A review on advances in doping with alkali metals in halide perovskite materials

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Abstract

Recent progress in doping of halide perovskite materials (HPM) by using targeted elements has provided a dimension beyond structural and compositional modification, for achieving desired properties and resulting device performance. Herein doping of alkali metal ions (Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+) in three-dimensional HPM is reviewed to lay a particular focus on advances in synthesis, doping-induced changes in optical and electrical properties, and their optoelectronic applications. The introduction of alkali metals in HPM shows an effective route for improved morphology, suppressed ion migration, reduction in non-radiative recombination, passivation of bulk and interface defects, and increased thermal stability. In the end, we provide our perspective that the effect of alkali metal incorporation on the efficiency and stability of HPM should be further investigated via in-situ characterization methods and doped HPM should be considered for more functional applications.

Graphical abstract

Keywords Halide perovskites · Doping · Alkali metals · Morphology · Defects · Stability

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1 Introduction

Halide perovskite materials (HPM) have emerged as a class of excellent semiconductors in high-performance optoelectronic applications. In 1839, the term “perovskite” was first coined by Gustav Rose for the CaTiO_3 mineral, who named it after nobleman Count Lev Alekseyevich von Perovski. These materials demonstrate unique optical and electrical properties such as tunable bandgap, high photoluminescence quantum yields (PLQYs), high light absorption coefficient, and efficient charge carrier mobility, hence could exhibit a promising future for next-generation electronic devices [1, 2]. The potential to combine all the listed properties in one material with low-cost solution processability has emerged HPM as a focus of current research. In recent years, perovskite materials have been used as a functional layer in light-emitting diodes (LEDs) with external quantum efficiency (EQE) up to 28.2% [3], highly sensitive photodetectors with low noise in photon detections, lasers with an ultralow lasing threshold of 220 nJ/cm^2 , and perovskite solar cells (PSCs) achieving certified power conversion efficiency (PCE) of 25.5% [4–6]. Such remarkable performance of perovskite materials has been made possible by the general perovskite structure ABX_3 , where A is monovalent cation (that can be either organic (e.g., CH_3NH_3^+ (methylammonium/ MA^+), $\text{CH}(\text{NH}_2)_2^+$ (formamidinium/ FA^+)) or inorganic e.g., Cs^+ (cesium)), B is a divalent cation mostly Pb^{2+} (lead), Sn^{2+} (tin) and Bi^{3+} (bismuth) or their co-alloying with Ge^{2+} (germanium) and Mn^{2+} (manganese), and X is a halide anion (Cl^- , Br^- , I^- or their mixtures) [7–9]. The crystal structure of ABX_3 type perovskite consists of a network of corner-shared lead halide octahedra $[\text{BX}_6]^{-4}$ with a 12-fold coordinated large size A-site cation fulfilling the voids to balance the charge. These materials can form multiple structural polymorphs from cubic to hexagonal complex phase depending on the connectivity to the $[\text{BX}_6]^{-4}$ octahedra [10–12]. HPM with such unique structures possess excellent photoelectric properties, low exciton binding energy, and solar light absorbance [13].

Doping engineering, a method to introduce impurity atoms into the target crystal lattice can optimize the perovskite materials performance without affecting their structure and inherent properties [14, 15]. Taking into account the inherent HPM related issues such as their long-term stability, defect states, and performance has attracted the doping strategy [16–18]. To fill these gaps, researchers [19–22] have been working on the incorporation of various ions into the HPM to study their effects. Only a small amount of dopants can modify the required characteristics of halide perovskites to the

required level without introducing deep energy levels. In addition, doping elements usually do not give rise to the quenched emission due to the surface defect states as reported in conventional II–VI, III–V, and IV–VI inorganic semiconductors [23, 24]. Therefore, the strategy to dope heteroatoms into the perovskite structure increases the ability to optimize the structural parameters and efficiency. Such as doping of A-site cation has been mostly reported to tune the bandgap, and ability to make the host perovskite more stable [25]. Moreover, B-site doping is used to reduce the toxicity of lead ions and extend the charge carrier lifetime of solar power conversion and light absorption process [26, 27]. Furthermore, mixing of X-site halide anions not only serve the purpose of desired shift in absorption band but also optimizes the electro luminescence (EL) spectrum of perovskites [28]. Hence, compared with pristine halide perovskites, doped HPM can improve the performances of solar cells, lasers, LEDs, photodetectors, and field-effect transistors [29].

For a stable doped perovskite structure, the ionic radii of all constituent elements should match well [30]. Notably, to predict the structural stability and lattice distortion of ABX_3 type perovskite materials, the Goldschmidt tolerance factor (T) has been widely used in applied studies. The T is determined by the ratios of effective ionic radii of the cation A (R_A), the cation B (R_B), and the X (R_X) anion using the following expression:

$$T = R_A + R_X / \sqrt{2} (R_B + R_X)$$

The perfect symmetry of perovskite compounds adopts a cubic close-packed crystal structure with $T = 1$. When the value of constituent ionic radii deviates from the ideal case ($T \neq 1$), the crystal distortion and structural strain occur. As this deviation arises, the crystal adopts a lower symmetry structure than the cubic one [31, 32]. To further describe the threshold of perovskite compounds stability, an additional octahedral factor (μ) which is the ratio of R_B to R_X is needed to show the structural map capable to display the formability of perovskites [33–35].

Recent research on doping halide perovskites with alkali metal ions such as Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+ has been acknowledged for polycrystalline and nanocrystalline thin films to maximize structural and optoelectronic properties i.e. to maximize luminance, facilitates charge injection, enhanced moisture resistance, and energy band alignment [36–38].

In this comprehensive review, we discussed advances in the doping of alkali metals for 3D ABX_3 type HPM, which are divided into two sections based on their polycrystalline and nanocrystalline nature. In detail, this review summarizes the impact of alkali metal ions on charge carrier dynamics, crystallinity, bulk and interface defects, and

their ability to influence optoelectronic device properties of HPM. Furthermore, a brief outlook about unresolved issues is also reviewed.

2 Influence of cesium ions doping in HPM

To date, cesium (Cs) is the only alkali metal that can substitute A-site cation in ABX_3 type perovskites due to its large ionic radii (1.67 Å) [39, 40]. Mixing of Cs ions with other A-site cations (MA^+ , FA^+) is considered as a milestone to address the problem of structural instability, thermal and moisture sensitivity of halide perovskite devices [41–43]. Among all HPM light harvesters, methylammonium lead triiodide ($MAPbI_3$) and formamidinium lead triiodide ($FAPbI_3$) have been considered as champion compounds in recent years due to their exceptional absorption coefficient, low exciton binding energy, and excellent photovoltaic properties. However, $MAPbI_3$ shows disturbing phase transition (tetragonal-cubic) at about 56 °C, while the operating temperature of solar cells is approximately 85 °C. Also, the bandgap of $MAPbI_3$ is 1.57 eV, which hinders the absorption of solar light above 800 nm and ultimately reduces the efficiency of PSCs. Although thermally stable $FAPbI_3$ with an appropriate bandgap of 1.48 eV shows potential in the presence of sunlight, however, its photoactive α -phase (black phase) transformation into undesired nonphotoactive δ -phase (yellow phase) at room temperature is a big issue [40, 44, 45]. Therefore, optimization of a photovoltaic device efficiency is challenging while using a single cation and it has been suggested to modify the perovskites by mixing of Cs-MA, Cs-FA or Cs-FA-MA cations [46, 47].

The incorporation of Cs ions into the $FAPbI_3$ perovskite system improves the phase stability, particularly its transformation from black to yellow phase [48, 49]. A report was published for stabilization of α phase of $FAPbI_3$, where a computational study was performed to check the influence of FA^+ cation substitution with monovalent cation MA^+ , Cs^+ , and Rb^+ . A series of simulation were performed for relative stabilization of α with respect to δ phase as a function of chemical nature of the dopant, doping amount, and temperature. It was suggested that α perovskite phase of $FAPbI_3$ can be best stabilized at ambient temperature by 42–50% of mixed Cs/Rb doping and MA^+ can be avoided as it is directed to make the α phase less stable. Furthermore, the substitution of these alkali ions into the target system blue shift the onset of optical spectra by 0.1–0.2 eV with respect to pristine $FAPbI_3$. This study paves the way towards the replacement of organic cation with Cs and Rb ions which are efficient in stabilizing its photoactive phase [38]. In a recent study, two-step spin coating for sequential doping of Cs and GA (guanidinium) cations was adopted

to demonstrate the control on crystallization kinetics of $FAPbI_3$ perovskite thin film with an average grain size of ≈ 300 nm for solar cell application. The addition of Cs cations in the first step induces the formation of δ - $CsPbI_3$ which provides an alternative phase transition pathway for perovskite α -phase. However, slightly larger crystalline grains of about 600 nm with several pinholes are formed due to nonuniform nucleation by sparse δ - $CsPbI_3$ crystals. This problem is solved in the second step where doping of GA cations eliminates the pinholes and further enhanced grain boundaries of ≈ 1 μm , hence solar cell device efficiencies above 23% were recorded [50]. Another study was reported about the addition of cesium chloride ($CsCl$) in mixed cation formulation of $FA_{0.80}Cs_{0.20}PbI_3$ results in high-quality photoactive layer, large grain size (≈ 1 μm), longer carrier lifetime (108.4 ns), with perovskite solar cell devices showed PCE of 19.85% [51].

It is now well established from a variety of studies [52–56] that the doping of Cs ions into $MAPbX_3$ perovskites optimizes the optical and electrical parameters of the materials while retaining their fundamental properties. Guangcheng and Rui claimed that doping of Cs into the $MAPbI_{3-x}Cl_x$ perovskite films enhances the grain morphology, lifts the valence and conduction band edges, passivate the trap states, and hence promote the flow of charge carriers [57].

Most importantly, the HPM among which the mixed cation (FAMA) perovskites showed many outstanding properties such as improved carrier diffusion length, broad absorption spectrum give rise the solar power conversion efficiency over 22% [58, 59]. According to recent studies, partial replacement of FA with smaller size cations (MA^+ , Cs^+ , and Rb^+) can be the most suitable strategy to work with photoelectric characteristics of FAMA mixed cation perovskites. Shihao et al. treated mixed cation $FA_{0.85}MA_{0.15}PbI_3$ with cesium acetate ($CsAc$) and doped perovskite films exhibited a large grain size of about 1.39 μm (Fig. 1a), longer carrier lifetime of 61.5 ns is benefited from the reduction in trap assisted recombination (Fig. 1b). The maximum PCE of 21.95% and 97% retention in initial PCE values after aging for 55 days was recorded after alloying with Cs^+ and Ac^- (Fig. 1c, Table 1) [60]. After that, Bowen claimed highest reported PCE (22.81%) of PSCs based on four components $Rb_xCs_{1-x}MA_{(1-2x)/2}FA_{(1-2x)/2}PbI_3$. The reason behind enhanced efficiency is controlled doping of Rb^+ and Cs^+ into the precursor solution which facilitates the transformation of δ phase into α phase, improve the photovoltaic performance (Fig. 1e, Table 1), and reduced PL lifetimes from 115 ns to 90 and 30 ns for 10 and 20% doping concentration (Fig. 1d) [61]. The most recent research studies available on alkali doped HPM for photovoltaic applications are summarized in Table 1.

Fig. 1 **a** SEM images of perovskite films deposited on FTO substrates with 0, 0.4, 0.8, 1.2, and 1.6 mol% CsAc alloying (left–right). **b** Time-resolved PL of perovskite films wo/w CsAc alloying. **c** Stable output curves of current densities and efficiencies of the best-performing PSCs wo/w CsAc alloying. Adapted with permission from

ref. [60], copyright 2019, WILEY-VCH. **d** Time-resolved PL **e** and photovoltaic performance of perovskite thin films doped with different proportion of Rb+ and Cs+ ions. Adapted with permission from ref. [61], copyright 2020, Elsevier

Nanocrystalline HPM can be characterized as minimizing the exciton dissociation and increasing the radiative recombination because of the quantum confinement effect [75–77]. However, their structural stability and physicochemical-related issues may drop the efficiency of perovskite devices within a few operating hours [78, 79]. To address these issues, mixed cation (Cs^+/FA^+) based $\text{FA}_{(1-x)}\text{Cs}_x\text{PbBr}_3$ perovskites nanocrystals (NCs) have been prepared to study the influence of Cs doping on the performance of LEDs. This study also offers some important insights into the different chemical composition range (Fig. 2a) with variable ratio of FA/Cs ($x=0-0.6$), crystal formation, and tuning of the optical bandgap. X-ray diffraction (XRD) analysis (Fig. 2b) of all composition range of these NCs showed standard perovskites crystal phase. The peak shift from 15.01° to 15.39° was displayed, which shows the shrinkage of d-spacing due to smaller size Cs insertion into the crystal lattice (Fig. 2c). To further confirm the effect of Cs doping, high-resolution transmission electron microscopy (TEM) is conducted and observe the reduction in lattice spacing and confirm the

presence of smaller size Cs cation. All the perovskite NCs crystallize with the cubic shape and a negligible effect was observed on their sizes after Cs doping. As the content of Cs increases, a blue shift in absorption band from 525 to 503 nm (Fig. 2a), corresponds to a shift in bandgap towards high energy levels from 2.27 to 2.33 eV. Moreover, the PL peak (Fig. 2e) was finely tuned from 531 to 519 nm, with varying ratios of Cs cation doping. Finally, Fig. 2f–i and Table 2 show the overview of current density to voltage (J–V) characteristics of LEDs based on $\text{FA}_{(1-x)}\text{Cs}_x\text{PbBr}_3$. The best efficiency is achieved when $x=0.2$ with maximum luminance $55,005 \text{ cd m}^{-2}$, the current efficiency of 10.09 cd A^{-1} , and EQE of 2.80% [80].

The approach used in this study was also reported by Bin Xu et al., to support the stance of commercialization of perovskites LEDs [88]. The ligand-assisted reprecipitation (LARP) technique was used to prepare colloidal $\text{MA}_{1-x}\text{Cs}_x\text{PbBr}_3$ NCs with the varying amount ($x=0-0.4$) of Cs doping in the mixed cation. The precursor solution was prepared by dissolving MABr, CsBr, PbBr_2 , oleic acid and oleylamine and in

Table 1 Summary of alkali metal ions doped perovskite solar cell performance

Perovskite active layer	Doped alkali metal	V_{OC} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]	Ref.
CsMAFAPbI _{3-x} Br _x	Rb	1.18	22.80	81.00	21.80	[62]
MAFAPbI _{3-x} Br _x	Rb	1.125	23.24	71.90	18.80	[63]
(Cs,FA,MA)Pb(I _{0.85} Br _{0.15}) ₃	K	1.17	23.20	79.00	21.50	[64]
FA _{0.83} MA _{0.17} Pb(I _{0.83} Br _{0.17}) ₃	K	1.15	23.50	75.00	20.40	[65]
MA _{0.17} FA _{0.83} Pb(I _{0.83} Br _{0.17}) ₃	Rb	1.16	22.80	78.00	21.00	[66]
CsPbI ₂ Br	Rb	1.24	14.02	69.00	12.00	[67]
CsPbI ₂ Br	Rb	1.32	16.25	80.03	17.16	[68]
FA _{0.83} MA _{0.17} Pb(I _{0.83} Br _{0.17}) ₃	Rb	1.14	19.97	72.00	16.51	[69]
	Cs	1.16	20.56	74.00	17.75	
MAPbI ₃	Na	1.10	21.16	78.00	18.16	[70]
	K	1.10	20.88	78.00	17.81	
FA _{0.85} MA _{0.15} Pb(I _{0.85} Br _{0.15}) ₃	K	1.16	22.99	76.00	20.32	[71]
Cs _{0.05} FA _{0.79} MA _{0.16} Pb(I _{0.6} Br _{0.4}) ₃	K	1.26	19.19	76.00	18.38	[72]
CH ₃ NH ₃ PbI ₃	K	0.92	19.07	68.00	12.07	[73]
MAPbI _{3-x} Cl _x	Cs	0.99	21.10	79.30	16.60	[57]
FAPbI ₃	Cs + MDA*	1.16	26.17	80.10	24.40	[74]
FA _{0.85} MA _{0.15} PbI ₃	Cs	1.16	24.92	78.64	21.95	[60]
MA _{0.5} FA _{0.5} PbI ₃	Cs + Rb	1.25	23.70	77.00	22.81	[61]

*Methylenediammonium

dimethylformamide (DMF) and controlled amount of this solution added in anti-solvent to form green colloidal solution of perovskite NCs. The as-synthesized perovskites NCs were single-crystalline of size between 8 and 12 nm (Fig. 3a). To study the effect of Cs doping amount on the optical properties of mixed cation perovskite NCs, UV–Vis absorption and photoluminance (PL) spectra were recorded (Fig. 3b–c). With the different amounts of Cs doping, the absorption band was blue-shifted from 515 to 505 nm and PL spectra also changed from 539 to 533 nm. The crystalline structure of all Cs doped samples was exhibited from XRD patterns (Fig. 3d) and the increase in (110) peak intensity shows the preferred crystal growth after the addition of dopant. The synthesized MACsPbBr₃ NCs were single crystalline with the sizes changing from 8 to 12 nm and had a cubic shape with no significant change observed after the addition of Cs ions into the samples. The J–V characteristics of optimized Cs doped perovskite LEDs showed the excellent value of luminance 24,500 cdm⁻² and the EQE of 1.3% (Fig. 3e–f, Table 2).

3 Role of incorporating rubidium ions in HPM

Rubidium (Rb) has been considered an emerging alkali metal that can be used as a functional dopant in HPM, which has a significant impact on the structural parameters of single or mixed cation perovskites [89].

The debate on whether Rb metal cations occupy the main A-site position in a perovskite crystal lattice or

not is still controversial. However, few studies showed the presence of Rb⁺ ions at the A-site of the perovskite crystal lattice. Saliba et al. [62] first embedded the Rb⁺ into the mixed A-site cation (CsMAFA) formulations to achieve stabilized PCE of 21.6%. This study opens the avenue to study the influence of rubidium ions for multi cation perovskites on solar cells, LEDs and photo-detection applications. Daniel et al. [66] worked on the doping of rubidium iodide (RbI) for state-of-the-art triple cation composition Cs₅(MA_{0.17}FA_{0.83})₉₅Pb(I_{0.83}Br_{0.17})₃ synthesized in the recently published study [90]. The addition of Rb⁺ ions to the mixed A-cation perovskite showed an improved PCE of about 21% mainly due to high open-circuit voltage (1.16 V) and fill factor (78%). Furthermore, different concentration of RbI (0.5–2%) for all in-organic perovskite (CsPbI₂Br) was analyzed in the construction of high-efficiency, low cost, and improved air stability of hybrid PSCs [67]. Compared with un-doped CsPbI₂Br perovskite films, excellent crystallinity, improved surface morphology, and enhanced absorbance were shown after incorporation of RbI, as had been reported in previously published studies [69, 91].

Recently, post passivation of multi cation perovskite Cs_{0.10}FA_{0.90}Pb(I_{0.83}Br_{0.17})₃ by rubidium butyrate (RbBu) was reported to explain the role of Rb⁺ and butyrate anion without affecting the perovskite crystallinity and surface morphology. After annealing of spin-coated Cs_{0.10}FA_{0.90}Pb(I_{0.83}Br_{0.17})₃ perovskite thin film, different concentrations (1, 5, 10, 50, and 100 mM) of RbBu sprinkled on it to study the charge carriers lifetime, diffusion length, resistance against

Fig. 2 **a** Photographs of different perovskite NCs in solution. **b** XRD patterns of $\text{FA}_{(1-x)}\text{Cs}_x\text{PbBr}_3$ ($x=0-0.6$). **c** Lattice fringe and peak position ($\approx 15^\circ$) as a function of Cs content, x , in $\text{FA}_{(1-x)}\text{Cs}_x\text{PbBr}_3$. **d** Absorption spectra and **e** PL spectra of $\text{FA}_{(1-x)}\text{Cs}_x\text{PbBr}_3$ ($x=0-0.6$).

f J–V **g** luminance–voltage, **h** EQE–current density, and **i** current efficiency–current density characteristics of perovskite LEDs, based on $\text{FA}_{(1-x)}\text{Cs}_x\text{PbBr}_3$ ($x=0, 0.1, 0.2$, and 0.3). Adapted with permission from ref. [80], copyright 2017, WILEY-VCH

Table 2 Summary of alkali metal-doped ions perovskite light-emitting diode

Perovskite emitting layer	Doped alkali metal	EL [nm]	Luminance [cd/m^2]	EQE %	CE [cd/A]	[Ref]
MAPbBr_3 (Polycrystalline)	Rb	527	7694	–	9.54	[81]
FAPbBr_3 (Polycrystalline)	Rb	532	66 353	7.17	24.22	[82]
CsFAPbBr_3 (QDs)	Rb	502	750	3.60	8.50	[83]
$\text{CsFAPbCl}_{1.25}\text{Br}_{1.75}$		466	39	0.61	0.45	
CsPbBr_3 [NCs]	Rb	490	183	0.69	–	[84]
		464	63	0.11		
CsPbBr_3 [NCs]	K	522	5759	5.60	–	[85]
$\text{CsPbI}_{3-x}\text{Br}_x$ [NCs]	K	637	2671	3.55	–	[86]
$\text{CsPb}(\text{Br}/\text{Cl})_3$ [NCs]	K	477	86.95	1.96		[87]
FAPbBr_3 [NCs]	Cs	525	55.005	2.80	10.09	[80]
MAPbBr_3 [NCs]	Cs	523	24,500	1.30	4.10	[88]

moisture, and photovoltaic performance. There is no obvious change in surface morphology from $\text{RbBu}=0-10$ mM and grain sizes between 0.4 and 1.2 μm were observed as shown in Fig. 4a. After that, rod-like crystals were noticed for the higher concentration of RbBu ($50-100$ mM) due to the presence of $\delta\text{-RbPb}(\text{Br}_x\text{I}_{1-x})_3$. To understand the effect of butyrate on the hydrophobicity of multi-cation perovskite, the maximum contact angle for $\text{RbBu}-10$ was recorded (Fig. 4b). As a general trend, the additives increases the charge carrier lifetime (τ_c), and RbBu (5 mM) showed a maximum lifetime of $\tau_c=210$ ns while

drop-in charge-carrier mobility from $\mu=31.9$ cm^2/Vs to from $\mu=12.9$ cm^2/Vs exhibiting the role of different RbBu molar concentrations (Fig. 4c). Diffusion length (L_D) measurements of the passivated films enhanced up to 5 μm for $\text{RbBu}=5$ mM and charge carrier diffusion length decreases to 2 μm for higher or non-passivated perovskite films [92].

Another interesting aspect of rubidium ions has been studied to successfully solve the crystals phase instability and high-temperature thermal instability problems of FAPbI_3 perovskite for high-performance photodetection. A large amount of Rb^+ ions (up to 30%) was added to reduce

Fig. 3 **a** TEM image of the $\text{MA}_{0.7}\text{Cs}_{0.3}\text{PbBr}_3$ NCs. **b** The absorption spectra, **c** PL spectra, **d** XRD patterns, **e** EQE versus current density and **f** luminance versus voltage, of $\text{MA}_{1-x}\text{Cs}_x\text{PbBr}_3$ ($x=0-0.4$).

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Fig. 4 **a** SEM images, **b** contact angle images and **c** charge-carrier lifetimes, **d** electron–hole sum mobilities from optical-pump terahertz-probe (OPTP) measurements, **e** charge-carrier diffusion

lengths considering front face excitation as a function of the RbBu concentration. Adapted with permission from ref. [92], copyright 2020, American Chemical Society

Fig. 5 **a** TEM images of synthesized $\text{Rb}_x\text{Cs}_{1-x}\text{PbBr}_3$ nanocubes **b** Photoluminescence (solid line) and absorption (dashed line) spectra of the synthesized solution. Inset is a picture of various solutions, illuminated by a UV-LED source ($\lambda = 374$ nm) displaying the tunable emission. **c** Current density (J) displayed by squares and

luminance (L) displayed by circles. **d** External quantum efficiency as a function of applied bias. **e** Devices that exhibited the largest luminance at their peak EQEs. Adapted with permission from ref. [84], copyright 2019, WILEY-VCH

the pin-holes, increase the crystallinity and absorption intensity of FAPbI_3 thin films. As a result, photodiode based on optimized $\text{Rb}_{0.3}\text{FA}_{0.7}\text{PbI}_3$ perovskite film exhibited high responsivity of 0.43 AW^{-1} , the ultrafast response speed of about 300 ns, and detectivity of more than 10^{12} Jones [93].

Rubidium doping has been widely studied for tuning of absorption range, low PLQY, and thermal instability issues of all-inorganic halide perovskites (CsPbX_3) nano geometries. Taking into account the importance of Rb^+ ions, Amgar et al. embedded the certain content of Rb ions into CsPbX_3 ($X = \text{Cl}$ or Br) nanoparticles to tune the absorption range in the near-ultraviolet and visible range (325–500 nm). Size distribution analysis of all samples presented the declining trend with an increase of Rb ions for CsPbX_3 ($X = \text{Cl}$ or Br) [94]. Another study to improve the emission of manganese (Mn) doped Mn: CsPbCl_3 NCs was conducted, where increased emission, highest PLQY (up to 63.18%), and thermal stability with the addition of Rb^+ ions was exhibited. The average size of Mn: CsPbCl_3 NCs without Rb doping was 11.37 nm which decreases to 7.7 nm after doping [95].

Similarly, different nanostructures of $\text{Rb}_x\text{Cs}_{1-x}\text{PbBr}_3$ (Fig. 5a) namely nanocubes and nanoplates with tunable emission (450–500 nm) were reported to fabricate blue-emitting LEDs (Fig. 5b). The as-prepared nanoplates were of varying thicknesses and smaller in size due to the presence of Rb ions. The addition of Rb ions into the pure bromine phase could provide a path to increase the bandgap without introducing phase segregation at high voltage as it tends to distort the PbX_6 octahedra and reduces the overall orbital overlap. As a result, high PLQY ($> 60\%$), improved luminance, and EQE of 0.11–0.87% for deep-blue and sky-blue (Fig. 5c–e) LEDs were displayed [84].

Fanyaun et al. studied the interplay of Rb^+ ions to realize the severe challenges of PL and EL in multi-cation blue-emitting perovskite quantum dots (QDs). It was noted that perovskite QDs exhibited cube-shaped and smaller size (5.17 nm vs 6.38 nm) structures since Rb ions were incorporated into them. The addition of Rb^+ realized to enlarge the bandgap due to octahedral distortion and strong quantum confinement resulted

Fig. 6 SEM images of **a** without, or with **b** Na⁺ **c** K⁺ doping **d** The X-ray diffraction patterns **e** the enlarged comparison of (110) diffraction peak **f** the steady-state photoluminescence (PL) **g** the current density–voltage characteristics and **h** external quantum efficiency (EQE) spectra with Na⁺, K⁺ doped and the control sample without

doping **i** The J–V curve of champion PSCs with 1.0 mol% Na⁺ doping measured at the AM 1.5G solar spectra of 100 mWcm^{−2} at a reverse scan. Adapted with permission from ref. [70], copyright 2017, WILEY-VCH

in outstanding PLQY of 64.5% and 49.8% for greenish-blue (Rb_{0.33}Cs_{0.67})_{0.42}FA_{0.58}PbBr₃ and deep-blue (Rb_{0.33}Cs_{0.67})_{0.42}FA_{0.58}PbCl_{1.25}Br_{1.75} perovskite QDs [83].

4 Incorporating other alkali metal ions (K⁺, Na⁺, and Li⁺) for enhanced performance of HPM

After studying beneficial aspects of rubidium, scientists were prompted to explore the other smaller alkali metal ions such as K⁺, Na⁺, and Li⁺. Previously published studies about polycrystalline perovskite thin films have been extensively reported about their high trap state density, enlarged grain boundaries, instability to heat, UV (ultra-violet), and humidity [96–98].

Wangen et al. investigated the role of alkali metal ions (Na⁺, K⁺) to make the MAPbI₃ polycrystalline thin films with fewer trap states, reduced grain boundaries, and increased built-in potential leading to enhanced PCE. It was observed from morphological analysis (Fig. 6a–c), the addition of Na⁺ and K⁺ ions helps in high coverage and increases the grain size from ≈140 nm to ≈220 nm and ≈230 nm, respectively. XRD analysis depicts (Fig. 6d–e) the typical tetragonal MAPbI₃ phase of all samples and enlarged (110) peak with significantly narrow width showed that large grain sizes were obtained after addition of Na⁺ and K⁺ ions. To check the trap states of the perovskite absorber layer, steady-state PL spectra were recorded (Fig. 6f). An obvious increase in PL intensity was detected, that assigned to the reduced trap centres due to the coverage of grain boundaries by alkali metal ions.

The J–V curves (Fig. 6g–i) showed that both alkali Na^+ and K^+ have a positive effect on the overall performance of perovskite photovoltaic devices. There was a significant improvement in PCE from 15.56 to 18.16%, an increase of 11.4% fill factor, and open circuit voltage improved from 1.06 to 1.10 V [70].

There is a large volume of published studies describing the impact of crystal native defects that can reduce the charge carrier lifetimes and stimulate the non-radiative recombination, hence reducing the device efficiency [99–102]. Lu et al. paved the way for the most common defect of iodine interstitials in the MAPbI_3 perovskite by doping of Li, Na, K, Rb, and Cs atoms. It was found that the presence of alkali metal as dopant increases the formation energies up to fourfold for the halide interstitials defect and helps in maintaining the high concentration of charge carriers. In addition, charge carrier recombination lifetime follow the trend, pristine $< \text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$ [103]. A brief list of radiative lifetime analysis of alkali doped HPM is given in Table 3.

Besides studying the influence of potassium on polycrystalline HPM, a considerable amount of literature has also been published on nanocrystalline HPM. It has been well reported as the passivating agent to form potassium halide layer to overcome halide segregation in mixed-halide perovskite thin films. Moreover, modification of grain boundaries and suppression of ions migration are the potential benefits of using potassium in HPM [64].

Halide segregation is a major problem in mixed HPM which results in poor electro luminance (EL) stability in LEDs. To overcome this problem, potassium bromide surface coated all inorganic $\text{CsPbI}_{3-x}\text{Br}_x$ NCs emitting at

640 nm were synthesized via hot-injection method. The resulting potassium passivated high-quality NCs showed above 90% PLQY and good dispersion stability for weeks. As a result, pure red-emitting LEDs at 637 nm exhibited a highly stable brightness of 2671 cdm^{-2} and EQE of 3.55% [86].

Several reports [105–108] have shown that blue perovskite LEDs still lag behind the red and green ones due to difficulties in synthesizing stable materials, maintaining high quantum efficiency, and halide segregation to get required emission parameters. The small amount of impurity ion doping has been considered as an effective strategy to improve the optical properties of nanocrystalline HPM. Several studies have been published on doping of a variety of ions including lanthanides [109] and manganese [110] with great success. However, the introduction of new emission due to additional ions cause the impurity in blue light. Smaller size alkali metal ions have the advantage to enhance the efficiency of blue-emitting devices without disturbing the original emission spectra. Given the low performance of CsPbCl_3 QDs, doping of potassium ions was introduced for controlling the emission properties of blue-violet light and a blue shift in absorption edge was observed. Only a small amount of potassium ions enhanced the PLQY of perovskite QDs at 408 nm from 3.2 to 10.3% [104].

To further study the role of potassium incorporation into the $\text{CsPb}(\text{Br}/\text{Cl})_3$ NCs, Fei et al. demonstrated the use of K^+ ions as metal–ligand to improve the nonradiative recombination and PLQY. It is clear from the XRD peaks (Fig. 7a) that all samples showed the characteristic peaks of typical cubic crystal planes of $\text{CsPb}(\text{Br}/\text{Cl})_3$, with no additional diffraction peak confirming the presence of K^+ ions as capping agent outside the crystal surface. The transmission electron microscopy (TEM) images (Fig. 7b–c) exhibit the lattice plane of (200) and (211), which further confirm that the addition of K^+ ions does not affect the crystal structure. The NCs exhibit a slight increase in size with the addition of K^+ as shown in size distribution histograms (Fig. 7b–c), where the average size for the untreated and K^+ treated is 9.94 nm and 10.92 nm respectively. It was demonstrated that alkali metal doping methods can accelerate the speed of reaction, leading to an increase of the NCs size.

Moreover, a schematic presentation (Fig. 7d) of K^+ ions bonding with halides verified the reduced amount of insulating ligands around the NCs. In terms of device performance (Fig. 7e–f, Table 2), the champion blue perovskite LED with 4.0% of K^+ ions showed the highest EQE of 1.96% and luminance of 86.95 cd m^{-2} [87].

In contrast to this study, Minh et al. demonstrated that potassium doping of NCs can enhance the coverage of capping ligands around CsPbBr_3 nanocrystal confirmed

Table 3 Radiative lifetime analysis for the alkali doped halide perovskite materials

Perovskite	Doped alkali element	Morphology of perovskite film	Radiative lifetime (ns)	Ref
$\text{CsPbI}_{3-x}\text{Br}_x$	K	Nanocrystalline	8.73	[86]
CsPbCl_3	K	Nanocrystalline	2.10	[104]
CsPbBr_3	K	Nanocrystalline	2.21	[85]
$\text{FA}_{0.85}\text{MA}_{0.15}\text{Pb}$ ($0.85\text{Br}0.15\text{I}$) ₃	K	Polycrystalline	32.7	[71]
$\text{CsPb}(\text{Br}/\text{Cl})_3$	K	Nanocrystalline	4.57	[87]
FAPbBr_3	Rb	Polycrystalline	2.77	[82]
CsPbBr_3	Rb	Nanocrystalline	4.7	[83]
CsFAPbBr_3			3.2	
$\text{CsFAPbCl}_{3-x}\text{Br}_x$			3.5	
CsPbBr_3	Rb	Nanocrystalline	5.47	[84]
MAFAPbBr_3	Rb	Polycrystalline	4.68	[63]
FAPbBr_3	Cs	Nanocrystalline	4.80	[80]

Fig. 7 **a** XRD patterns of perovskite films with different x values and standard XRD patterns of CsPbBr_3 and CsPbCl_3 . **b** and **c** TEM images of pristine and K^+ based (4.0% in terms of nominal K^+ ratio) NCs and size distribution analysis; the insets show the corresponding high-

resolution TEM images. **d** Schematic illustration of potassium passivation. **e** Current density–voltage–luminance curves and **f** EQE–luminance curve for LED device based on $x=4.0\%$. Adapted with permission from ref [87], copyright 2020, WILEY-VCH

by N–H stretching at 3356 cm^{-1} . The reason for increased stretching is due to better oleylamine coverage which could be ascribed to the formation of the bromide-rich surface due to potassium ions. Furthermore, Fourier transforms infrared (FTIR) peaks of 2.5% potassium doped sample showed nearly double intensity as compared to the sample without doping. Also, reduction in trap states and reduced surface energy of NCs were believed due to the more insulating ligands attached to the NCs surface [85].

5 Conclusion and outlook

In this review, we summarized comprehensive progress on doping of alkali metal ions (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+) in terms of their ability to markedly influence the electrical, optical, and doping induced charge carrier dynamics in halide perovskite materials. Alkali metals have been successfully doped in polycrystalline halide perovskites, giving rise to structural stability, reduced defect states, enlarged grain boundaries, and improved film morphology. Moreover, alkali metal-doped NCs have shown reduced crystal native defects, improved thermal and moisture stability, prolonged charge carrier lifetime, and high PLQY.

Looking forward, to fully exploring the potential benefits of alkali metals in perovskites, considerably more research work will need to be done to determine the true position of alkali metals ions, the influence of doping on crystal orientation, and the principle behind the improved optoelectronic properties. Also, there is a wide research gap in co-doping the high-band gap perovskite to enhance stability and to cover a wide luminance range. Thus, we expect that advanced characterization techniques such as in-situ transmission electron microscopy should be implemented to study the influence of the incorporation of alkali metal ions. At present, alkali metal-doped perovskites are mostly reported for solar cells and LEDs construction. Keeping in mind the unique properties of alkali metals in perovskites, doped perovskites should consider in other applications such as photodetectors, X-ray detectors, and single-photon sources.

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Declarations

Conflict of interest There are no conflicts of interest to declare.

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