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The collective and individual impacts in perovskite single crystals by cascade doping of alkal /DOTC03085F cations

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#### Abstract

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The alkali ions (Cs<sup>+</sup>, Rb<sup>+</sup> and K<sup>+</sup>) incorporated hybrid perovskite polycrystalline films have shown great potential in obtaining more efficient and stable perovskite solar cells. The intrinsic influence of different alkali ions on perovskites is urgently needed to gain insight into the optoelectronic performance improvement. Single crystals with less defects can be an ideal candidate for the intrinsic property study. Herein, for the first time, we prepared a series of perovskite (FA<sub>0.85</sub>MA<sub>0.15</sub>PbI<sub>2.55</sub>Br<sub>0.45</sub>) single crystals with Cs<sup>+</sup>, Rb<sup>+</sup>, K<sup>+</sup> cascade doping through "inverse temperature crystallization" method, and systematically characterized their structure and optoelectronic properties, as well as phase, humidity and thermal stability. Our work highlights the structure-property relationship, that is, the diversified A-site occupation (especially FAMACsRb system) can significantly promote the carrier transport behavior of perovskites, as well as obtaining better thermal and humidity stability, while K<sup>+</sup> doping weakens the intrinsic properties of perovskites which probably due to the interstitial occupation of K<sup>+</sup>. These findings deepen the understanding of alkali ions doping on the intrinsic properties influence of perovskite materials, which providing an exemplary paradigm for further explorations.

#### Introduction

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The power conversion efficiency (PCE) of organic-inorganic perovskite (ABX<sub>3</sub>, where A is a monovalent cation, such as methylammonium (MA<sup>+</sup>), formamidinium (FA<sup>+</sup>) or Cs<sup>+</sup>; B is divalent cation normally Pb<sup>2+</sup> or Sn<sup>2+</sup>; X is a halide ion, e.g. Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>) solar cells (PSCs) has achieved 25.2%, which mainly originated from the perovskite component optimization, process engineering, device structure adjustment and additive engineering, etc.<sup>1-5</sup> Particularly, alkali metal ions (Cs, Rb, K, etc.) doping has shown great potential in improving the efficiency and stability of PSCs, through either acting as the perovskite composition or serving as an additive. Previous studies have shown that the doping of alkali ions mainly brings the following effects:

1) To interfere carrier behavior in the material. For example, Saliba et al. doped Rb into (FA, MA, Cs)Pb(I, Br)<sub>3</sub> perovskites and proved that the density of defect states was greatly reduced and non-radiative recombination was suppressed.<sup>6</sup> Hu et al. studied the effect of Cs, Rb doping on the carrier transport and defects in the polycrystalline perovskite films, which had less defects, large carrier mobility, and thus the high stable output power of the devices.<sup>7</sup> With regard to K ion doping, Park et al. speculated that the formation energy of interstitial K was small due to its

2)

smaller ion radius, which inhibited the formation of Frankel I<sup>-</sup> defects, and reduced the/DOTC03085F hysteresis.<sup>8</sup> Abdi-Jalebi et al. demonstrated substantial mitigation of both non-radiative losses and photoinduced ion migration in perovskite films and interfaces by decorating the ((Cs<sub>0.06</sub>FA<sub>0.79</sub>MA<sub>0.15</sub>)Pb(I<sub>0.85</sub>Br<sub>0.15</sub>)<sub>3</sub> surfaces and grain boundaries with passivating KI layers.<sup>9</sup> To improve materials stability. On one hand, Cs and Rb can partially replace the A-site ions to participate in the lattice, which can improve the phase stability of the formamidinium (FA) based perovskite. On the other hand, appropriate amount of K and Na, as interstitial ions, can improve the stability by blocking the ion migration channel and reduce the device hysteresis.<sup>8</sup>.

- <sup>10, 11</sup> For instance, Lee et al. firstly studied the stability of (FA, Cs)PbI<sub>3</sub>, and found that the phase stability of perovskite film against illumination and moisture were significantly improved when 10% of FA was replaced by Cs, which was attributed to the enhanced interaction between FA and iodide due to contraction of cubo-octahedral volume.<sup>10</sup> Meanwhile, Zhou et al. introduced Cs into FA-based perovskite in a two-step method and obtained largely improved phase stability of polycrystalline perovskite films.<sup>12</sup> Further, MA-free (FA, Cs, Rb)PbI<sub>3</sub> perovskite system developed by Turrencruz et al. exhibited excellent stability due to improved crystal quality and the stability of the composition itself.<sup>13</sup>
- 3) To adjust film quality and crystal orientation. Many works have shown that alkali ions will participate in and affect the crystallization kinetics of perovskite films. For instance, Chang et al. found the Na or K doping could increase the grain size of the perovskite film and thus improved the charge carrier lifetime.<sup>14</sup> Zheng et al. reported a controllable approach to manipulate the facet orientation within the ABX<sub>3</sub> hybrid perovskites polycrystalline films by cation cascade doping at A-site, which was found to facilitate photocarrier transport across the absorber and pertaining interface in the resultant device.<sup>15</sup>

Despite the above-mentioned progress, most studies were conducted on perovskite polycrystalline films to improve the stability and efficiency of the resulting devices. However, the defects in polycrystalline films are difficult to be decoupled to understand the intrinsic properties of alkali ions-doped perovskites. Compared to polycrystalline films, single crystals are regarded as the best platform to reflect the intrinsic materials properties for fundamental understanding due to its low defects density and simple structure. Up to now, it lacks the understanding on the effect of the alkali ions doping on perovskite single crystals, and it is worthy to establish a correlation between doping ions and intrinsic properties of perovskite materials.

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In this work, we synthesized a series of  $FA_{0.85}MA_{0.15}Pb(I_{0.85}Br_{0.15})_3$  single crystals with series of alkali ions cascade doping, and systematically characterized the effect of these ions on the optoelectronic and stability properties of perovskites. First of all, we determined the exact content of alkali metal ions in each single crystals. Further, we found that all single crystals belonged to the simple cubic phase in the temperature range from 180 K to 360 K, except FAMACsRbK perovskite which changed to a body-centered cubic phase at 180 K. However, their carrier dynamics varied dramatically. Compared to FA0.85MA0.15Pb(I0.85Br0.15)3 (FAMA) single crystals, the alkali ions doped ones exhibit fewer defects, improved carrier lifetime and mobility. Interestingly, CsRb and Cs doping led to single crystals outperformed that of the CsRbK doping. Moreover, the CsRb doped single crystals possessed the best moisture and thermal stability. Deep study revealed that the alkali ions occupied different sites of the perovskite lattice, which mainly contributed to the properties variation. Simply, the richer occupant diversity at A-sites (CsRb), the more improvement in materials properties, but the interstitial occupants of alkali cations (K) will decrease materials performance. The mechanism of K doping effects is discussed in detail. The understanding about the alkali doping on the intrinsic materials properties shed light on the application of perovskite in the various optoelectronic devices, such as solar cells, light-emitting diode, lasers and photodetectors.

#### **Results and Discussion**

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The Cs, Rb, K cascade doped FA<sub>0.85</sub>MA<sub>0.15</sub>Pb(I<sub>0.85</sub>Br<sub>0.15</sub>)<sub>3</sub> single crystals in this work were simply marked as FAMACs, FAMACsRb, FAMACsRbK, respectively. Due to retrograde solubility of perovskite in γ-butyrolactone solvent, we adopted "inverse temperature crystallization" method to synthesize the single crystals as showed in **Figure 1a**, and introduced Cs, Rb, K cations through the addition of KI, RbI and CsI compounds to keep the fixed ratio of I/Br in the precursors solutions.<sup>16, 17</sup> After forming the single crystal seeds by continuously heating the solutions, we lifted the solution temperature by 1 °C at interval of 1 h. Since the nucleation consumed solutes then reduced the supersaturation of solution and the growth speed of crystals, increasing the temperature during the growth process could provide enough supersaturation and supply the solutes timely, which accelerated the growth process and improved the quality of single crystals. More growth details can be found in experimental section.



**Figure 1.** (a) Schematic diagram of perovskite single crystal growth. The photos of single crystals: (b) FAMA, (c) FAMACs, (d) FAMACsRb, and (e) FAMACsRbK. The (0kl) diffraction patterns of single crystals at different temperature: (f) FAMA, (g) FAMACs, (h) FAMACsRb, (i) FAMACsRbK single crystals at room temperature; (j) FAMA, (k) FAMACs, (l) FAMACsRb, (m) FAMACsRbK single crystals at 180 K. (n) FAMA, (o) FAMACs, (p) FAMACsRb, (q) FAMACsRbK single crystals at 360 K.

The photos of various single crystals (**Figure 1b-e**) showed that they had an average size of A3mm/DOTCO3085F with uniform size distribution. All crystals were black with regular rhombic dodecahedron shapes, indicating the availability of the inverse temperature crystallization method. Most importantly, this phenomenon suggested that the involvement of alkali ions had no dramatically impact on the nucleation and growth process of FAMA single crystals.

We first performed a detailed characterization of its actual alkali metal ions content through inductively coupled plasma-atomic emission spectrometry (ICP-AES). The ratio of each alkali ion to Pb determined by ICP-AES was shown in **Table 1**. In order to eliminate the influence of surface residues, the newly prepared crystals were washed three times with  $\gamma$ -butyrolactone before the test. **Table 1**. The actual ratio of each alkali ion to Pb in the perovskite single crystal.

	Cs/Pb	Rb/Pb	K/Pb
FAMACs	4.1%	0	0
FAMACsRb	4.2%	0.11%	0
FAMACsRbK	4.1%	0.07%	0.2%

The actual content of Cs was about 4.1%, which was close to the feed ratio in the precursor. Due to the mismatched ion radius, the actual doping content of Rb and K was very low (~0.1%), but not zero, which indicated that the cascade doping method could introduce a small amount of Rb or K into the bulk perovskite. In contrast, Rb could hardly be detected in FAMARb samples (only Rb doped, see the experimental section for details). However, the actual positions occupied by different alkali metal ions in the perovskite lattice may be different, which will be discussed later.

To further demonstrate the phase evolution of single crystals, we performed single crystal X-ray diffraction (XRD) characterization under different temperature. The *(0kl)* diffraction patterns of single crystals at room temperature (~300 K) were listed in the **Figure 1 f-i**, and the corresponding patterns at low (180 K) and high (360 K) temperature were listed in **Figure 1 j-m** and **Figure 1 n-q**, respectively. The diffraction patterns of all single crystals were clear, indicating the high quality of single crystals. Previous studies have shown that the FA<sub>x</sub>MA<sub>1-x</sub>PbI<sub>3</sub> perovskite single crystal would change from a cubic phase to a tetragonal phase when the temperature reduced from room temperature to 255-285 K.<sup>18</sup> However, our results indicated that the FAMA single crystals always maintained a pure cubic phase at varied temperatures (**Figure 1, f, j, n**). This may be related to the 15% bromine substitution in the composition, which brought into stabilizing effect on the cubic

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phase due to the reduced defect density.<sup>19</sup> In addition, both FAMACs and FAMACsRb: single/DOTC03085F crystals maintained the pure cubic phase at all temperature points, further proving that Cs and CsRb doped perovskites obtained good phase and thermal cycling stability. However, FAMACsRbK perovskite maintained a cubic phase at 300K and 360K, while they changed to a body-centered cubic phase at 180K, indicating the phase instability associated with K ions doping. We speculated that K ions actually occupied interstitial instead of the A-site due to the unmatched ionic radius of K ion to accommodate the A-site occupation, which led to phase instability. The effect of interstitial K ions will be discussed further below.

In order to observe the effect of Cs, Rb, K cascade doping on the perovskite lattice constant, we grinded single crystals and performed the powder X-ray diffraction (PXRD) measurement. The normalized PXRD data were shown in the **Figure 2**, and the diffraction peak at 14.1°, 20.0°, 24.6°, 28.4°, 31.87°, 35.0° (**Figure 2a**) was assigned to the (001), (011), (111), (002), (012), (112) crystal plane<sup>20</sup> of the cubic phase perovskites, respectively. We then selected the peak of (012) which centered at 31.8-32° to analyze the peak position shift in detail. (**Figure 2b**) The positions of the (012) peak corresponding to FAMA, FAMACs, FAMACsRb, and FAMACsRbK were 31.85°, 31.89°, 31.91°, and 31.90°, respectively, which clearly indicated that the decrease of lattice parameter in cascade doped single crystals followed the sequence from FAMA, FAMACs, to FAMACsRb.

It was also observed that the peak shift from the FAMACs to FAMACsRb is smaller than that from FAMA to FAMACs sample, which indicated that Cs could easily incorporate into the lattice of the FAMA sample to significantly reduce the perovskite lattice constant, while Rb could only partially enter the lattice and occupy the A-site so that the peak shift tendency upon Rb doping was decreased. Further analyzing FAMACsRbK, we found that the corresponding lattice constant did not decrease further, which indicated that K cannot substitute the A-site within perovskite lattice due to its too small size. We speculated that K may be incorporated into the lattice in the form of interstitial ions and then affected the carrier behavior of perovskites as shown in following characterizations.<sup>8</sup> **Figure 2c** showed the possible occupation of different alkali metal ions in the FAMA based crystal lattice.



**Figure 2.** (a) The powder X-ray diffraction (PXRD) data of single crystals: FAMA, FAMACs, FAMACsRb, and FAMACsRbK; (b) The magnified PXRD at the range of 31.4 ° to 32.3 °. And (c) Schematic diagram of lattice with speculated alkali ions occupation.

We characterized the optoelectronic properties of single crystals by measuring their UV-Vis absorption, photoluminescence (PL), and the time-resolved photoluminescence (TRPL) spectra. It can be seen from **Figure 3a** that the absorption band edge was located at 820 nm, which was about 50 nm red-shifted compared to the PL peak position. This anti-Stokes shift was always observed in perovskite crystals with a certain thickness, which was caused by below-bandgap absorption.<sup>21</sup> Thus, the absorption spectrum of the single crystals cannot reflect its optical band gap well. At the same time, PL always originated from the direct band gap. Therefore, for perovskite single crystals, PL was a more reliable method to determine the optical band gap due to the existence of large anti-Stokes shift. The PL emission peaks of FAMA, FAMACs, FAMACsRb, FAMACsRbK single crystals were located at 762 nm, 765 nm, 767 nm, and 768 nm, and the corresponding band gaps were 1.627, 1.621, 1.617 and 1.615 eV, respectively. This red-shift along with the Cs, Rb, K cascade

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doping indicated the reduced bandgap of corresponding single crystals. It is generally recognized/DOTC03085F that for hybrid ABX<sub>3</sub> perovskite, the conduction band minimum (CBM) and valance band maximum (VBM) are mainly composed of Pb 6p orbitals, hybrid orbitals of Pb 6s and X 5p, respectively.<sup>22</sup> However, the size of A-site ions still can affect the orbitals overlapping of Pb and X, then resulting in the band gap variations of perovskites. Therefore, we speculated that the small amount of Cs, Rb, K cascade doping induced the shrinking of crystal lattice (**Figure 2b**), thus increasing the overlap of Pb and X and then decreasing the band gap.<sup>23</sup>

The TRPL spectra of single crystals are shown in **Figure 3b**, and carrier lifetime extracted from the bi-exponential fitted TRPL spectra are listed in the **Table 2**. The short lifetime ( $\tau_1$ ) corresponds to the surface recombination process, where the surface traps assisted the carrier recombination.<sup>24</sup> The long lifetime  $(\tau_2)$  resulted from the bulk recombination process, in which the electron from CBM recombined with the hole from VBM.<sup>25</sup> The long  $\tau_1$  and  $\tau_2$  indicated low surface defects and high quality of single crystals. Compared to FAMA single crystals with  $\tau_1$ =16.30 ns and  $\tau_2$ =971.67 ns, both  $\tau_1$  and  $\tau_2$  greatly improved in FAMACsRb and FAMACs single crystals (FAMACs:  $\tau_1$ =24.13 ns,  $\tau_2$ =1832.52 ns; FAMACsRb:  $\tau_1$ =29.14 ns,  $\tau_2$ =1739.20 ns), while the FAMACsRbK single crystals exhibited shorter  $\tau_1$ =10.55 ns and longer  $\tau_2$ =1537.31 ns. In addition, the proportions of  $\tau_1$ and  $\tau_2$  components in FAMA were 77% and 23%, respectively, indicating strong surface nonradiative recombination. The proportion of the  $\tau_1$  component decreased from 77% to 74%/70% after the Cs/CsRb doping, while that of FAMACsRbK rose to 80%. It was concluded that Cs, Rb cascade doping could improve the bulk quality of single crystals, among them, the FAMACsRb and FAMACs single crystals exhibited the highest carrier lifetime, which was in line with previous work that doped alkali metal ions into polycrystalline perovskite thin films.<sup>7</sup> Meanwhile, longer  $\tau_1$  and lower proportion of  $\tau_1$  in FAMACsRb and FAMACs single crystals suggested that the surface defects recombination was effectively inhibited in these samples, which may be due to the better defects passivation of Cs and Rb. Compared with Cs and CsRb, the cascade doping of K ions weakened both  $\tau_1$  and  $\tau_2$ , which fully proved that interstitial doping will have a negative impact on carrier lifetime.

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**Figure 3.** (a) The photoluminescence (PL) emission / UV-Vis absorption spectra, and (b) the timeresolved photoluminescence spectra (TRPL) of single crystals: FAMA, FAMACs, FAMACsRb, FAMACsRbK single crystals. (c) X-ray absorption near edge structure (XANES) and (d) extended Xray absorption fine structure (EXAFS) of Pb(FAMACs) and Pb(FAMACsRb).

Lifetime	FAMA	FAMACs	FAMACsRb	FAMACsRbK
$\tau_1 / ns$	16.30	24.13	29.14	10.55
$\tau_2$ / ns	971.67	1832.52	1739.20	1537.31

Table 2. The carrier lifetime extracted from bi-exponential fitted TRPL in Figure 3b.

In addition, in order to understand the influence of the alkali metal ions cascade doping on the microstructure of perovskites, we performed X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) characterization on the FAMACs and FAMACsRb single crystals. The experimental details were shown in the characterization section. XANES is useful in identifying the chemical state of the absorbing element and hence inferring its chemical species. For FAMACs and FAMACsRb, the Pb L<sub>3</sub> edge energy positions ( $E_0 = 13035.0$  eV) were not changed as showed in **Figure 3c**, which indicated there were no detectable changes in

the oxidation state of Pb(II) in these two samples. Further, the fine structure from the X-ray/DOTCO3085F absorption spectra in the high energy range (beyond the ionization potential) is a powerful tool to determine the chemical environment such as interatomic distances.<sup>26, 27</sup> Thus based on the R space EXAFS data (**Figure 3d**), we could conclude that FAMACs and FAMACsRb have the same local coordination structure around Pb sites. Therefore, the microstructure of alkali metal ions doped perovskites showed no visible difference, which excluded the possible interaction between alkali metal ions and Pb ions.



Figure 4. The dark current-voltage curve of ITO/NiOx/perovskite/Au devices according to the SCLC model: (a) FAMA, (b) FAMACs, (c) FAMACsRb, (d) FAMACsRbK.

To explore the effect of Cs, Rb, K cascade doping on the carrier mobility of perovskite single crystals, we performed space-charge-limited current (SCLC) measurement. The dark J–V curves were obtained based on the ITO/NiO<sub>x</sub>/perovskite single crystal/Au structure. The traps density ( $n_{trap}$ ) and mobility ( $\mu$ ) was estimated according to the equation  $J_D = 9\epsilon\epsilon_0\mu V^2/8L^3$  and  $V_{TFL} = en_t L^2/2\epsilon\epsilon_0$ , respectively. **Figure 4** showed the measured and calculated results for all single crystals. It can be seen that the mobility of FAMA single crystals approached 21.69 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, which was consistent

with our previous reports<sup>28</sup>, while the mobility of Cs, CsRb, CsRbK doped perovskite single@crystals/DOTC03085F were 41.69 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, 46.43 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, 36.21 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, respectively. The enhanced mobility and reduced traps density for Cs, Rb, K cascade doped perovskites implied the higher quality of corresponding single crystals, which was in accordance with our TRPL results.

Based on these results, we speculated that FAMACsRb and FAMACs single crystals had higher quality than the FAMA, and we contribute this to the contraction of cubo-octahedral volume upon Cs and Rb doping, which in turn enhancing the interaction between A-site ions and iodide, and greatly reducing the trap density. However, although FAMACsRb single crystals exhibited the highest carrier mobility which was consistent with the results of the CsRb doped polycrystalline films,<sup>7</sup> we still argued that there are some difference between the published results and our work: the doped Rb ions mainly located at the grain boundaries (GBs) of the polycrystalline film, however, the doping of Rb in single crystals (without GBs) still improved the corresponding carrier mobility, indicating that Rb could also play a positive role in the perovskite bulk through partial A-site substitution. The stable cubic phase and large carrier mobility of CsRb doped perovskite system highlight the potential application in fabricating high-efficiency PSCs. Unexpectedly, K cascade doping significantly reduced carrier mobility compared to FAMACs and FAMACsRb, which was not consistent with the trend in polycrystalline films of previous report<sup>9, 14</sup>. The results based on single crystal platform fully indicated that interstitial doping will decrease the carrier mobility of perovskite, but K ions may had a passivating effect on the interface and grain boundaries of the polycrystalline film, so their overall effect is positive.

For further application of perovskite materials toward commercialization, the highly-efficient PSCs should also have the competitively intrinsic stability of absorber. To characterize the humidity and thermal stability of alkali metal ions doped perovskites, we measured the PXRD after heating the single crystals powder at 300 °C under 85% relative humidity (RH) for 5 min (**Figure 5a**). The intensity of perovskite (001) diffraction peak were normalized to compare the relative content of secondary phase (PbI<sub>2</sub>). For freshly prepared single crystals, the signal of PbI<sub>2</sub> was absent (**Fig. 2a**), however, PbI<sub>2</sub> emerged in all aged single crystals at 300 °C under 85% RH for 5 min, indicating the partial decomposition of perovskites after humidity and thermal stressors.



**Figure 5.** (a) PXRD of FAMA, FAMACs, FAMACsRb, FAMACsRbK single crystals powder after heating at 300 °C and 85% relative humidity for 5 min. (b) the ratio of the (001) peak intensity of  $PbI_2$ at 12.7° compared to the (001) peak intensity of each perovskite at 14.1°. (c) Proposed mechanism diagram of alkali ions doping improves the humidity and thermal stability of perovskite.

Further, we used the ratio of the (001) peak intensity of PbI<sub>2</sub> at 12.7° compared to the (001) peak intensity of perovskite at 14.1° to quantify the decomposition degree of single crystal (**Figure 5b**). The FAMA single crystal exhibited the most severe decomposition, with the ratio of PbI<sub>2</sub>/perovskite reaching 12%. Fortunately, all alkali metal ions doped single crystals could effectively suppress the decomposition of perovskites. Among them, FAMACsRb showed the best resistance to humidity and heat, and the PbI<sub>2</sub>/perovskite ratio was only 3%. The other two kind of perovskite single crystals, FAMACsRbK and FAMACs had relatively poor resistance to heat and humidity, with the PbI<sub>2</sub>/perovskite ratio keeping at 5% and 7%, respectively. Specifically, the doped Cs and Rb could occupy the A-site and reduce the intrinsic defects (most of which are vacancy defects) density of single crystals, which was proved by our SCLC measurement.<sup>29, 30</sup> Combining with the reported

View Article Online results<sup>31, 32</sup>, we reasonably speculated that vacancy defects are the important channels for watep/DOTCO3085F molecules invading on perovskite single crystals, so FAMACs and FAMACsRb with fewer vacancy defects and tighter lattices exhibited significantly improved moisture and heat resistance stability. Proposed mechanism diagram was showed in **Figure 5c**. On the contrary, the cascade doping of CsRbK reduced the resistance to moisture and heat. According to previous studies, we attributed this phenomenon to the microstrain increasing caused by a small amount of K ions which occupied interstitial sites of perovskite crystal.<sup>15</sup> Overall, the FAMACsRb perovskite exhibits excellent humidity and thermal stability, as well as the best carrier performance, which ensure its greater prospect of wide application.

#### Conclusion

We systematically synthesized FA<sub>0.85</sub>MA<sub>0.15</sub>PbI<sub>2.55</sub>Br<sub>0.45</sub> single crystals doped with Cs<sup>+</sup>, Rb<sup>+</sup>, K<sup>+</sup> in a cascade manner to analyze their collective and individual impacts on the intrinsic properties of perovskite. The results revealed that the cascade doping of alkali ions with smaller size could reduce the lattice constant and shrink the energy band gap. With various characterizations, it was found that the optoelectronic and carrier transport properties were improved profoundly upon CsRb and Cs cation doping, while the effect is reduced upon CsRbK doping. Among all perovskite single crystals, the FAMACsRb perovskite exhibited the best stability in courses of humidity and thermal stressors. We explain these differences in the structure-property relationship. Diversified occupants at A-site will improve the intrinsic properties of perovskite, while additional interstitials such as Kinterstitial will decrease the materials properties. It thus suggests to introduce A-site doping with rational materials design to avoid introducing extra interstitial defects. This understanding about the intrinsic properties of perovskite doped by alkali ions may shed light on further applications of hybrid halide perovskite with alkali doping.

#### **Experimental**

#### Chemicals

CH<sub>3</sub>NH<sub>2</sub> aqueous solution (40% w/w), HI aqueous solution (57% w/w, stabilized with 1.5% H<sub>3</sub>PO<sub>2</sub>), HBr aqueous solution (48% w/w), HN=CHNH<sub>2</sub>·CH<sub>3</sub>COOH (FAAC, 99%, Aladdin), γbutyrolactone (GBL, 99%, Aladdin), PbI<sub>2</sub> (99.9%, Aladdin), PbBr<sub>2</sub> (99.999%, sigma), CsI (99.98%, sigma), RbI (99.9%, sigma), KI (99.9%, sigma).

#### Synthesis of FAI<sup>33</sup>

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FAI was synthesized by stirring 14 g FAAC and 32.3 MI HI in the 250 mL three-neck round bottom flask at 0 °C ice bath under the N<sub>2</sub> atmosphere. After 2 h, the solvent was removed by Rotary evaporation at 50 °C, and the remained yellow solids were washed by ether. Then the solids was dissolved in ethanol at 80 °C to form saturation solution. Decreasing the temperature of solutions could precipitate white solids. Dissolving and recrystallization process were repeated three times to obtain the pure products. After heating at 30 °C for 24 h in the vaccum oven for 24 h, the final products were stored in the N<sub>2</sub> glove box. *Synthesis of MABr*<sup>34</sup>

MABr was synthesized similar to FAI, except by stirring 30 mL CH<sub>3</sub>NH<sub>2</sub> and 36 mL HBr.

Synthesis of Cs, Rb, K cascade doped FA<sub>0.85</sub>MA<sub>0.15</sub>PbI<sub>2.55</sub>Br<sub>0.45</sub> single crystals

FA<sub>0.85</sub>MA<sub>0.15</sub>PbI<sub>2.55</sub>Br<sub>0.45</sub> single crystals

0.5 mL GBL and the molar ratios of FAI,  $PbI_2$ , MABr,  $PbBr_2$  were inputted in the 5 mL vial to form 1.2 M precursor solutions. After heating the solutions at 78 °C for 2 h, there were few small crystal seeds in the vial. Increasing the temperature at the speed of 1 °C/h could obtain millimeter sized single crystals, which were then heated at 100 °C for 15 min in the glove box to remove the remained solvent on the crystal surface The products were marked as FAMA single crystals.

 $Cs_{0.05}(FA_{0.85}MA_{0.15})_{0.95}PbI_{2.55}Br_{0.45}$  single crystals

Except the different molar ratios of CsI, FAI, PbI<sub>2</sub>, MABr, PbBr<sub>2</sub> and the different initial heating temperature (80 °C), the other processes were the same as FAMA single crystals. The products were marked as FAMACs single crystals.

Rb<sub>0.05</sub>(Cs<sub>0.05</sub>(FA<sub>0.85</sub>MA<sub>0.15</sub>)<sub>0.95</sub>)<sub>0.95</sub>PbI<sub>2.55</sub>Br<sub>0.45</sub> single crystals

Except the different molar ratios of RbI, CsI, FAI, PbI<sub>2</sub>, MABr, PbBr<sub>2</sub> and the different initial heating temperature (84 °C), the other processes were the same as FAMA single crystals. The products were marked as FAMACsRb single crystals.

K<sub>0.05</sub>(Rb<sub>0.05</sub>(Cs<sub>0.05</sub>(FA<sub>0.85</sub>MA<sub>0.15</sub>)<sub>0.95</sub>)<sub>0.95</sub>)PbI<sub>2.55</sub>Br<sub>0.45</sub> single crystals

Except the different molar ratios of KI, RbI, CsI, FAI, PbI<sub>2</sub>, MABr, PbBr<sub>2</sub> and the different initial heating temperature (87 °C), the other processes were the same as FAMA single crystals. The products were marked as FAMACsRbK single crystals.

#### Characterization

The test samples of inductively coupled plasma-atomic emission spectrometry (ICP-AES, Prodigy

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acid solutions. The actual concentration measured was shown in the table below. Pb Cs/Pb Rb/Pb K K/Pb Sample Cs Rb (ug/ml) (ug/ml) (ug/ml) (mole (ug/ml) (mole (mole ratio) ratio) ratio) 0.0009 FAMACs 17.7219 0.4711 4.1% 0.0962

0.0086

0.0056

0.0014

0.11%

0.07%

 $\approx 0$ 

0.1043

0.1182

0.1007

~0.2%

7-Leeman) were obtained by dissolving a certain amount of perovskite single crystals in 5% inite (DOTCO3085F

In order to compare with cascade doping, we also tested the actual content of Rb in samples doped with Rb (5%) only. Compared with FAMACsRb samples, Rb could hardly be detected in FAMARb samples. The results confirmed the effectiveness of cascade doping.

4.2%

4.1%

Single crystal X-ray Diffraction patterns were obtained by measuring the single crystal particle at different temperature (180 K, 300 K, 360 K) through single crystal X-ray diffractometer with Mo Ka ray ( $\lambda$ = 0.071073 nm). Powder X-ray Diffraction (PXRD) data of single crystals were obtained on the Rigaku D/MAX-2400 diffractometer. Absorption of perovskite single crystal particles were measured by UV-Visible/NIR Spectrophotometer UH4150. Photoluminescence (PL) spectrum of single crystal particles were characterized by FLS980 (Edinburgh Instruments Ltd), and Time-Resolved Photoluminescence (TRPL) spectrum was obtained by 470 nm excitation wavelength. We measured the dark current-voltage of Au/perovskite/Au devices through Keithley 4200 system to calculate the mobility of single crystals according to the Space-Charge-Limited Current (SCLC) model. Both sides of the single crystals sheets cleaved from big particles was deposited 80 nm Au to form the hole-only device. The X-ray absorption fine structure (XAFS) spectra at Pb L3 ( $E_0 =$ 13035.0 eV) edge was performed at BL14W1 beamline of Shanghai Synchrotron Radiation Facility(SSRF) operated at 3.5 GeV under "top-up" mode with a constant current of 200 mA. The XAFS data were recorded under transmission mode with Oxford ion chambers. The energy was calibrated accordingly to the absorption edge of pure Pb foil. Athena and Artemis codes were used to extract the data and fit the profiles.

#### Acknowledgments

FAMACsRb

FAMARb

FAMACsRbK

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17.7363

19.5133

18.9004

0.4804

0.5187

< 0.0001

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