A-Site Management for Highly Crystalline Perovskites

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An in-depth understanding and effective suppression of nonradiative recombination pathways in perovskites are crucial to their crystallization process, in which supersaturation discrepancies at different time scales between CH$_3$NH$_3$I (MAI, methylammonium iodide) and PbI$_2$ remain a key issue. Here, an A-site management strategy via the introduction of an A-site placeholder cation, NH$_4^+$, to offset the deficient MA$^+$ precipitation by occupying the cavity of Pb–I framework, is proposed. The temporarily remaining NH$_4^+$ is substituted by subsequently precipitated MA$^+$. The temperature-dependent crystallization process with the generation and consumption of a transient phase is sufficiently demonstrated by the dynamic changes in crystal structure characteristic peaks through in situ grazing-incidence X-ray diffraction and the surface potential difference evolution through temperature-dependent Kelvin probe force microscopy. A highly crystalline perovskite is consequently acquired, indicated by the enlarged grain size, lowered nonradiative defect density, prolonged carrier lifetime, and fluorescence lifetime imaging. Most importantly, it is identified that the A-site I$_{MA}$ defect is responsible for such crystal quality optimization based on theoretical calculations, transient absorption, and deep-level transient spectroscopy. Furthermore, the universality of the proposed A-site management strategy is demonstrated with other mixed-cation perovskite systems, indicating that this methodology successfully provides guidance for synthesis route design of highly crystalline perovskites.

Significant progress in perovskite solar cells (PSCs) has been made over the past few years, with the solar-to-electric power conversion efficiency (PCE) rapidly evolving from 3.8% to the state-of-the-art value of 25.2%.[1] Unfortunately, restricted by the perovskite crystal quality, further shortening the distance from the theoretical value of 30% is difficult.[2] Specifically, the energy loss due to charge recombination via nonradiative channels has been identified as a major roadblock.[1,4] Thus, an in-depth understanding and effective suppression of nonradiative recombination pathways in hybrid organic–inorganic perovskites (HOIPs) are crucial to their crystallization management, which will enable continuous boosting of device performances.[3]

Generally, HOIP materials have a chemical formula of ABX$_3$, in which A and B are organic and metal cations of different sizes, respectively, while X is a halogen anion that coordinates to B.[6] The A-site cation is located in the B–X framework cavities. On this basis, the versatility of perovskite materials originating from such composition cooperation and various processing routes offers substantial opportunities for tailoring their crystal quality.[7–9] To date, a series of strategies has been proposed to manipulate the A-, B-, and X-sites to optimize perovskite materials.[10–17] Especially, the A-site organic components in HOIPs confer exotic properties different from those of traditional inorganic perovskites, which further imparts manifold functionalities to A-site management.[18] For instance, in addition to small alkali element doping for perovskite crystal facet orientation control, the bandgap, environmental stability, and dimensionality of HOIPs have been manipulated by incorporating HC(NH$_3$)$_3^+$, CH$_3$NH$_2^+$, and bulky organic alkylammonium cations, respectively.[19–25] Such composition engineering, as a widely proposed A-site management strategy, eventually gave rise to improvements in the HOIP performance and the diversity of perovskite material systems. However, for multiferrous HOIP materials, an essential issue concerning the A-site still remains: deficient precipitation of A-site cations aggravates the crystal quality deterioration. The different physical properties of inorganic BX$_3$ and organic AX result in mismatched precipitation at different time scales, which tends to induce A-site vacancies. Though such A-site vacancies are shallow defects, they can potentially decrease the energetic cost associated with unexpected A-site-related deep defects.[26]

To date, substantial efforts have been devoted to decreasing A-site-related defects by balancing such supersaturation...
discrepancies. Specifically, a straightforward approach is to introduce excess methylammonium iodide (MAI) to compensate for insufficient precipitation of MA during the growth process.[27,28] From the perspective of the preparation process, the antisolvent-induced precipitation method has been widely proposed to decrease the solubility of MAI by selectively extracting the solvent.[29] Similarly, the vacuum-flash solution processing method attempts to balance the precipitation times through the sudden and well-controlled removal of the solvent.[30] Additionally, post-passivation treatment with quaternary ammonium ions successfully decreases undesired MA vacancies.[31] However, such methods are not only sensitive to rigorous experimental conditions but also increase the fabrication complexity. Thus, the perovskite crystal quality is still plagued by unfavorable A-site-related defects. An alternative A-site management strategy is expected to eliminate the influence of the mismatched solubility on the perovskite crystal quality.

Herein, we have proposed an A-site management strategy to improve the perovskite quality via the introduction of an A-site placeholder cation, NH4+, during the crystallization process. NH4+ with a size of 1.61 Å could easily occupy the cavity of the PbI2 octahedral structure to compensate for the lack of MA+ precipitation and easily be substituted by the subsequently precipitated MA+, with the feasibility verified based on the density functional theory (DFT)-calculated formation energy. Such NH4+ entrance and exit corresponded to the generation and consumption of the transient phase NH4PbX3 (X = I, Br). The temperature-dependent crystallization process with the transient phase was sufficiently demonstrated by the dynamic changes in the characteristic peaks through in situ grazing-incidence X-ray diffraction (GIXRD) and the surface potential difference evolution through temperature-dependent Kelvin probe force microscopy (KPFM). The A-site placeholder eventually resulted in improved crystallization of the perovskite film, which was indicated by an enlarged grain size, a lowered nonradiative defect density, obtained from steady-state photoluminescence (PL) spectra and Kelvin probe measurements, and a prolonged carrier lifetime, obtained from time-resolved PL (TRPL) spectra and fluorescence lifetime imaging microscopy (FLIM). To further identify the phase transformation process, in situ KPFM measurements of the perovskite without and with NH4Br were performed. For the perovskite film without NH4Br, the surface potential difference changed slightly, accompanying the extension of the annealing time, as shown in Figure S2a in the Supporting Information. However, with NH4Br, the surface potential difference of the perovskite film declined with increasing annealing time to the lowest level at 5 min. Afterward, the surface potential started to inversely change, as shown in Figure 1c. This trend indicated that the transient phase with a low surface potential difference (−1.2669 V) decreased the surface potential difference of the perovskite film in the initial stage. The surface potential difference of the NH4Br additive is larger than those of the perovskite and transient phase, which excludes its impact on the above surface potential difference evolution (as shown in Figure S2b–e, Supporting Information). With extension of the annealing time, the transient phase was consumed and transformed to the NH4PbX3-to-MAPbX3 transformation process occurred via organic-cation exchange between MA+ and NH4+ (process II, in Figure 1a), similar to the reported interaction behavior between CH3NH2 and NH4+.[32] The bonding between protonated MA+ and lead coordination complexes is stronger than that between CH3NH2 and lead coordination complexes. Thus, such a cation displacement reaction between MA+ and NH4+ readily occurs. Additionally, the NH4+ produced as a byproduct further facilitated the proposed cation exchange process, and no external residue remained, even without any posttreatment (process III, in Figure 1a). The temperature-dependent crystallization process with a transient phase was also identified by in situ GIXRD, as illustrated in Figure 1b.d. For the NH4Br-perovskite sample before annealing, in addition to the characteristic perovskite peak, another strong diffraction peak, (101), occurred at 2θ = 9.4°, which was associated with NH4PbI3.[33] When the perovskite was heated from room temperature to 100 °C within 35 min, the NH4PbI3-diffraction peak gradually disappeared after heating for 25 min, which effectively verified the formation and disappearance of the NH4PbI3 phase. The intensity of the (101) peak decreased until the peak disappeared during the annealing treatment, as shown in Figure S1b (Supporting Information). At the same time, the narrowing full-width at half-maximum (FWHM) of the (110) reflection of the perovskite indicated the enhanced crystallinity of the perovskite. Therefore, the in situ GIXRD results indicated the formation of NH4PbI3 after adding the lower-solubility NH4Br and the consumption of the transient phase via organic-cation exchange. The transient phase was also investigated by electron backscatter diffraction.[34] By comparing the test Kikuchi patterns and the transient dynamic patterns, we further verified the formation of the transient phase in the unannealed perovskite (Figure S6, Supporting Information).

To further identify the phase transformation process, in situ KPFM measurements of the perovskites without and with NH4Br during annealing were performed. For the perovskite film without NH4Br, the surface potential difference changed slightly, accompanying the extension of the annealing time, as shown in Figure S2a in the Supporting Information. However, with NH4Br, the surface potential difference of the perovskite film declined with increasing annealing time before reaching the lowest level at 5 min. Afterward, the surface potential started to inversely change, as shown in Figure 1c. This trend indicated that the transient phase with a low surface potential difference (−1.2669 V) decreased the surface potential difference of the perovskite film in the initial stage. The surface potential difference of the NH4Br additive is larger than those of the perovskite and transient phase, which excludes its impact on the above surface potential difference evolution (as shown in Figure S2b–e, Supporting Information). With extension of the annealing time, the transient phase was consumed and transformed to the

to compensate for the absent MA+, leading to the NH4PbX3 transient phase (process I, in Figure 1a). Compared with other ions in perovskite precursors, the doses of Br− and NH4+ were very low. In consideration of the low addition dose, the transient phase was mainly the NH4PbI3 phase, which was identified by X-ray diffraction (XRD) measurements, as shown in Figure S1a (Supporting Information). Then, the temporarily remaining NH4+ was substituted by the subsequently precipitated MA+. After annealing, the transient phase disappeared, leaving only the perovskite phase. This indicated that the NH4PbX3-to-MAPbX3 transformation process occurred via organic-cation exchange between MA+ and NH4+ (process II, in Figure 1a), similar to the reported interaction behavior between CH3NH2 and NH4+.[32] The bonding between protonated MA+ and lead coordination complexes is stronger than that between CH3NH2 and lead coordination complexes. Thus, such a cation displacement reaction between MA+ and NH4+ readily occurs. Additionally, the NH4+ produced as a byproduct further facilitated the proposed cation exchange process, and no external residue remained, even without any posttreatment (process III, in Figure 1a). The temperature-dependent crystallization process with a transient phase was also identified by in situ GIXRD, as illustrated in Figure 1b.d. For the NH4Br-perovskite sample before annealing, in addition to the characteristic perovskite peak, another strong diffraction peak, (101), occurred at 2θ = 9.4°, which was associated with NH4PbI3.[33] When the perovskite was heated from room temperature to 100 °C within 35 min, the NH4PbI3-diffraction peak gradually disappeared after heating for 25 min, which effectively verified the formation and disappearance of the NH4PbI3 phase. The intensity of the (101) peak decreased until the peak disappeared during the annealing treatment, as shown in Figure S1b (Supporting Information). At the same time, the narrowing full-width at half-maximum (FWHM) of the (110) reflection of the perovskite indicated the enhanced crystallinity of the perovskite. Therefore, the in situ GIXRD results indicated the formation of NH4PbI3 after adding the lower-solubility NH4Br and the consumption of the transient phase via organic-cation exchange. The transient phase was also investigated by electron backscatter diffraction.[34] By comparing the test Kikuchi patterns and the transient dynamic patterns, we further verified the formation of the transient phase in the unannealed perovskite (Figure S6, Supporting Information).

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perovskite. The consumption of the transient phase was further validated by DFT, as shown in Figure S3 (Supporting Information), and the detailed calculation process is described in Note S1 in the Supporting Information. The DFT results show that the formation energy of MAPbI$_3$ from NH$_4$PbI$_3$ is $-0.6$ eV, which suggests the feasibility of the proposed phase transformation.[35] Additionally, thermogravimetric analysis (TGA), as depicted in Figure S4a (Supporting Information), was carried out to investigate the thermal stability of the transient phase. The TGA results further indicated that the introduced NH$_4^+$ disappeared in the form of NH$_3$ gas release, and no external residue remained, even without any posttreatment. Thus, the phase transformation based on the generation and consumption of NH$_4$PbX$_3$ has been verified via the aforementioned theoretical and experimental data.

To investigate the impact of NH$_4$Br on the morphology, field-emission scanning electron microscopy (FESEM) was used to collect the surface information. Mixed halide perovskites were prepared via a one-step spin deposition process based on the stoichiometric mixture of MAI and PbI$_2$ with additional NH$_4$Br in various molar ratios (mol%) relative to PbI$_2$. A wide range of surface morphologies of the perovskites was observed with increased NH$_4$Br dose at low magnification, as shown in Figure S4 (Supporting Information). Dense and full-coverage perovskite films were deposited after adding a small dose of NH$_4$Br. However, the unexpected precipitation marked by the circle emerged when the dose was increased to 10%. Additionally, detailed morphology information was observed at low magnification. As Figure S4b (Supporting Information) shows, compact and homogenous perovskite layers with an enlarged grain size owing to the increase of CNH$_4$Br were observed. Upon adding excess NH$_4$Br to the precursor solution, the average grain size increased from 164 to 804 nm, as estimated from the corresponding SEM images.

Figure 1. Schematic diagram of the A-site management strategy and in situ analysis. a) Schematic depiction of the perovskite formation process with NH$_4^+$ in the starting precursor solution. Process i: the entrance of NH$_4^+$ into the Pb–I framework to form the transient phase; process ii: the MA$^+$ and NH$_4^+$ cation exchange process; process iii: NH$_4^+$ disappearance in the form of NH$_3$ gas release. b) 2D intensity–time color mapping following the phase transformation process through the $(t$–$T)$ XRD profile. c) Surface potential difference evolution of the MA-based perovskite with NH$_4$Br as a function of the annealing time. d) 2D-GIXRD profiles of NH$_4$Br-perovskite films at different annealing temperatures. e) AFM morphology and f) surface potential difference of MA-based perovskite films with NH$_4$Br during annealing (for 20 min). Scale bar: 100 nm.
To further explore the perovskite film quality, XRD was employed, as shown in Figure 2a. The intensity of the (110) diffraction peak became stronger with increased additive dose, and its FWHM decreased from 0.18° to 0.13°. This result shows that the addition of NH₄Br can effectively improve the crystal quality of the perovskite with an enlarged grain size and preferred orientation (Figure S5d, Supporting Information). Such improved crystal quality is ascribed to A-site management. Additionally, the sample without the additive showed a tetragonal perovskite phase with distinctive (110), (220), and (310) diffraction peaks centered at 14.12°, 28.44°, and 31.88°, respectively, consistent with reported results. However, the crystal structure gradually changed with increasing NH₄Br dose. Generally, the introduction of Br ions with a small ionic radius (1.96 Å) into a perovskite instead of I ions (ionic radius: 2.2 Å) decreases the lattice parameters and results in a transition to an MAPbI₃₋ₓBrₓ structure. The magnified XRD patterns in the range of 27° to 30° show an apparent shift to higher 2θ values after NH₄Br addition, as shown in Figure 2b. At a 2% NH₄Br dose, the tetragonal (220), (200), and (211) peaks systematically shifted to higher 2θ values due to the...
decreased lattice spacing. Therefore, the perovskite structure changed from the tetragonal phase to a cubic phase when the NH4Br dose exceeded 2%. Such changes in the diffraction peak position indicated that the I ions in MAPbI3 were partially substituted by Br ions. Moreover, X-ray absorption fine-structure (XAFS) measurements were carried out to investigate the bond length between the Pb and I atoms in the perovskites. The XAFS curves in k-space (Figure 2c) demonstrate the interatomic distance between the lead and the adjacent iodide in the perovskites with and without NH4Br. Generally, the first peak (>1 Å) corresponds to the length between Pb and the nearest I atom. The Pb–I bond length of the perovskite with NH4Br decreased compared with that of the pristine perovskite, which indicated that the introduction of NH4Br changed the lead coordination complex framework by gradually replacing I with Br.

The charge separation and recombination dynamics of the perovskites were also investigated. The steady-state PL spectra in Figure 2d show that the intensities of the perovskite increased with increasing NH4Br concentration before reaching the highest level at a 2% dose. Afterward, the PL intensities began to inversely change. This phenomenon clearly reveals that the perovskite with 2% NH4Br addition has a relatively low nonradiative recombination loss, which supports the crystal quality improvement. Notably, though the introduction of 10% NH4Br enlarged the perovskite grain size, the unexpected precipitation severely deteriorated the crystal quality. Thus, the introduction of 10% NH4Br led to a high XRD intensity but a low PL intensity and a low device efficiency. Moreover, the arranged PL spectra in Figure 2e present a shift toward short wavelengths with increased NH4Br dose, consistent with the absorption spectra results. Additionally, TRPL spectra were collected (Figure 2f). By fitting the TRPL curves with a biexponential decay function, two time components were observed for both perovskite films. Generally, the fast-decay component (τ1) and long-decay component (τ2) are attributed to surface and bulk recombination, respectively. Both τ1 and τ2 increased with 2% NH4Br addition (see Table S1, Supporting Information). The calculated average charge carrier lifetime (τavg) of the pristine sample (34.08 ns) was prolonged to 192.18 ns in the 2% NH4Br-perovskite sample, demonstrating the reduced recombination in the perovskite film. For quantification analysis, the trap density was analyzed by fitting the PL decay curves based on the theoretical model (Note S2, Supporting Information). The fitted results demonstrated that the trap densities of the pristine sample and NH4Br-perovskite film were 2.78 × 1016 and 6.02 × 1015 cm−3, respectively, indicating that the trap density declined by an order of magnitude with NH4Br addition (Figure S5f, Supporting Information).

To trace the perovskite quality on the nanoscale, FLIM was employed to detect the variations in the PL intensity and the PL lifetime. Figure 2g shows a confocal fluorescence image of the perovskite film without the additive (average PL counts = 472.12). The confocal fluorescence lifetime image of the perovskite without the additive shows an average lifetime of 5.94 ns. The corresponding TRPL decay curve of the film is shown in Figure S8 (Supporting Information). With NH4Br addition, a higher average PL intensity (average PL counts = 2860.79) was observed, as shown in Figure 2i. In addition, the NH4Br additive could activate previously green regions in the film and prolong the average lifetime to 17.66 ns, as shown in Figure 2j. Both the higher PL intensity and the longer PL lifetime are associated with NH4Br addition. Normally, the spatial variation in the PL intensity indicates the local nonradiative recombination rates. Therefore, the NH4Br additive effectively improved the crystal quality, with reduced nonradiative recombination sites. Importantly, the above trends are consistent with the macroscopic steady-state and TRPL decays in Figure 2d,f. The difference between the fluorescence microscopy results and the macroscopic PL results can be ascribed to the different excitation fluences.

For the surface defect investigation, Kelvin probe measurements were performed in the dark under different light intensity conditions to monitor the surface photovoltage (SPV) of the perovskites without and with the NH4Br additive. The difference in the work functions under dark and illumination conditions is defined as the SPV, which indicates the surface redistribution of photogenerated charges. As shown in Figure 3a, the trap states at the perovskite surface accumulate electrons, subsequently giving rise to surface band bending. Under illumination, the photogenerated carriers are swept to the surface to screen the trapped carriers, which mitigates the degree of band bending. The change in the magnitude of the band bending at the surface can be represented by the SPV. Consequently, the SPV is indicative of the density of the surface states. Generally, more surface states lead to a larger magnitude of band bending and higher SPV. As shown in Figure 3b, we performed SPV measurement of the perovskites without and with the NH4Br additive and found that the work functions of both perovskite films declined with increasing illumination intensity. The corresponding surface potential differences of the perovskite films on fluorine-doped tin oxide (FTO) glass are shown in Figure 3c. The SPV of the perovskites was reduced from 251.98 to 157.68 mV after NH4Br addition, which manifested a lower density of trap states at the surface.

We constructed solar cells based on the MAPbI3 perovskite films with different CNH4Br to identify the perovskite quality improvement, as shown in Figure 3d. The PCE was enhanced with increased NH4Br dose and reached the highest level in the 2% NH4Br-perovskite sample. The statistical data on the NH4Br concentration effect on the PV parameters are presented in Table S2 (Supporting Information). With 2% NH4Br, the PSC yielded the best PCE of 20.61% in the reverse-scan direction. To obtain the real PCE, we measured the stabilized power output of PSCs without and with the NH4Br additive over a 250 s time span. As shown in Figure S9c (Supporting Information), a stabilized photocurrent density of 21.11 mA cm−2 and a stabilized efficiency of 20.26% were achieved at the maximum power point (0.96 V) for the PSC with 2% NH4Br. The corresponding external quantum efficiency spectra of the 2% NH4Br-based device indicated a high quantum yield across a wide spectral range, and the integrated photocurrent density was 23.06 mA cm−2, in agreement with the aforementioned PV result, as presented in Figure S9d (Supporting Information). In addition to the PCE, the open-circuit voltage (Voc), short-circuit current density (Jsc), and fill factor (FF) were also initially augmented and subsequently decreased with increasing additive dose, as illustrated in Figure S9e (Supporting Information). The NH4Br-based PSCs exhibited a higher Voc due to the increased bandgap resulting from Br substitution and improved crystal
Photocurrent mapping was also used to trace the enhanced photoresponse of PSCs with NH$_4$Br addition, as shown in Figure S11 (Supporting Information). In addition, stability testing of both pristine and NH$_4$Br-based PSCs stored in the dark was carried out, as depicted in Figure 3g. The NH$_4$Br-based PSC showed improved device stability, with a retention of almost over 90% of the initial level after 1000 h of exposure. Moreover, we introduced other NH$_4^+$-based additives...
(NH₄I and NH₄Cl) into the MA perovskite and confirmed the corresponding positive effects on the perovskite crystal quality and PSC performance, as shown in Figure S10a (Supporting Information). We also fabricated mixed-cation PSCs to study the influence of the NH₄Br additive, as shown in Figure 3e. Compared with the pristine sample, the mixed-cation perovskite with A-site management showed an enhanced $J_{sc}$ of approximately 23.64 mA cm$^{-2}$, a high $V_{oc}$ of 1.139 V, and an improved FF of approximately 80.45%, which eventually contributed to the high PCE of 21.67%. Therefore, we have demonstrated the feasibility of using this type of additive for MA-based perovskite improvement, as well as the universality of introducing such a protocol into other mixed-cation perovskite systems.

To gain further insight into the influence of the A-site management strategy on the perovskite crystal quality, both theoretical and experimental methods have been proposed. DFT calculations were used to investigate the band structures. The calculated bandgap of a perfect perovskite crystal was $\approx 1.62$ eV, which was close to the experimental value, as shown in Figure 4a.$^{[18]}$ We further confirmed the energy levels of related A-site defects, including MA$^+$ vacancy ($V_{MA}$), I$^{-}_{MA}$, and Pb-on-MA antisite (Pb$^{\text{MA}}$) defects. As shown in Figure 4b, the formation of $V_{MA}$ induced a shallow defect level located 0.505 eV below the valence band maximum (VBM). According to the band structure plots in Figure 4c,d, the I$^{-}_{MA}$ and Pb$^{\text{MA}}$ defects created deep defect levels within the bandgap, located 0.634 and 0.457 eV below the conduction band minimum (CBM), respectively. Experimentally, the TA technique was conducted to investigate the defect states by monitoring the bleach signals.$^{[50,51]}$ Figure 4e,f shows pseudocolor TA plots of the perovskite films as a function of the pump wavelength and pump-probe delay time. Each perovskite sample was photoexcited by a pump laser pulse at 400 nm and probed by a white-light supercontinuum. The $-\Delta T/T_0$ values above 850 nm are multiplied by a factor of 2. Pump: 400 nm, $\approx 120$ fs, 30 µW. Probe: white-light supercontinuum, $\approx 200$ fs, $\leq 0.1$ µJ cm$^{-2}$ pulse energy density. $g$) DLTS spectra of MA-based perovskites without and with NH₄Br, measured from 380 to 150 K.

![Image of Figure 4: A-site defect analysis.](image-url)

- **a)** Calculated band structure of the perfect perovskite. **b-d)** The calculated defect levels for the $V_{MA}$ (b), I$^{-}_{MA}$ (c), and Pb$^{\text{MA}}$ (d). The red lines represent the defect levels. The insets are the local structures of the perovskite with A-site-related defects. **e,f)** Pseudocolor TA plots at varying probe wavelengths and probe delay times for MA-based perovskites without (e) and with (f) NH₄Br. The $-\Delta T/T_0$ values above 850 nm are multiplied by a factor of 2. Pump: 400 nm, $\approx 120$ fs, 30 µW. Probe: white-light supercontinuum, $\approx 200$ fs, $\leq 0.1$ µJ cm$^{-2}$ pulse energy density. **g)** DLTS spectra of MA-based perovskites without and with NH₄Br, measured from 380 to 150 K.
the transient phase \( \text{NH}_4\text{PbX}_3 \). Then, the temporarily remaining \( \text{NH}_4^+ \) was substituted by the subsequently precipitated MA\(^+\). Such an A-site management strategy eventually resulted in a highly crystalline perovskite with an enlarged grain size, a lowered nonradiative defect density, and a prolonged carrier lifetime. Most importantly, the sharp decrease in the number of A-site-related \( \text{I}_\text{MA} \) defects indicated that this defect should be responsible for such crystal optimization. Additionally, the universality of the proposed A-site management strategy was verified in other mixed-cation perovskite systems. Such a methodology of introducing a placeholder cation for A-site management may provide an impetus to effectively promote perovskite evolution.

**Experimental Section**

**Materials and Device Fabrication:** All the materials were used directly as received without further purification. For details on the materials used for the MA perovskite and the corresponding fabrication procedure, the reader can refer to the previously reported work.[27] The CsFAMA perovskite was prepared by mixing \( 1.35 \text{ mF A}^+, \text{FABr}^-, \text{MAI}, \text{CsI}, \text{PbI}_2^-, \text{and \ PbBr}_2 \) in anhydrous dimethylformamide/dimethylsulphoxide (4:1 volume ratio). This perovskite precursor solution was deposited onto the prepared substrate at 1000 and 6000 rpm for 30 s. Then, 250 \( \mu \text{L} \) chlorobenzene solution was dropped onto the substrate. Thereafter, the films were placed on a hotplate for 35 min at 150 °C. For the \( \text{NH}_4\text{Br}\)-perovskite solution, different amounts of \( \text{NH}_4\text{Br} \) were added to the perovskite solution (at molar ratios of \( \text{NH}_4\text{Br} \) to \( \text{PbI}_2 \) of 1%, 2%, 3%, and 10%). Before use, these prepared solutions were filtered using a hydrophilic PTFE syringe filter. For the complete devices, the electron-transporting layer of \( \text{TiO}_2 \) was treated with \( \text{TiCl}_4 \) solution according to previous work.[36] The hole-transporting solution prepared by dissolving 85 mg \( 2,2'7,7' \text{tetrakis(N,N-di-p-methoxyphenylamine)-9,9' \text{spirofluorenone (spiro-MeOTAD)} \), 28.8 \( \mu \text{L} \) \( 4 \text{-tert-butylpyridine, and 17.8 } \mu \text{L of a stock solution (520 mg mL}^{-1} \text{lithium bis(trifluoromethanesulfonfyl)imide in acetonitrile)} \text{ in } 1 \text{ mL chlorobenzene was spin coated (4000 rpm, 20 s)} \) onto the perovskite film in a glovebox. Finally, an 80 nm thick gold electrode was deposited on the hole-transporting materials (HTM) surface by thermal evaporation. All devices were stored and tested in an atmospheric environment. The synthesized transient phase was obtained by spin coating a solution of \( \text{NH}_4\text{I} \) and \( \text{PbI}_2 \) at an equal molar ratio onto the FTO substrate.

**Characterization:** The current–voltage characteristics were recorded using an electrochemical workstation (Solartron SI1287/SI 1260) under simulated solar illumination (Oriel, 91159A, 100 mW cm\(^{-2}\)) and ambient environment. The current–voltage curves were measured through forward (–0.3 to 1.3 V forward bias) or reverse (1.3 to –0.3 V) scans in air. A mask of 0.09 cm\(^2\) was used for the current–voltage measurements. Before each measurement, the exact light intensity was determined using a calibrated Si reference diode. All devices were stored in the dark with a relative humidity of approximately 20 ± 5 RH%. The devices were tested without encapsulation (the devices were exposed directly to the environment, without any cover) in ambient environment at 26 °C with 20–30 RH% humidity. The morphologies of the samples were characterized by FESEM (FEI QUANTA 3D FESEM). XRD patterns were used to identify the crystal phases of the materials and were collected by a Rigaku DMAX-RB equipped with a Cu Kα X-ray radiation source. The Fourier-transform infrared spectroscopy spectra were recorded on an Excalibur 3100 spectrophotometer with the perovskite on calcium fluoride glass. The elemental contents of the perovskite samples were determined using energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy (ThermoFisher Scientific, ESCALAB250Xi). Time-correlated single-photon counting data sets were acquired on an inverted OLYMPUS FV1000 microscope with a 100x/1.4 NA lens equipped with a PicoQuant picoHarp 300 (Germany) controller. Samples were excited by 485 nm picosecond pulses generated by a 40 MHz laser. The non-descanned emission was collected from a 561 nm longpass filter (PicoQuant, Germany) and detected by an MPD SPAD detector (PicoQuant, Germany). Images of 512 × 512 pixel size were obtained. Photon data were analyzed using the SymPhoTime 64 image software. A commercial atomic force microscope (AFM; Bruker Dimension, ICON) was employed to investigate the surface potential. Doped silicon PFQNE-Al cantilevers were used for KPFM to improve the spatial resolution of the surface potential. The samples were deposited onto FTO glass. SPV measurements were carried out under illumination in ambient conditions. The work function of the AFM probe was calibrated by clean gold with a known work function (5.1 eV). The incident photon conversion efficiency spectra were measured using a Keithley 2400 source meter with a 1/4 m monochromator (Spectral Product DK240) under the irradiation of a 150 W tungsten lamp. The UV-visible absorption spectra were obtained on an UV–vis–NIR spectrophotometer (HITACHI, U-2800 122-0003). XAFS measurements (Pb K-edge) were performed at the Wiggler beamline BL14W1 of the Shanghai Synchrotron Radiation Facility. The electron beam energy of the storage ring was 3.5 GeV with a maximum stored current of 300 mA. The static PL spectra were obtained on a PL spectrometer, HORIBA, FL3 1097C-4608, under excitation at 514 nm. TRPL measurements were performed using a PL spectrometer (Edinburgh Instruments, FLS 900) with a pulsed diode laser (EPL-470, pulse width 91.5 ps) at a pulse frequency of 1 MHz. The samples for the PL experiments were prepared on FTO substrates. The excitation wavelength for the PL measurements was 470 nm, with an emission wavelength of 774 nm.

**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.

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