## **Supporting Information**

## Effects of cation size and concentration of cationic chlorides on the properties of formamidinium lead iodide based perovskite solar cells

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**Fig. S1** *EQE* data of perovskite films as a function of wavelength for all 21 compositions; perovskite films prepared with (a) FACl, (b) CsCl, (c) RbCl, or (d) KCl with concentrations: 0 mol%, 10 mol%, 20 mol%, 30 mol%, 40 mol%, and 50 mol%.



Fig. S2 Certification from the Newport Corp.



Fig. S3 Storage stability of device with and without CsCl.



Fig. S4 Reciprocal values of FWHM obtained from films prepared with different additive concentrations at the diffraction peak  $13.9^{\circ}$  for the  $\alpha$ -phase perovskite.



Fig. S5 SEM images of (a) Pristine, (b) Gu-10, (c) Gu-20, (d) Gu-30, (e) Gu-40, and (f) Gu-50. Note that the scale bar is 1  $\mu$ m.



**Fig. S6** SEM images of (a) Pristine, (b) FA-10, (c) FA-20, (d) FA-30, (e) FA-40, and (f) FA-50. Note that the scale bar is 1 μm.



**Fig. S7** SEM images of (a) Pristine, (b) Rb-10, (c) Rb-20, (d) Rb-30, (e) Rb-40, and (f) Rb-50. Note that the scale bar is 1 μm.



Fig. S8 SEM images of (a) Pristine, (b) K-10, (c) K-20, (d) K-30, (e) K-40, and (f) K-50. Note that the scale bar is 1  $\mu$ m.



**Fig. S9** PL intensities as a function of wavelength for all 26 compositions; perovskite films prepared with (a) GuCl, (b) FACl, (c) CsCl, (d) RbCl, and (e) KCl with additive concentrations: 0 mol%, 10 mol%, 20 mol%, 30 mol%, 40 mol%, and 50 mol%.



**Fig. S10** Model systems of  $\alpha$ -phase FAPbI<sub>3</sub> perovskite structure including (a) GuCl, (b) FACl, (c) CsCl, (d) RbCl and (e) KCl additives. Note that  $3 \times 3 \times 1$  supercell system of  $\alpha$ -phase FAPbI<sub>3</sub> perovskite unit cell was used. In each system, all possible configurations of Cl doping were calculated for obtaining the most stable system with maintaining the  $\alpha$ -phase structure. It was used as a representative system. The doping sites of Cl are described as A, B and C aligned along the *x*-, *y*- and *z*-axes, respectively.



Fig. S11 Model systems of reference states for calculating the formation energy.

In this study, the formation energy ( $\Delta E_f$ ) of  $\alpha$ -phase FAPbI<sub>3</sub> perovskite including the cationic chloride or cation was calculated through the following equation (s1),

$$\Delta E_{\rm f} = E_{\alpha \text{-phase system}} - aE_{\rm FA} - bE_{\rm Pb} - cE_{\rm I} - dE_{\rm cation} - eE_{\rm Cl} \tag{s1}$$

where,  $E_{\alpha\text{-phase system}}$  is the total system energy of  $\alpha$ -phase perovskite structure including the cationic chloride or cation.  $E_{\text{FA}}$ ,  $E_{\text{Pb}}$ ,  $E_{\text{I}}$ ,  $E_{\text{cation}}$  and  $E_{\text{Cl}}$  are the system energies per unit of reference states (*i.e.*, FA, Pb, I<sub>2</sub>, cation (Gu, FA, Cs, Rb and K) and Cl<sub>2</sub>). *a*, *b*, *c*, *d* and *e* are the number of atoms in the perovskite structure system.



**Fig. S12** The cell optimized structure of FAPbI<sub>3</sub> perovskite containing five types of cation (*i.e.*, Gu, FA, Cs, Rb and K cations) through the DFT calculation. Note that for the system including (a) Gu cation, the  $\alpha$ -phase perovskite structure was collapsed. On the other hand, (b) FA, Cs, Rb and K cations maintained the  $\alpha$ -phase perovskite structures.



**Fig. S13** Projected density of states (PDOS) of  $\alpha$ -phase FAPbI<sub>3</sub> perovskite structures including the four types of cation (*i.e.*, FA, Cs, Rb and K cations).



**Fig. S14** Total volumes of  $\alpha$ -phase FAPbI<sub>3</sub> perovskite structures including the four types of cation (*i.e.*, FA, Cs, Rb and K cations).



Fig. S15 Volumes of cubo-octahedral sites of  $\alpha$ -phase FAPbI<sub>3</sub> perovskite structures including the four types of cation (*i.e.*, FA, Cs, Rb and K cations). The cubo-octahedral volume was calculated by Connolly surface method<sup>1</sup> with 2 Å radius of probe atom. Red colored boxes indicate the cubo-octahedral volumes of site 5, which were the main distribution of volume shrinkage of Cs, Rb or K-incorporated system.



**Fig. S16** Volume differences of cubo-octahedral sites of the perovskite structure with Cs cation compared to the FA-incorporated system of Fig. S15.



**Fig. S17** Model systems of  $\alpha$ -phase FAPbI<sub>3</sub> perovskite structures including one (11 % concentration), two (22 % concentration) and three (33 % concentration) FACl additives to construct the systems including two, three and four cations, which describe 22 %, 33 % and 44 % concentration systems, respectively. Based on 11 %, 22 % and 33 % concentration systems (left side) obtained from Fig. S10(b), S17(a), and S17(b), all possible configurations that FACl additive can be doped into the  $\alpha$ -phase FAPbI<sub>3</sub> perovskite structure, are calculated in order to obtain the most stable systems with maintaining the  $\alpha$ -phase structure (right side). They were used as representative systems. Note that the doping configuration of FACl additive considered the doping combination of FACl having the most stable system with maintaining the  $\alpha$ -phase structure which was found in Fig. S10(b). The doping sites of Cl is described as A.



**Fig. S18** Model systems of  $\alpha$ -phase FAPbI<sub>3</sub> perovskite structures including one (11 % concentration), two (22 % concentration) and three (33 % concentration) CsCl additives to construct the systems including two, three and four cations, which describe 22 %, 33 % and 44 % concentration systems, respectively. Based on 11 %, 22 % and 33 % concentration systems (left side) obtained from Fig. S10(c), S18(a), and S18(b), all possible configurations that CsCl additive can be doped into the  $\alpha$ -phase FAPbI<sub>3</sub> perovskite structure, are calculated in order to obtain the most stable systems with maintaining the  $\alpha$ -phase structure (right side). They were used as representative systems. Note that the doping configuration of CsCl additive considered the doping combination of CsCl having the most stable system with maintaining the  $\alpha$ -phase structure which was found in Fig. S10(c). The doping sites of Cl and Cs are described as A and C, respectively.



Fig. S19 Model systems for reference states for calculating the doping formation energy.

To investigate the formation energy to dope the cationic chloride additive into the  $\alpha$ -phase FAPbI<sub>3</sub> perovskite structure, we calculated the doping formation energy ( $\Delta E_{doping}$ ) through the following equation (s2),

$$\Delta E_{\text{doping}} = E_{\text{cationic chloride doping}} - E_{\text{pristine}} + a(\mu_{\text{anion out}} - \mu_{\text{anion in}}) + b(\mu_{\text{cation out}} - \mu_{\text{cation in}}) \quad (s2)$$

where  $E_{\text{cationic chloride doping}}$  is the total system energy of  $\alpha$ -phase perovskite structure including cationic chloride additive (*i.e.*, FACl and CsCl).  $E_{\text{pristine}}$  is the total system energy of pristine  $\alpha$ -phase FAPbI<sub>3</sub> perovskite structure, which does not include the cationic chloride additive.  $\mu_{\text{anion out}}(\mu_{\text{cation out}})$  and  $\mu_{\text{anion in}}(\mu_{\text{cation in}})$  are the chemical potentials of anions (cations) that are removed from or included to the perovskite structure based on the reference states of cationic iodide and cationic chloride. *a* and *b* are the number of anions and cations, respectively.



Fig. S20 (a) Model systems of  $\alpha$ -phase FAPbI<sub>3</sub> perovskite structures including cationic chloride additive (*i.e.*, FACl or CsCl) according to its doping concentration (*i.e.*, 11 % ~ 44 %). These systems were obtained from Fig. S17 and S18. Note that red and orange colored regions indicate the doped sites of FA and Cs cations, respectively. (b) Formation energy of  $\alpha$ -phase FAPbI<sub>3</sub> perovskite structure including FACl or CsCl additive. (c) Doping formation energy of FACl or CsCl additive into the  $\alpha$ -phase FAPbI<sub>3</sub> perovskite structure.

To elucidate why the lower concentration of CsCl additive was needed to achieve the high performance of solar cell device compared to the FACl additive, we investigated the concentration effect of FACl and CsCl additives on the formation of the  $\alpha$ -phase FAPbI<sub>3</sub> perovskite structure. We constructed the model systems of  $\alpha$ -phase perovskite including each cationic chloride additive according to its doping concentration (11 % ~ 44 % concentration

in Fig. S20(a)). We found that the formation energy decreased as the additive concentration increased (Fig. S20(b)), indicating that the improvement of device performance was induced by increasing the stability of the perovskite structure. Moreover, the formation energy of CsCl case was more favorable thermodynamically compared to the FACl case. However, in the case of CsCl, we found that the absolute value of the doping formation energy was large compared to FACl (Fig. S20(c)), implying that the additive concentration eventually became low. The experiment result also showed the best performance at lower additive concentration (*i.e.*, 20 % concentration) compared to the FACl additive.

Voc (V)	Isc (A)	FF (%)	Efficiency (%)
1.1245	0.002037	79.6	22.65
$\pm 0.0087$	$\pm \ 0.000043$	$\pm 1.6$	$\pm 0.74$

 Table S1. Certified IV parameters of the perovskite solar cell.

Tolerance factor $(t)$	10 mol%	20 mol%	30 mol%	40 mol%	50 mol%
GuCl	1.013	1.018	1.024	1.029	1.035
FACl	1.007	1.007	1.007	1.007	1.007
CsCl	0.988	0.968	0.949	0.930	0.911
RbC1	0.984	0.962	0.939	0.917	0.894
KC1	0.980	0.953	0.926	0.900	0.873

**Table S2.** Tolerance factors of the films prepared with different additives in various concentrations.

$$T = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \tag{s3}$$

ABX<sub>3</sub> perovskites prepared with A = Gu, FA, Cs, Rb or K, B = Pb, and X = I or Cl compositions had tolerant factors that depended on the size of the A cation and X anion. The Goldschmidt tolerance factor (*t*) could be calculated from equation (s3), where  $r_A$ ,  $r_B$ , and  $r_X$  are the effective ionic radii of A, B, and X ions, respectively. The chloride ions might evaporate during annealing (see Fig. 5(c)); therefore, the composition of the X ions was fixed at 197 pm (I). The cation could be substituted with Gu, FA, Cs, Rb or K ions in the FA-based perovskite (see Fig. 5). Therefore, the size of the cation could provide a formula of FA<sub>1</sub>. <sub>x</sub>Cation<sub>x</sub>, for example, the 20 mol% CsCl could have a formula of FA<sub>0.8</sub>Cation<sub>0.2</sub>. The effective radii of the cation ( $r_{cation}$ ) could be estimated using equation (s4).

$$A = r_{cation} = (1 - x) \times FA + x \times cations$$

$$B = Pb^{2+} = 119 \text{ pm}$$

$$C = r_{anion} = \Gamma = 198 \text{ pm}$$
(s4)

	Pristine		10 mol%		20 mol%		30 mol%		40 mol%		50 mol%	
	τ <sub>1</sub> (ns)	τ <sub>2</sub> (ns)										
GuCl			513	227	476	187	418	238	330	164	276	112
FACl			479	218	702	49.7	594	248	773	201	737	206
CsCl	509	262	526	256	1275	623	964	312	581	257	340	187
RbC1			510	224	451	149	444	148	357	9.27	229	379
KCl			411	126	351		264		122		114	102

**Table S3.** Decay profiles of perovskite prepared with different additives as a function ofadditive concentration: 10 mol%, 20 mol%, 30 mol%, 40 mol%, and 50 mol%.

## References

[1] Connolly, M. L. Solvent-accessible surfaces of proteins and nucleic acids. *Science*, 1983, *221*, 709-713.