Stabilizing Perovskite Light-Emitting Diodes by Incorporation of Binary Alkali Cations

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The poor stability of perovskite light-emitting diodes (PeLEDs) is a key bottleneck that hinders commercialization of this technology. Here, the degradation process of formamidinium lead iodide (FAPbI$_3$)-based PeLEDs is carefully investigated and the device stability is improved through binary-alkalization incorporation. Using time-of-flight secondary-ion mass spectrometry, it is found that the degradation of FAPbI$_3$-based PeLEDs during operation is directly associated with ion migration, and incorporation of binary alkali cations, i.e., Cs$^+$ and Rb$^+$, in FAPbI$_3$ can suppress ion migration and significantly enhance the lifetime of PeLEDs. Combining experimental and theoretical approaches, it is further revealed that Cs$^+$ and Rb$^+$ ions stabilize the perovskite films by locating at different lattice positions, with Cs$^+$ ions present relatively uniformly throughout the bulk perovskite, while Rb$^+$ ions are found preferentially on the surface and grain boundaries. Further chemical bonding analysis shows that both Cs$^+$ and Rb$^+$ ions raise the net atomic charge of the surrounding I anions, leading to stronger Coulomb interactions between the cations and the inorganic framework. As a result, the Cs$^+$–Rb$^+$-incorporated PeLEDs exhibit an external quantum efficiency of 15.84%, the highest among alkali cation-incorporated FAPbI$_3$ devices. More importantly, the PeLEDs show significantly enhanced operation stability, achieving a half-lifetime over 3600 min.

In recent years, solution-processed metal halide perovskites have attracted tremendous interests in the scientific community including the field of light-emitting diodes (LEDs).\textsuperscript{[1–5]} Besides low fabrication cost and tunable emission wavelength, metal halide perovskites show great potential of achieving high-performance LEDs due to high photoluminescence (PL) quantum efficiency, narrow emission linewidth (i.e., high color purity), and low density of sub-gap electronic trap states.\textsuperscript{[6–9]} Significant breakthroughs have been achieved in perovskite LEDs (PeLEDs) in the past 5 years, with the external quantum efficiency (EQE) boosted from 0.76% in 2014 to over 21% recently,\textsuperscript{[1,10,11]} comparable to the state-of-the-art performance of organic LEDs (OLEDs).\textsuperscript{[12]}

Nevertheless, despite rapid development of electroluminescence (EL) efficiency, the commercialization of PeLEDs is still challenging due to the poor device stability,\textsuperscript{[13]} which mainly stems from degradation of perovskite materials upon air exposure or electrical bias. As demonstrated in perovskite-based photovoltaic (PV) devices, migration of mobile ions under electrical bias stress causes destruction of the perovskite lattices and infiltration of mobile ions into adjacent layers.\textsuperscript{[14,15]} In PeLEDs, a higher electric-field is present and may aggravate the ion migration issue. In particular, in contrast to the thick perovskite absorber layer in PV devices, the perovskite light-emitting layer in PeLEDs is much thinner (typically a few tens of nanometers) as required for spatial confinement of charge carriers and efficient radiative recombination.\textsuperscript{[1]}

Therefore, mobile ions in the thin perovskite layer would be...
more likely to migrate into adjacent charge injection layers in PeLEDs, resulting in defect generation and gradually deteriorating EL efficiency.[26] Besides, ion migration could promote halide separation in mixed halide PeLEDs, resulting in the splitting of EL peaks and color instability.[27] As demonstrated in the previous studies, halide ions dominate ion migration in perovskites due to lower activation energy (0.1 eV) of the motion as compared with that of A-site cations (0.5 eV) and B-site metal cations (0.8 eV).[18] and that halide ions mainly migrate via halide vacancies rather than interstitial sites.[19,20]

In addition, compared with in the bulk, ions migrate faster on grain boundaries (GBs) in the polycrystalline perovskite films due to higher ionic diffusivity at GBs, which might provide the main channel for ion migration in perovskite materials.[21,22]

Thus, suppressing defects-assisted ion migration, especially the motion of halide ions, is of vital importance to stabilize the EL efficiency during operation of PeLEDs.

So far, amine-based agents have been explored to passivate defects and block ion migration in PeLEDs, leading to improved EL performance and operation stability. Ethylenediamine and branched polyethyleneimine treatment on MAPbBr3 films inhibited the Br− migration-induced corrosion of Ag on top of MAPbBr3 as a result of passivated defect sites through coordinate bonding between nitrogen atoms and undercoordinated lead ions.[23] Amino-functionalized molecules were also designed as additives for FAPbI3, which improved passivation efficiency through enhanced interaction with defects; the work achieved a record EQE of 21.6% among the near-infrared (NIR) PeLEDs and a half-lifetime ($T_{50}$) defined as the time to half of the initial EQE) of 20 h at 25 mA cm$^{-2}$.[18] Besides, benzylamine (BA) treatment on FAPbI3 perovskites was demonstrated to reduce perovskite surface defects and resulted in a $T_{50}$ of 23.7 h at 100 mA cm$^{-2}$; however, the peak EQE (EQEmax) was decreased from 14% to 11.8% after the BA treatment, likely due to the increased roughness of treated perovskite films.[24]

In this work, we carefully examine the degradation of FAPbI3-based NIR PeLEDs under bias stress, and provide direct evidence of halide ion migration in the operated device through time-of-flight secondary ion mass spectrometry (TOF-SIMS) depth profiling. Further, inspired by the finds in the perovskite PV field,[25–27] wherein the doped alkali cations prompt the enhanced structure stability of FA-based perovskites, we explore a composition tuning method by incorporating alkali cations (Cs+ and Rb+) in FAPbI3 perovskite and investigate effects of the modified structures on the operation stability of PeLEDs. With incorporation of Cs+ and Rb+ in the neat FAPbI3 perovskites, the ion migration is greatly suppressed and the lifetime of the PeLEDs is significantly improved. Interestingly, the combined experimental data and first principle density functional theory (DFT) calculations reveal that although both Cs+ and Rb+ play a positive role in improving operation stability of PeLEDs, the underlying mechanisms of Cs-induced and Rb-induced enhancement are different. The results show that Cs+ ions are present throughout the bulk while Rb+ ions are spontaneously located on the surface and GBs of the perovskite films. By further chemical bonding analysis, both Cs+ and Rb+ raise net atomic charges of surrounding I− anions, leading to stronger Coulomb interactions between the cations and the inorganic framework and potentially increasing the formation energy of I− vacancies. As such, the presence of Cs+ and Rb+ ions efficiently blocks the pathways of ion migration in the bulk and along the GBs, respectively. In consequence, the NIR PeLEDs exhibited improved EQEmax from 12.06% for the pure FAPbI3 device to 15.84% for the Cs+-Rb+-incorporated device. The operation stability is significantly promoted with a half-lifetime ($T_{50}$ over 3600 min), comparable to that of the state-of-the-art NIR OLEDs.

We first fabricated FAPbI3-based PeLEDs with a typical device structure (inset scheme in Figure 1a), employing polyethyleneimine (PEIE)-modified zinc oxide (ZnO) and poly(9,9-dioctyl-fluorene-co-N-(4-butylphenyl)diphenylamine) (TFB) as the electron-transport layer and the hole-transport layer, respectively. The detailed solution preparation and device fabrication processes are described in the Experimental Section. Note that Pb(SCN)$_2$ was introduced as an additive in the perovskite precursor and its effects on device performance are shown in Figures S1 and S2 in the Supporting Information. Figure 1a,b illustrates the characteristics of the device performance, exhibiting a high radiance of 493.1 W sr$^{-1}$ m$^{-2}$ at 4 V, an energy conversion efficiency (EQE) of 9.1%, and an EQEmax up to 12.06% with a current density of 214.5 mA cm$^{-2}$ at 2.4 V, which indicate effective carrier injection and transport in the light-emitting devices. To evaluate operation stability of the fabricated devices, we applied a constant current density of 100 mA cm$^{-2}$ on the device with a modulated voltage. As shown in Figure 1c, the radiance and EQE decline rapidly under the continuously applied electric field and reach a value below 6 W sr$^{-1}$ m$^{-2}$ and 1% after 100 min, respectively, with a $T_{50}$ of 18 min. The severe decay of the EL efficiency motivates us to investigate the internal mechanism in the operated device. Here, we employed the TOF-SIMS depth profiling to probe the degradation process of the devices. TOF-SIMS depth profiling is considered as a powerful technique to probe evolution of compositional inhomogeneity and chemical gradients in perovskite-based and other optoelectronic devices.[28–30]

We measured the depth profiling in devices before and after applied with a constant current density of 100 mA cm$^{-2}$ for 100 min (Figure S3a, S3b, Supporting Information), to reveal the vertical distribution of species in the fresh and degraded devices. Note that the detected ion intensity extends to adjacent layers and overlaps at the interfaces, which is inevitable due to the instrumental limitation of the TOF-SIMS measurements and the rough interfaces.[11] As shown in Figure S3 in the Supporting Information and Figure 1d, from the fresh device to the degraded device, the I− ion intensity shows a prominent change with a sharp increase at the MoO$_3$/Au interface, which indicates the dissociation of I− ions from the perovskite emitting layer and further transport of the dissociated ions through the TFB and MoO$_3$ layers under the external electric field. The I− migration and formation of iodide vacancies could induce nonradiative recombination centers and decrease light emission.[14,18,23]

In particular, the accumulation and reaction of the ions with the Au electrode could further result in deterioration of the perovskite layer under long-term operation and aggragate the decay of EL efficiency and thus EQE. We also note that the driving voltage for keeping the constant current density is decreased during operation (Figure 1c), this might be related to the modification of carrier injection barrier or formation of leakage paths after I− migration and metal-halide reaction.
The TOF-SIMS results suggest that the degradation of PeLEDs is probably associated with the $I^−$ dissociation from the perovskite layer accompanied by generation and migration of halide defects. Herein, we explore the incorporation of binary alkali cations (Cs$^+$ and Rb$^+$) into FAPbI$_3$ as the method has previously been shown to stabilize FA-based perovskite materials as well as the perovskite solar cell performance. For simplification, we abbreviate the names of the perovskites according to their A-site cations, i.e., FA, FACs, FARb, and FACsRb. The film morphology was first examined by scanning electron microscopy (SEM). The doping molar ratio of Rb$^+$ is optimized to be 5% since a higher ratio would cause generation of undesired branch-like morphologies (Figure S4, Supporting Information) and separation of RbPbI$_3$ phase (Figure S5, Supporting Information). As illustrated in Figure 2a–d, both the neat FA film and the incorporated films present islanded domain morphology on the PEIE-modified ZnO substrates. Incorporation of Cs$^+$ or Rb$^+$ could readily increase the grain size, while co-incorporation of Cs$^+$ and Rb$^+$ appears to result in the largest grain size. The larger grains may suppress ion migration due to the reduced defect sites at GBs. Compared with the neat FA film, the incorporated films exhibit improved crystallinity with slight peak shift (Figure S4, Supporting Information) and separation of RbPbI$_3$ phase (Figure S5, Supporting Information). As illustrated in Figure 2a–d, both the neat FA film and the incorporated films present islanded domain morphology on the PEIE-modified ZnO substrates. Incorporation of Cs$^+$ or Rb$^+$ could readily increase the grain size, while co-incorporation of Cs$^+$ and Rb$^+$ appears to result in the largest grain size. The larger grains may suppress ion migration due to the reduced defect sites at GBs. Compared with the neat FA film, the incorporated films exhibit improved crystallinity with slight peak shift (Figure S4, Supporting Information) and separation of RbPbI$_3$ phase (Figure S5, Supporting Information).

To investigate how the structural and morphology variations affect the charge recombination process in the films, we performed steady-state PL and time-resolved PL (TRPL) measurements. The PL peaks show a similar blue-shift trend (Figure S8, Supporting Information) as the absorption onset, and the drastically enhanced PL intensity in the FACs, FARb, and FACsRb films reveals decreased nonradiative recombination, likely due to the improved morphology and crystallinity of the mixed cation perovskite films reducing defect states. Moreover, we observe more stable PL emission under the continuous 405 nm light excitation in the incorporated films (Figure S9, Supporting Information), suggesting enhanced phase stability of the mixed-cation perovskites in ambient air. The TRPL data of the fabricated perovskite films (Figure 2f) is plotted and fitted with a bi-exponential decay function, where the fast and slow components have previously been assigned to trap-assisted recombination at GBs and radiative recombination inside the bulk perovskite, respectively.$^{[33,34]}$ As summarized in Table S1 in the Supporting Information, both the fast decay component and the low decay component show a longer lifetime after incorporation of Cs$^+$ or Rb$^+$. With the co-incorporation of Cs$^+$ and Rb$^+$, the average lifetime is prolonged from 686.35 to 1883.58 ns, again pointing to remarkably reduced nonradiative recombination centers in the perovskite layer.

Next, we discuss whether the roles of Cs$^+$ and Rb$^+$ in enhancing the perovskite properties are the same. Interestingly, the depth profiling of X-ray photoelectron spectra (XPS; Figure 2g) reveals that Rb$^+$ ions predominantly distribute at the perovskite film surface, while Cs$^+$ ions disperse relatively uniformly throughout the bulk film. (Note that the local Cs$^+$ accumulation near ZnO is probably due to the limited solubility of CsI and PbI$_2$ in the solution, which could lead to the partial precipitation of Cs-rich phases during the film formation.
process.\(^{[15]}\) Besides, the Rb 3d signal overlaps with the signals of Zn 3p and In 4s and the XPS test area with a diameter of 400 µm includes the exposed ZnO/ITO substrates between the isolated perovskite grains, therefore apparent Rb signals at the ZnO/ITO side are actually Zn 3p and In 4s signals.

In order to understand the different distribution patterns of Cs\(^+\) and Rb\(^+\) ions and their subsequent effects on the perovskites, we carried out first principle DFT calculations to study the perovskite systems. To model the FACs and FARb perovskites, we substituted one FA\(^+\) cation for one Cs\(^+\) or Rb\(^+\) cation at the FAI-terminated surface, PbI\(_2\)-terminated surface, and in the bulk, respectively (Figures S10 and S11, Supporting Information). In Figure 3a–c, we illustrate the most stable FA, FACs, and FARb structures, where Cs\(^+\) is more stable in the

![Figure 2. Perovskite films characterizations. a–c) Surface SEM images of: a) FA, b) FACs, c) FARb, and d) FACsRb films. The scale bars of the SEM images are 1 µm. e) XRD patterns, and f) time-resolved PL spectra of the as-prepared films. g) Vertical depth distribution of A-site inorganic cation in incorporated films.](image)

![Figure 3. Locations of Cs\(^+\) and Rb\(^+\) cations in FA perovskites and their effects on the net atomic charges of I\(^-\) anions surrounding Cs\(^+\) and Rb\(^+\) cations. a–c) The most stable structures of: a) the neat FA, b) FACs, and c) FARb perovskite. d) Comparisons of the net atomic charges of the 12 nearest-neighbor I\(^-\) ions surrounding the Cs\(^+\) cation with those of neat FA perovskite. e) Comparisons of the net atomic charges on the eight nearest-neighbor I\(^-\) ions surrounding the Rb\(^+\) cation with those of neat FA perovskite.](image)
bulk than on both surfaces by 0.10–0.33 eV, while Rb$^+$ is more stable on the PbI$_2$-terminated surface than in the bulk and on the FAI-terminated surface by 0.15–0.50 eV (Table S2, Supporting Information). The DFT results agree with the findings from the experimental XPS depth profiling, where preference of distribution of Rb$^+$ on the surface and GBs and distribution of Cs$^+$ in the bulk are observed.

To further investigate the passivation role of Cs$^+$ and Rb$^+$ in the FAPbI$_3$ perovskite, we carried out the atomic population analysis\[36–39\] based on the most stable structures of FA, FACs, and FARb perovskites. It should be noted here that in FACs perovskites, the Cs$^+$ cation in the bulk preferentially occupies an A-site and forms bonds with 12 surrounding I$^-$ anions. For FARb perovskite, the Rb$^+$ occupies a site between the A-site and a surface interstitial site on the PbI$_2$-terminated surface and closely interacts with eight nearest-neighbor I$^-$ anions. Compared with the I$^-$ in the neat FAPbI$_3$, the average net atomic charges of I$^-$ surrounding Cs$^+$ and Rb$^+$ in the incorporated perovskites increase by 4.6% and 5.9% (Figure 3d,e), respectively, a sign of enhanced Coulomb interaction of the cations with the inorganic framework. The increased Coulomb interactions upon the incorporation of Cs$^+$ and Rb$^+$ is expected to increase the formation energy of iodide vacancies, effectively suppressing the creation and diffusion of the halide defects.\[40,41\] Using Rb-modified perovskite as an example, we found an increase of about 200 meV in the defect formation energy of one of the iodide vacancies near Rb or Cs would increase in a similar magnitude, i.e., within a few hundreds meV. Further, the passivation roles of the Cs$^+$ and Rb$^+$ could be distinguished by different mechanisms. The Cs$^+$ is supposed to probably reduce the I$^-$ vacancies in the bulk and retard the ion migration inside the grains, whereas the Rb$^+$ primarily passivate the vacancy defects at the GBs and block the I$^-$ migration channels along the GBs.

The devices based on the incorporated films were further fabricated to examine the roles of doped Cs$^+$ or Rb$^+$ cations in the device performance and operation stability. As illustrated in Figure 4a,b, incorporation of either Cs$^+$ or Rb$^+$ cations can lead to an improvement of EQE and ECE, while the most significant improvement results from co-incorporation of Cs$^+$ and Rb$^+$. The champion device exhibits an EQE$_{\text{max}}$ of 15.84% at a current density of 277 mA cm$^{-2}$, one of the highest among alkali-cation-incorporated FAPbI$_3$-based PeLEDs\[42,43\] together with an ECE$_{\text{max}}$ of 11.65% at 93 mA cm$^{-2}$ and a high radiance of 626.94 W sr$^{-1}$ m$^{-2}$ at 4 V (Table S3 in the Supporting Information and Figure 4c). The sharp rise of the current density and radiance after the device turn-on reveals efficient charge injection and transport, as well as fast trap-filling and suppressed nonradiative recombination in the FACsRb devices. The statistic histogram of 40 devices in Figure 4d shows an average EQE$_{\text{max}}$ of 14.34%, suggesting reasonable fabrication reproducibility. It is also worth noting that higher Rb$^+$ doping ratio results in reduction of the EL efficiency (Table S4, Supporting Information), possibly caused by the phase inhomogeneity (i.e., generation of RbPbI$_3$ phase)-induced nonradiative recombination centers.

To examine the device stability, we recorded EQE of the fabricated devices at a constant current density of 100 mA cm$^{-2}$.

Figure 4. Performance comparison of PeLEDs. a) EQE-current density curves and b) ECE-current density curves of PeLEDs based on the FA, FACs, FARb, and FACsRb perovskites. c) Current density and radiance versus driving voltage and d) EQE$_{\text{max}}$ statistic distribution of the FACsRb-based devices.
The incorporated devices exhibit remarkably improved operation stability at the high current density in comparison with the neat FA-based device. Through the TOF-SIMS depth profiling of the mixed cation perovskite PeLEDs in Figure S12 in the Supporting Information, in comparison with the accumulated I⁻ at the MoO₃/Au interface in the degraded FA-based device (Figure 1d), no visible sign of I⁻ re-distribution is observed in the FACsRb-based device after operation (Figure 5b,c), confirming suppressed halide ion migration during device operation and the stress test. Surprisingly, the FACsRb-based PeLEDs achieve a T50 over 60 h at 10 mA cm⁻² (Figure S13, Supporting Information), comparable to the lifetime of NIR OLEDs. The stability test and composition distribution analysis well support the predictions from our DFT calculations. As a result of the increased net atomic charges of I⁻ anions in the Cs⁺-incorporated perovskites, the Coulomb interaction of the cations with the inorganic frame is enhanced and hence raises the formation energy of I⁻ vacancy defects and increases the energy barrier for ion migration both in the bulk and at GBs. In the meantime, the improved crystallinity of the incorporated perovskites with reduced nonradiative recombination also suppresses ion migration through defective pathways.⁹⁻¹² Taking together, the best performance and operation stability is achieved with the optimized FACsRb composition. We also note that the FARb device appears to have a better stability than the FACs device. This suggests that the Rb-induced surface passivation may play a more important role in the stability improvement.

To conclude, we examined the degradation mechanism of FAPbI₃-based PeLEDs during operation and explored ways of improving the PeLED stability via composition engineering. Through TOF-SIMS depth profiling, we show severe accumulation of I⁻ ions at the MoO₃/Au interface, providing a direct evidence of ion migration during PeLED operation. To mitigate this degradation process induced by migration of I⁻ ions, we investigated the effects of incorporating alkali cations in FA-based perovskites. We carefully controlled the types of alkali cations and found that the perovskites with co-incorporation of binary alkali cations (spontaneous incorporation of Rb⁺ and Cs⁺ in FA perovskites) show the most significant improvement in the perovskite film quality and the PeLED device performance. Interestingly, our XPS profiling experiments and DFT calculations indicate that Rb⁺ ions primarily locate at the GBs and surfaces while Cs⁺ mainly distribute in the bulk. Further atomic population analysis indicates that Cs⁺ and Rb⁺ ions increase net atomic charges of I⁻ anions and enhance the Coulomb interaction between the cations and the inorganic framework, potentially retarding the formation of I⁻ vacancy and blocking the I⁻ migration both in the bulk and at GBs. Using the binary-alkali-cation-incorporated FA perovskite, we obtain a record EQEₘₐₓ of 15.84%, one of the highest among alkali-cation-incorporated FAPbI₃-based PeLEDs. The device also shows superior durability with a T₅₀ over 3600 min, comparable to that of the NIR OLEDs. Our work provides a new approach to the fabrication of highly efficient and stable PeLEDs.

Experiment Section

Materials: Lead iodide was purchased from TCI. Formamidinium iodide and 5-ammonium valeric acid iodide (5-AVAI) were purchased...
from Dyessol. PEIE (80% ethoxylated, 37% solution in H2O) was supplied by J&K. The hole transport polymer, TFb was purchased from American Dye Source, Inc. Other chemicals were purchased from Sigma Aldrich. All chemicals were used without further purification. Colloidal ZnO nanocrystals were synthesized by a solution–precipitation process as reported in the literature.[44]

Solution Preparation: The FAPbI3 precursor solution was prepared by mixing 0.15 M A solution (molar ratio FAI: PbI2 = 1:1 in N,N-dimethylformamide (DMF)/dimethyl sulfoxide (DMSO) mixed solvent) and 0.15 M B solution (molar ratio FAI: Pb(SCN)2 = 3:1 in DMF/DMSO mixed solvent) with a volume ratio of 4:1. The FACs precursor solution was prepared by mixing 0.15 M C solution (molar ratio Cst:FAI: PbI2 = 0.17:0.83:1 in DMF/DMSO mixed solvent) and 0.15 M D solution (molar ratio Cst:FAI: Pb(SCN)2 = 0.17:2.83:1 in DMF/DMSO mixed solvent) with a volume ratio of 4:1. For the FARB and FACsRb precursor solution, Rbl (1 M in DMF/DMSO mixed solvent) with certain molar ratio was added in the mixed FAPbI3 and FACs solution, respectively. 5% AVAI and 30% FAI (molar ratio) were further introduced in all the precursor solutions as additives.

ReLEDS Fabrication and Characterization: Indium tin oxide (ITO) glass (15 Ω sq−1) was cleaned by sequential sonication with a detergent solution, deionized water, acetone, ethanol, and isopropyl alcohol for 15 min, respectively. After dried by a nitrogen flow, the substrates were further treated with UV ozone for 15 min before use. ZnO films were fabricated onto the ITO substrates by spin coating the colloidal solution at 4000 rpm for 45 s, followed by annealing at 150 °C for 30 min in air. PEIE (0.4 wt% in 2-methoxyethanol) as a modification layer was spin coated on the ZnO films at 5000 rpm for 45 s and annealed at 90 °C for 10 min to decrease the work function of ZnO.[45] After cooled down to the room temperature, ZnO films were transferred into the N2 glovebox. DMF washing was applied to the films before the deposition of the perovskite layers to leave an ultrathin PEIE on ZnO films. Subsequently, the perovskite precursor solution was spin coated with two stages, at 500 rpm for 5 s and 8000 rpm for 45 s, and 100 ul chlorobenzene was dropped onto the substrates at the last 17 s, followed by annealing at 100 °C for 15 min. Then the TFb solution was spin coated at 2000 rpm for 40 s as the hole transport layer. Finally, 7 nm MoO3 and 50 nm Au were evaporated as the electrode through a shadow mask under high vacuum (<1 × 10−8 Torr).

The morphology and structure of the perovskite films were characterized by a high-resolution field emission SEM (HR-FESEM) and an X-ray diffraction (XRD) system with a Rigaku RU-300 diffractometer (Cu Kα irradiation, λ = 1.5406 Å), respectively. The absorption spectra were collected by a Hitachi U-3501 UV–Vis–NIR spectrophotometer. The steady-state PL spectra were measured using a continuous-wave laser source with a wavelength of 405 nm and a power density of 20 mW cm−2. The TRPL spectra were collected by an FLS980 spectrophotometer (Edinburgh) with the excitation sources of a 488 nm laser. The XPS was performed using a VG ESCALAB 220-iXL surface analysis system equipped with a monochromatic Al Kα X-ray gun (hv = 1486.6 eV). The TOF-SIMS measurements (Model TOF-SIMS 5–100, ION-TOF GmbH) were performed with the pulsed primary ions from a Cs+ (1 keV) liquid-metal ion gun for the sputtering and a Bi+ pulsed primary ion beam for the analysis (30 keV) with analysis area of 100 um × 100 um. For the device performance and stability test, the J–V curves, radiance, EQE, and ECE were recorded with a Keithley 2400 source meter and a QE-Pro spectrometer coupled with a fiber integration sphere (FOIS-1).

Computational Method: The role of alkali cations (Cs+ and Rb+) in stabilizing FAPbI3 perovskite was investigated by using DFT and the DDEC6 atomic population analysis.[46–48] All structures were optimized using DFT implemented in the Vienna ab initio simulation package.[46–49] The Perdew–Burke–Ernzerhof functional[50] at the level of the generalized gradient approximation was used to describe exchange and correlation. The outermost s, p, and d (in the case of Pb) electrons were treated as valence electrons whose interactions with remaining ions were described using the projector-augmented wave method.[51,52] A 500 eV kinetic energy cutoff was chosen for the plane-wave basis set, and the Monkhorst–Pack scheme 3 × 3 × 1 k-point sampling was used for the integration in the irreducible Brillouin zone. During the structural optimizations, all ions were allowed to relax and the energy and force convergence criteria were set to 10−5 eV and 0.01 eV Å−1, respectively. A five-layer slab model containing (2 × 2) cells along the x–y–directions was built to simulate the FAPbI3 perovskite. The slab was created using the starting structure with cubic symmetry with a DFT-optimized lattice parameter of 6.360 Å. A vacuum of 23 Å was chosen along the z-direction to avoid the interactions between the slabs. One FA+ cation in FAPbI3 perovskite was replaced by one Cs+ or one Rb+ cation to model the Cs+ or Rb+-modified FA perovskite.

In addition to the energy calculations, the DDEC6 atomic population analysis was carried out[46–49] to calculate the net atomic charges of the neat FA, FACs, and FARb perovskites. The net atomic charge[53] assigned to each atom in material was defined as the difference between the nuclear charge (i.e., element number) of the atom and the number of electrons assigned to the atom which could concisely summarize key information about the partitioning of electrons among atoms in materials.[53] The sign of the net atomic charge indicated the positive or negative character of the charge assigned to the atom. Since the interaction between positively charged FA+ and negatively charged I− ions was of electrostatic nature,[53,54] the net atomic charge could indicate the strength of the Coulomb interaction of cations with the inorganic framework and further revealed how the Cs+ or Rb+ cations influenced the stability of the perovskite.

The I defect formation energy is defined as

$$\Delta E_{\text{I}} = E_{\text{I}} - E_{\text{vac}}$$

where $E_{\text{I}}$ and $E_{\text{vac}}$ are the total energies of the surfaces with and without I vacancy, respectively, and $E_{\text{Fermi}}$ and $\mu[I]$ are the Fermi energy and the chemical potential of I2, respectively. Since it is not straightforward to calculate the exact value of the defect formation energies due to the need to determine the last two terms, the suppression of I vacancy formation was defined due to the alkali ions by calculating the relative defect formation energies as

$$\Delta E_{\text{rel}} = \frac{\Delta E_{\text{I}}(\text{Rb/Cs}) - \Delta E_{\text{I}}(\text{ref})}{\Delta E_{\text{I}}(\text{ref})}$$

where positive value indicates increased defect formation energy compared with that in pristine perovskite.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.
