with an average PCE of 8.2%. The stability has also been improved compared to the reference CsPbI2Br devices. The incorporation of potassium was proved to be beneficial to the formation and transportation of photoexcited charge carriers. A contraction of the volume of PbX₆ octahedron was observed with K⁺, thus increasing the bond strength and improving the phase stability. The results of energy dispersive spectroscopy (EDS) exhibited a shift of the peak position to higher binding energy in Cs_{0.925}K_{0.075}PbI₂Br for Pb 4f and Br 3d orbitals, which might be due to more positive potassium ions in the perovskite because of the contraction of perovskite cubic volume associated with the difference between the ionic radius of cesium (1.67 Å) and potassium (1.38 Å). Currently, the research on the stability of PSCs with alkali metals is mainly focused on Cs⁺, along with a few studies on Rb⁺ and K⁺, but the in-depth mechanism has not yet been explored. Research in this area is highly urgent. For example, the mechanism of the phase stability with K⁺ incorporation and the interaction of Rb⁺ and K⁺ with halide anions are urgently needed to be discovered.

8. Conclusion and prospects

Tremendous progress has been made over the past few years in metal halide perovskite optoelectronic devices. Interface and defect engineering will be critical to address the current bottleneck and further improve the photovoltaic performance of PSCs. In this review, we summarized important research progress on understanding alkali metal (Li⁺, Na⁺, K⁺ and Rb⁺) incorporation in metal halide perovskite materials from the aspect of electronic properties, film morphology, energy level alignment, and carrier recombination dynamics. Various approaches from theoretical to experimental characterization have identified and quantified the beneficial effect of alkali metal doping in perovskite films. By doping alkali metals into perovskite precursor solution, the electronic properties of the resultant perovskite film can be improved, the energy level can be adjusted, and the defect density can be reduced. Furthermore, doping alkali metals in perovskite films is indeed an effective defect passivation method to improve the carrier mobility and to reduce the ion migration. In terms of stability,

the alkali metal cation Cs^+ with similar radius to $CH_3NH_3^+$ significantly improves the thermal stability, photostability and environmental stability. Moreover, the incorporation of positive potassium ions causes shrinkage of the PbX₆ octahedral volume, thereby improving the phase stability of the perovskite film. In summary, Rb⁺, K⁺, and Na⁺ have been shown to reduce ion migration and accumulation and thus reduce *J*–*V* hysteresis and PL aging effects. Moreover, alkali metal doping has an important influence on the long-term operation of perovskite optoelectronic devices.

The tremendous role of alkali metal doping in perovskite is undeniable. However, an in-depth understanding of the structure and photophysical properties of alkali metal cation-doped perovskites is still lacking in this field. The underlying mechanism of doping of alkali metals to improve the efficiency of PSCs has not been explicitly explained, although improved devices have fewer defects, reduced ion migration, increased carrier lifetime, etc. This is most likely due to the complexity of the alkaline additives, and the limited experimental and characterization techniques. For example, more detailed work about the form of potassium ions in perovskites is still needed. The incorporation of Li^+ (0.076 nm), Na^+ (0.102 nm), and K^+ (0.138 nm) resulted in an increase in the lattice constant; however, the locations of these small cations remained unclear. Also, the indepth mechanism of the phase stability with K⁺ incorporation and interactions of Rb⁺ and K⁺ with halide anions are urgently needed to be explored.

Looking forward, alkali metal doping in perovskite has great development space in the related optoelectronic device. Simple and inexpensive inorganic alkali metal ions provide a facile platform to improve the stability of perovskite-based materials and the performance of the corresponding photovoltaic devices. We expected that this strategy can be implemented in other deposition technologies based on high-flux solution techniques like inkjet-printing, slot-die coating, or aerosol-jet printing. In addition, it is expected that alkali metal doping can be extended from single elements to multiple elements. It is believed that perovskite layers doped with alkali metal ions can be widely used in the fabrication of perovskite-based optoelectronic devices, such as field-effect transistors, photodetectors, and light-emitting diodes on flexible polymer substrates. Existing optoelectronic devices can be improved to further reduce performance loss and instability issues, realizing the true industrial application potential of metal halide perovskite optoelectronic devices.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China NSFC (51702038) and the Recruitment Program for Young Professionals.

Note and references

- 1 M. Long, T. Zhang, Y. Chai, C.-F. Ng, T. C. Mak, J. Xu and K. Yan, *Nat. Commun.*, 2016, 7, 13503–13514.
- 2 A. Kojima, K. Teshima, Y. Shirai and T. Miyasaka, J. Am. Chem. Soc., 2009, 131, 6050–6051.
- 3 M. Saliba, T. Matsui, J.-Y. Seo, K. Domanski, J.-P. Correa-Baena, M. K. Nazeeruddin, S. M. Zakeeruddin, W. Tress, A. Abate and A. Hagfeldt, *Energy Environ. Sci.*, 2016, 9, 1989–1997.
- 4 H. S. Kim, S. H. Im and N. G. Park, *J. Phys. Chem. C*, 2014, **118**, 5615–5625.
- 5 M. Ye, X. Wen, M. Wang, J. Iocozzia, N. Zhang, C. Lin and Z. Lin, *Mater. Today*, 2015, **18**, 155–162.
- 6 Q. Zhang, F. Hao, J. Li, Y. Zhou, Y. Wei and H. Lin, *Sci. Technol. Adv. Mater.*, 2018, **19**, 425-442.
- 7 L. Xie, J. Wang, K. Liao, J.-a. Yang, A. Wang, X. Deng, C. Li, T. Li, X. Niu and F. Hao, *J. Mater. Chem. A*, 2019, 7, 18626– 18633.
- 8 P. Schulz, ACS Energy Lett., 2018, 3, 1287-1293.
- 9 A. Rajagopal, K. Yao and A. K. Y. Jen, *Adv. Mater.*, 2018, **30**, 1800455–1800489.
- 10 X. Dai, Z. Zhang, Y. Jin, Y. Niu, H. Cao, X. Liang, L. Chen, J. Wang and X. Peng, *Nature*, 2014, **515**, 96–99.
- 11 L. Dou, Y. M. Yang, J. You, Z. Hong, W. H. Chang, G. Li and Y. Yang, *Nat. Commun.*, 2014, 5, 5404–5409.
- 12 L. Meng, E. P. Yao, Z. Hong, H. Chen, P. Sun, Z. Yang, G. Li and Y. Yang, *Adv. Mater.*, 2017, **29**, 1603826–1603832.
- 13 C. V. V. M. Gopi, M. Venkata-Haritha, Y. S. Lee and H. J. Kim, *J. Mater. Chem. A*, 2016, 4, 8161–8171.
- 14 S. P. Senanayak, B. Yang, T. H. Thomas, N. Giesbrecht, W. Huang, E. Gann, B. Nair, K. Goedel, S. Guha, X. Moya, C. R. McNeill, P. Docampo, A. Sadhanala, R. H. Friend and H. Sirringhaus, *Sci. Adv.*, 2017, 3, 1601935–1601944.
- 15 M. A. Green, A. Ho-Baillie and H. J. Snaith, *Nat. Photonics*, 2014, **8**, 506–514.
- 16 S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza and H. J. Snaith, *Science*, 2013, 342, 341–344.
- 17 M. He, D. Zheng, M. Wang, C. Lin and Z. Lin, J. Mater. Chem. A, 2014, 2, 5994–6003.
- 18 M. He, X. Pang, X. Liu, B. Jiang, Y. He, H. Snaith and Z. Lin, Angew. Chem., Int. Ed., 2016, 55, 4280–4284.
- 19 NREL Chart, https://www.nrel.gov/pv/cell-efficiency.html, 2019.
- 20 X. Zheng, C. Wu, S. K. Jha, Z. Li, K. Zhu and S. Priya, *ACS Energy Lett.*, 2016, **1**, 1014–1020.
- 21 Q. Wang, M. Lyu, M. Zhang, J. H. Yun, H. Chen and L. Wang, J. Phys. Chem. Lett., 2015, 6, 4379-4384.
- 22 T.-B. Song, Q. Chen, H. Zhou, C. Jiang, H.-H. Wang, Y. M. Yang, Y. Liu, J. You and Y. Yang, *J. Mater. Chem. A*, 2015, **3**, 9032–9050.
- 23 W. Zhao, Z. Yao, F. Yu, D. Yang and S. F. Liu, *Adv. Sci.*, 2018, 5, 1700131–1700137.
- 24 M. Ye, C. He, J. Iocozzia, X. Liu, X. Cui, X. Meng, M. Rager, X. Hong, X. Liu and Z. Lin, *J. Phys. D: Appl. Phys.*, 2017, 50, 373002–373016.

- 25 H.-S. Duan, H. Zhou, Q. Chen, P. Sun, S. Luo, T.-B. Song,
 B. Bob and Y. Yang, *Phys. Chem. Chem. Phys.*, 2015, 17, 112–116.
- 26 Q. Jiang, D. Rebollar, J. Gong, E. L. Piacentino, C. Zheng and T. Xu, *Angew. Chem., Int. Ed.*, 2015, 54, 7617–7620.
- 27 Y. Y. Dang, Y. Liu, Y. X. Sun, D. S. Yuan, X. L. Liu, W. Q. Lu, G. F. Liu, H. B. Xia and X. T. Tao, *CrystEngComm*, 2015, 17, 665–670.
- 28 L. Li, Y. Chen, Z. Liu, Q. Chen, X. Wang and H. Zhou, *Adv. Mater.*, 2016, 28, 9862–9868.
- 29 H. Zhou, Q. Chen, G. Li, S. Luo, T.-b. Song, H.-S. Duan, Z. Hong, J. You, Y. Liu and Y. Yang, *Science*, 2014, 345, 542–546.
- 30 H. Zhang, H. Chen, C. C. Stoumpos, J. Ren, Q. Hou, X. Li, J. Li, H. He, H. Lin, J. Wang, F. Hao and M. G. Kanatzidis, ACS Appl. Mater. Interfaces, 2018, 10, 42436–42443.
- 31 L. Mao, H. Tsai, W. Nie, L. Ma, J. Im, C. C. Stoumpos,
 C. D. Malliakas, F. Hao, M. R. Wasielewski and
 A. D. Mohite, *Chem. Mater.*, 2016, 28, 7781–7792.
- 32 L. Wang, H. Zhou, J. Hu, B. Huang, M. Sun, B. Dong, G. Zheng, Y. Huang, Y. Chen and L. Li, *Science*, 2019, 363, 265–270.
- 33 J.-A. Yang, T. Qin, L. Xie, K. Liao, T. S. Li and F. Hao, J. Mater. Chem. C, 2019, 7, 10724–10742.
- 34 C. B. Fei, L. X. Guo, B. Li, R. Zhang, H. Y. Fu, J. J. Tian and G. Z. Cao, *Nano Energy*, 2016, 27, 17–26.
- 35 B. B. Wang, Z. G. Zhang, S. Y. Ye, H. X. Rao, Z. Q. Bian, C. H. Huang and Y. F. Li, *J. Mater. Chem. A*, 2016, 4, 17267–17273.
- 36 N. De Marco, H. Zhou, Q. Chen, P. Sun, Z. Liu, L. Meng, E.-P. Yao, Y. Liu, A. Schiffer and Y. Yang, *Nano Lett.*, 2016, 16, 1009–1016.
- 37 J.-W. Lee, H.-S. Kim and N.-G. Park, Acc. Chem. Res., 2016, 49, 311–319.
- 38 Y. Zhang, P. Gao, E. Oveisi, Y. Lee, Q. Jeangros, G. Grancini, S. Paek, Y. Feng and M. K. Nazeeruddin, *J. Am. Chem. Soc.*, 2016, **138**, 14380–14387.
- 39 Y. Guo, W. Sato, K. Shoyama and E. Nakamura, J. Am. Chem. Soc., 2016, 138, 5410–5416.
- 40 Q.-Q. Ge, J. Ding, J. Liu, J.-Y. Ma, Y.-X. Chen, X.-X. Gao, L.-J. Wan and J.-S. Hu, *J. Mater. Chem. A*, 2016, 4, 13458– 13467.
- 41 W. Zhu, T. Yu, F. Li, C. Bao, H. Gao, Y. Yi, J. Yang, G. Fu, X. Zhou and Z. Zou, *Nanoscale*, 2015, 7, 5427–5434.
- 42 Z. Xiao, Q. Dong, C. Bi, Y. Shao, Y. Yuan and J. Huang, *Adv. Mater.*, 2014, **26**, 6503–6509.
- 43 F. Hao, C. C. Stoumpos, P. Guo, N. Zhou, T. J. Marks, R. P. Chang and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2015, 137, 11445–11452.
- 44 Z. Li, M. Yang, J.-S. Park, S.-H. Wei, J. J. Berry and K. Zhu, *Chem. Mater.*, 2015, **28**, 284–292.
- 45 Y. Hu, E. M. Hutter, P. Rieder, I. Grill, J. Hanisch, M. F. Aygüler, A. G. Hufnagel, M. Handloser, T. Bein, A. Hartschuh, K. Tvingstedt, V. Dyakonov, A. Baumann, T. J. Savenije, M. L. Petrus and P. Docampo, *Adv. Energy Mater.*, 2018, 8, 1703057–1703067.

- 46 Y. Hu, M. F. Aygüler, M. L. Petrus, T. Bein and P. Docampo, ACS Energy Lett., 2017, 2, 2212–2218.
- 47 S.-H. Turren-Cruz, M. Saliba, M. T. Mayer, H. Juárez-Santiesteban, X. Mathew, L. Nienhaus, W. Tress, M. P. Erodici, M.-J. Sher, M. G. Bawendi, M. Grätzel, A. Abate, A. Hagfeldt and J.-P. Correa-Baena, *Energy Environ. Sci.*, 2018, 11, 78–86.
- 48 M. Abdi-Jalebi, Z. Andaji-Garmaroudi, S. Cacovich, C. Stavrakas, B. Philippe, J. M. Richter, M. Alsari, E. P. Booker, E. M. Hutter, A. J. Pearson, S. Lilliu, T. J. Savenije, H. Rensmo, G. Divitini, C. Ducati, R. H. Friend and S. D. Stranks, *Nature*, 2018, 555, 497–501.
- 49 S. Bag and M. F. Durstock, *ACS Appl. Mater. Interfaces*, 2016, 8, 5053–5061.
- 50 M. Abdi-Jalebi, Z. Andaji-Garmaroudi, A. J. Pearson,
 G. Divitini, S. Cacovich, B. Philippe, H. Rensmo,
 C. Ducati, R. H. Friend and S. D. Stranks, ACS Energy Lett., 2018, 3, 2671–2678.
- 51 Z. Tang, T. Bessho, F. Awai, T. Kinoshita, M. M. Maitani, R. Jono, T. N. Murakami, H. Wang, T. Kubo and S. Uchida, *Sci. Rep.*, 2017, 7, 12183–12189.
- 52 C. Bi, X. Zheng, B. Chen, H. Wei and J. Huang, *ACS Energy Lett.*, 2017, **2**, 1400–1406.
- 53 S. Dastidar, C. J. Hawley, A. D. Dillon, A. D. Gutierrez-Perez, J. E. Spanier and A. T. Fafarman, *J. Phys. Chem. Lett.*, 2017, 8, 1278–1282.
- 54 R. E. Beal, D. J. Slotcavage, T. Leijtens, A. R. Bowring, R. A. Belisle, W. H. Nguyen, G. F. Burkhard, E. T. Hoke and M. D. McGehee, *J. Phys. Chem. Lett.*, 2016, 7, 746–751.
- 55 A. Swarnkar, A. R. Marshall, E. M. Sanehira,
 B. D. Chernomordik, D. T. Moore, J. A. Christians,
 T. Chakrabarti and J. M. Luther, *Science*, 2016, 354, 92–95.
- 56 M. Luan, J. Song, X. Wei, F. Chen and J. Liu, *CrystEngComm*, 2016, 18, 5257–5261.
- 57 N. Onoda-Yamamuro, T. Matsuo and H. Suga, J. Phys. Chem. Solids, 1990, 51, 1383–1395.
- 58 W.-J. Yin, T. Shi and Y. Yan, *Appl. Phys. Lett.*, 2014, **104**, 063903–063906.
- 59 Z. Cheng and J. Lin, CrystEngComm, 2010, 12, 2646-2662.
- 60 F. Hao, C. C. Stoumpos, D. H. Cao, R. P. Chang and M. G. Kanatzidis, *Nat. Photonics*, 2014, 8, 489–494.
- 61 F. Hao, C. C. Stoumpos, R. P. Chang and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2014, **136**, 8094–8099.
- 62 L. Ma, F. Hao, C. C. Stoumpos, B. T. Phelan, M. R. Wasielewski and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2016, **138**, 14750–14755.
- 63 C. C. Stoumpos, L. Frazer, D. J. Clark, Y. S. Kim, S. H. Rhim,
 A. J. Freeman, J. B. Ketterson, J. I. Jang and
 M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2015, 137, 6804–6819.
- 64 P.-P. Sun, Q.-S. Li, S. Feng and Z.-S. Li, *Phys. Chem. Chem. Phys.*, 2016, **18**, 14408–14418.
- 65 G. Giorgi and K. Yamashita, Chem. Lett., 2015, 44, 826-828.
- 66 X.-G. Zhao, J.-H. Yang, Y. Fu, D. Yang, Q. Xu, L. Yu, S.-H. Wei and L. Zhang, *J. Am. Chem. Soc.*, 2017, **139**, 2630–2638.
- 67 T. Shi, W.-J. Yin and Y. Yan, J. Phys. Chem. C, 2014, 118, 25350–25354.

- 68 M. R. Filip, G. E. Eperon, H. J. Snaith and F. Giustino, *Nat. Commun.*, 2014, 5, 5757–5765.
- 69 P. Zhao, W. Yin, M. Kim, M. Han, Y. J. Song, T. K. Ahn and H. S. Jung, *J. Mater. Chem. A*, 2017, 5, 7905–7911.
- 70 J. Cao, S. X. Tao, P. A. Bobbert, C. P. Wong and N. Zhao, *Adv. Mater.*, 2018, **30**, 1707350–1707358.
- 71 H. J. Snaith, A. Abate, J. M. Ball, G. E. Eperon, T. Leijtens, N. K. Noel, S. D. Stranks, J. T.-W. Wang, K. Wojciechowski and W. Zhang, *J. Phys. Chem. Lett.*, 2014, 5, 1511–1515.
- 72 B. Chen, M. Yang, S. Priya and K. Zhu, J. Phys. Chem. Lett., 2016, 7, 905–917.
- 73 N. J. Jeon, J. H. Noh, W. S. Yang, Y. C. Kim, S. Ryu, J. Seo and S. I. Seok, *Nature*, 2015, **517**, 476–480.
- 74 Z. Tang, S. Uchida, T. Bessho, T. Kinoshita, H. Wang,
 F. Awai, R. Jono, M. M. Maitani, J. Nakazaki, T. Kubo and
 H. Segawa, *Nano Energy*, 2018, 45, 184–192.
- 75 D. Y. Son, S. G. Kim, J. Y. Seo, S. H. Lee, H. Shin, D. Lee and N. G. Park, *J. Am. Chem. Soc.*, 2018, **140**, 1358–1364.
- 76 Y. Hu, M. F. Aygüler, M. L. Petrus, T. Bein and P. Docampo, *ACS Energy Lett.*, 2017, **2**, 2212–2218.
- 77 D. J. Kubicki, D. Prochowicz, A. Hofstetter,
 S. M. Zakeeruddin, M. Grätzel and L. Emsley, *J. Am. Chem. Soc.*, 2017, 139, 14173–14180.
- 78 D. J. Kubicki, D. Prochowicz, A. Hofstetter, S. M. Zakeeruddin, M. Grätzel and L. Emsley, J. Am. Chem. Soc., 2018, 140, 7232–7238.
- 79 L. Kuai, Y. Wang, Z. Zhang, Y. Yang, Y. Qin, T. Wu, Y. Li, Y. Li, T. Song, X. Gao, L. Wang and B. Sun, *Sol. RRL*, 2019, 3, 1900053–1900061.
- 80 J. K. Nam, S. U. Chai, W. Cha, Y. J. Choi, W. Kim, M. S. Jung, J. Kwon, D. Kim and J. H. Park, *Nano Lett.*, 2017, **17**, 2028– 2033.
- 81 T. Bu, X. Liu, Y. Zhou, J. Yi, X. Huang, L. Luo, J. Xiao, Z. Ku, Y. Peng and F. Huang, *Energy Environ. Sci.*, 2017, **10**, 2509– 2515.
- 82 C. Li, A. Guerrero, Y. Zhong and S. Huettner, *J. Phys.:* Condens. Matter, 2017, 29, 193001–193020.
- 83 X. Liu, Y. Zhang, L. Shi, Z. Liu, J. Huang, J. S. Yun, Y. Zeng, A. Pu, K. Sun, Z. Hameiri, J. A. Stride, J. Seidel, M. A. Green and X. Hao, *Adv. Energy Mater.*, 2018, **8**, 1800138–1800149.
- 84 T. Bu, X. Liu, Y. Zhou, J. Yi, X. Huang, L. Luo, J. Xiao, Z. Ku, Y. Peng, F. Huang, Y.-B. Cheng and J. Zhong, *Energy Environ. Sci.*, 2017, **10**, 2509–2515.
- 85 T. J. Jacobsson, J.-P. Correa-Baena, E. Halvani Anaraki,
 B. Philippe, S. D. Stranks, M. E. Bouduban, W. Tress,
 K. Schenk, J. l. Teuscher and J.-E. Moser, *J. Am. Chem. Soc.*, 2016, 138, 10331–10343.
- 86 W. Tress, N. Marinova, T. Moehl, S. M. Zakeeruddin, M. K. Nazeeruddin and M. Grätzel, *Energy Environ. Sci.*, 2015, 8, 995–1004.
- 87 E. L. Unger, E. T. Hoke, C. D. Bailie, W. H. Nguyen,
 A. R. Bowring, T. Heumüller, M. G. Christoforo and
 M. D. McGehee, *Energy Environ. Sci.*, 2014, 7, 3690–3698.
- 88 Y. Zhang, M. Liu, G. E. Eperon, T. C. Leijtens, D. McMeekin, M. Saliba, W. Zhang, M. de Bastiani, A. Petrozza and L. M. Herz, *Mater. Horiz.*, 2015, 2, 315–322.

- 89 Y. Zhou, X. Yin, Q. Luo, X. Zhao, D. Zhou, J. Han, F. Hao, M. Tai, J. Li and P. Liu, *ACS Appl. Mater. Interfaces*, 2018, 10, 31384–31393.
- 90 T. J. Jacobsson, S. Svanström, V. Andrei, J. P. H. Rivett, N. Kornienko, B. Philippe, U. B. Cappel, H. Rensmo, F. Deschler and G. Boschloo, *J. Phys. Chem. C*, 2018, 122, 13548–13557.
- 91 G. Sabouret, F. Bradbury, S. Shankar, J. Bert and S. A. Lyon, *Appl. Phys. Lett.*, 2008, **92**, 082104–082106.
- 92 Y. Yang, X. Zou, Y. Pei, X. Bai, W. Jin and D. Chen, J. Mater. Sci.: Mater. Electron., 2017, 29, 205–210.
- 93 J. Zhang, R. Chen, Y. Wu, M. Shang, Z. Zeng, Y. Zhang,
 Y. Zhu and L. Han, *Adv. Energy Mater.*, 2018, 8, 1701981– 1701988.
- 94 W. Zhao, D. Yang and S. F. Liu, *Small*, 2017, **13**, 1604153–1604161.
- 95 S. Mabrouk, B. Bahrami, A. Gurung, K. M. Reza, N. Adhikari, A. Dubey, R. Pathak, S. Yang and Q. Qiao, *Sustainable Energy Fuels*, 2017, 1, 2162–2171.
- 96 K. M. Boopathi, R. Mohan, T.-Y. Huang, W. Budiawan, M.-Y. Lin, C.-H. Lee, K.-C. Ho and C.-W. Chu, *J. Mater. Chem. A*, 2016, 4, 1591–1597.
- 97 J. Chang, Z. Lin, H. Zhu, F. H. Isikgor, Q.-H. Xu, C. Zhang, Y. Hao and J. Ouyang, *J. Mater. Chem. A*, 2016, 4, 16546– 16552.
- 98 Z. Zhang, Y. Zhou, Y. Cai, H. Liu, Q. Qin, X. Lu, X. Gao, L. Shui, S. Wu and J.-M. Liu, *J. Power Sources*, 2018, 377, 52–58.
- 99 P. Wang, J. Wang, X. Zhang, H. Wang, X. Cui, S. Yuan, H. Lu, L. Tu, Y. Zhan and L. Zheng, *J. Mater. Chem. A*, 2018, 6, 15853–15858.
- 100 M. Saliba, T. Matsui, K. Domanski, J.-Y. Seo, A. Ummadisingu, S. M. Zakeeruddin, J.-P. Correa-Baena, W. R. Tress, A. Abate and A. Hagfeldt, *Science*, 2016, 354, 206–209.
- 101 P. Yadav, M. I. Dar, N. Arora, E. A. Alharbi, F. Giordano, S. M. Zakeeruddin and M. Grätzel, *Adv. Mater.*, 2017, 29, 1701077–1701083.
- 102 Y. H. Park, I. Jeong, S. Bae, H. J. Son, P. Lee, J. Lee, C. H. Lee and M. J. Ko, *Adv. Funct. Mater.*, 2017, 27, 1605988– 1605996.
- 103 C. Wehrenfennig, G. E. Eperon, M. B. Johnston, H. J. Snaith and L. M. Herz, *Adv. Mater.*, 2014, **26**, 1584–1589.
- 104 C. C. Stoumpos, C. D. Malliakas and M. G. Kanatzidis, *Inorg. Chem.*, 2013, 52, 9019–9038.
- 105 J. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal and S. I. Seok, *Nano Lett.*, 2013, **13**, 1764–1769.
- 106 G. Xing, N. Mathews, S. Sun, S. S. Lim, Y. M. Lam, M. Grätzel, S. Mhaisalkar and T. C. Sum, *Science*, 2013, 342, 344–347.
- 107 S. De Wolf, J. Holovsky, S.-J. Moon, P. Löper, B. Niesen, M. Ledinsky, F.-J. Haug, J.-H. Yum and C. Ballif, *J. Phys. Chem. Lett.*, 2014, 5, 1035–1039.
- 108 T. Leijtens, G. E. Eperon, N. K. Noel, S. N. Habisreutinger,
 A. Petrozza and H. J. Snaith, *Adv. Energy Mater.*, 2015, 5, 1500963–1500985.

- 109 Y. Deng, Z. Xiao and J. Huang, *Adv. Energy Mater.*, 2015, 5, 1500721–1500726.
- 110 C. Li, S. Tscheuschner, F. Paulus, P. E. Hopkinson, J. Kiessling, A. Kohler, Y. Vaynzof and S. Huettner, Adv. Mater., 2016, 28, 2446–2454.
- 111 Y. Yuan and J. Huang, Acc. Chem. Res., 2016, 49, 286-293.
- Y. Zhao, C. Liang, H. Zhang, D. Li, D. Tian, G. Li, X. Jing, W. Zhang, W. Xiao, Q. Liu, F. Zhang and Z. He, *Energy Environ. Sci.*, 2015, 8, 1256–1260.
- 113 T. Y. Yang, G. Gregori, N. Pellet, M. Gratzel and J. Maier, Angew. Chem., Int. Ed., 2015, 54, 7905–7910.

- 114 J. W. Lee, D. H. Kim, H. S. Kim, S. W. Seo, S. M. Cho and N. G. Park, *APL Mater.*, 2015, 5, 1501310–1501318.
- 115 D. Ghosh, P. Walsh Atkins, M. S. Islam, A. B. Walker and C. Eames, *ACS Energy Lett.*, 2017, 2, 2424–2429.
- 116 T. Matsui, T. Yamamoto, T. Nishihara, R. Morisawa, T. Yokoyama, T. Sekiguchi and T. Negami, *Adv. Mater.*, 2019, **31**, 1806823.
- 117 S.-Q. Wang, S. Shen, X.-X. Xue, Y. He, Z.-W. Xu, K. Chen and Y. Feng, *Appl. Phys. Express*, 2019, **12**, 051017.