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## Effect of alkaline earth metal chloride additives $\text{BCl}_2$ (B = Mg, Ca, Sr and Ba) on the photovoltaic performance of $\text{FAPbI}_3$ based perovskite solar cells†

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Additive engineering is known to be an effective method for inducing a simultaneous effect of enlarging the grain size and surface passivation. As compared to the monovalent halides frequently used as additives, divalent halides are relatively less investigated in the role of additives. In this work, we report effects of alkaline earth metal halides  $\text{BCl}_2$  (B = Mg, Ca, Sr, Ba) as additives on the opto-electronic properties and photovoltaic performance of  $\text{FAPbI}_3$  based perovskite solar cells (PSCs). A significant improvement in power conversion efficiency (PCE) from 17.27% to 21.11% is observed by  $\text{MgCl}_2$  addition in the  $\text{FAPbI}_3$  precursor solution, while a marginal increment for  $\text{CaCl}_2$  or  $\text{BaCl}_2$  and a negative effect for  $\text{SrCl}_2$  is observed. The lattice constant of cubic  $\text{FAPbI}_3$  is hardly changed by additives, while the crystallinity is improved by  $\text{MgCl}_2$ . The carrier lifetime increases from 40 ns to 287 ns and the trap density is reduced from  $1.08 \times 10^{16} \text{ cm}^{-3}$  to  $3.19 \times 10^{15} \text{ cm}^{-3}$  by addition of 5 mol%  $\text{MgCl}_2$ , which is responsible for the enhancement in photovoltaic parameters. The steady-state PCE of the PSC with the  $\text{MgCl}_2$ -additive-treated  $\text{FAPbI}_3$  measured under continuous illumination at the maximum power point remains unchanged for 1500 s.

## Introduction

Since the report of a 9.7% efficient and 500 h stable solid-state perovskite solar cell (PSC) in 2012,<sup>1</sup> developed to solve the instability of methylammonium lead iodide ( $\text{MAPbI}_3$ ) in a liquid electrolyte,<sup>2,3</sup> a swift surge in perovskite photovoltaics led to a certified power conversion efficiency (PCE) of 25.2% in 2019.<sup>4</sup> The inherently excellent opto-electronic properties of organic lead halide perovskites<sup>5–7</sup> are responsible for the superb photovoltaic performance, which might be better than the well-known thin film solar cell materials such as  $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ , multi-crystalline Si and CdTe because of higher PCE. Among the

### New concepts

Formamidinium lead iodide ( $\text{FAPbI}_3$ ) perovskite is known to be an ideal material among the studied compositions in terms of optical bandgap. The precursor solution is suggested to include an additive – normally, the monovalent cationic chlorides, such as  $\text{MACl}$  or  $\text{CsCl}$ , are frequently used as additives – to improve the photovoltaic performance of  $\text{FAPbI}_3$  perovskite solar cells (PSCs). However, a change in bandgap is expected because MA or Cs cations can replace the FA cations. Thus, it is required to keep the bandgap of  $\text{FAPbI}_3$  even after modification by additive engineering. As compared to the monovalent halides, no systematic investigation on the role of divalent halides has been reported in  $\text{FAPbI}_3$  based PSCs. In this work, we first report the effects of alkaline earth metal halide  $\text{BCl}_2$  (B = Mg, Ca, Sr, Ba) additives on the opto-electronic properties and photovoltaic performance of  $\text{FAPbI}_3$  based PSCs. We have found that the addition of  $\text{MgCl}_2$  improves the power conversion efficiency significantly due to a large increase in carrier lifetime and a significant reduction in trap density. In addition, no change in bandgap is observed because of the higher oxidation state and much smaller ionic radius of  $\text{Mg}^{2+}$  than FA and Pb cations.

studied compositions for PSCs,  $\text{FAPbI}_3$  (FA = formamidinium) has been regarded as an ideal perovskite because of suitable bandgap ( $\sim 1.47$  eV) and no structural phase transition at the operating temperature.<sup>8</sup> However, the photoactive  $\text{FAPbI}_3$  is known to be in the high-temperature stabilized  $\alpha$  phase, and tends to undergo phase transition from  $\alpha$  to photo-inactive  $\delta$  phase at ambient temperature.<sup>9</sup> It was first reported that a substitution of a certain amount of FA cations with Cs cations can stabilize the  $\alpha$  phase at ambient temperature.<sup>10</sup> In general, substitution with smaller monovalent cations ( $\text{Cs}^+$ ,  $\text{Rb}^+$  or MA) and/or halide anion ( $\text{Br}^-$ ) was found to stabilize the  $\alpha$  phase of  $\text{FAPbI}_3$  thermodynamically.<sup>11–14</sup> Thus, these cations can be referred to as “stabilizers” in  $\text{FAPbI}_3$ .<sup>12</sup>

The stabilizers can be incorporated compositionally by stoichiometrically mixing FA with a certain amount of stabilizer, which is called “compositional engineering”. The incorporation of stabilizer is also possible by “additive engineering” in which an adequate amount of additive is mixed with  $\text{FAPbI}_3$  precursor. The difference between compositional engineering

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and additive engineering is that additive engineering is a non stoichiometric approach and elements that may not be involved in the composition can be used as additives. Additive engineering has been found to be also beneficial for both surface passivation and growth of grain size.<sup>15</sup> It is well-known that addition of MAI additive in a perovskite precursor solution shows a positive effect on the photovoltaic performance of FAPbI<sub>3</sub> based PSCs.<sup>16–18</sup> Although it has been argued whether or not chloride is incorporated in iodide sites, it is widely accepted that chloride plays an important role in enlarging the grain size and improving crystallinity.<sup>19</sup> Since there is a positive effect of chloride in additives, we have been motivated to systematically investigate the effect of divalent alkaline earth metal chlorides, BCl<sub>2</sub> (B = Mg, Ca, Sr and Ba), on the photovoltaic performance and stability of FAPbI<sub>3</sub> based PSCs. Since the divalent cations in BCl<sub>2</sub> are smaller in ionic radius (Mg<sup>2+</sup> = 72 pm, Ca<sup>2+</sup> = 100 pm, Sr<sup>2+</sup> = 118 pm, and Ba<sup>2+</sup> = 135 pm) and have higher formal charge than the FA cation, the surface passivation effect is expected rather than the substitution effect. In addition, the chloride content of BCl<sub>2</sub> is twice that of monovalent chloride when the same quantity is dissolved in the precursor solution, which may also affect the opto-electronic properties of the PSCs. To the best of our knowledge, no systematic studies have been reported on the additive engineering of FAPbI<sub>3</sub> with BCl<sub>2</sub>.

Here, we report on the effects of BCl<sub>2</sub> additives on the photovoltaic parameters and opto-electronic properties of the FAPbI<sub>3</sub> based PSCs. The additive BCl<sub>2</sub> is mixed with a pre-synthesized FAPbI<sub>3</sub> powder,<sup>20</sup> where the concentration of BCl<sub>2</sub>, [BCl<sub>2</sub>], is varied with respect to [FAPbI<sub>3</sub>]. Among the studied additives, MgCl<sub>2</sub> is found to improve the photovoltaic performance and stability. Crystal structure, film morphology, band alignment and carrier lifetime are comparatively investigated to understand the basis for the improvement. A pristine FAPbI<sub>3</sub> device shows a PCE of 17.27% which is significantly improved to 21.11% by addition of MgCl<sub>2</sub> in the FAPbI<sub>3</sub> precursor solution.

## Results and discussion

### Effect of BCl<sub>2</sub> (B = Mg, Ca, Sr and Ba) on the opto-electronic properties of FAPbI<sub>3</sub> and photovoltaic performance

The perovskite precursor solutions are prepared by mixing the pre-synthesized FAPbI<sub>3</sub> powder (yellow  $\delta$  phase) with BCl<sub>2</sub> with

different molar ratios (see Experimental details). In order to investigate how the metal precursor additives change the reactivity of the perovskite precursors, UV-vis absorption spectroscopy of the precursor solution is studied. Fig. S1 (ESI<sup>†</sup>) shows that the absorption band around 310 nm is due to the iodoplumbate (probably PbI<sub>2</sub>(DMF)<sub>x</sub>(DMSO)<sub>4–x</sub> species), where peak intensity is higher for the MgCl<sub>2</sub> additive than for other additives. A strong absorption is indicative of an increase in iodoplumbate concentration and thereby an improvement of photovoltaic performance.<sup>21</sup> Another weak absorption peak at around 380 nm (inset in Fig. S1, ESI<sup>†</sup>) is related to PbI<sub>3</sub><sup>–</sup>.<sup>22</sup> This peak is also relatively intense for the MgCl<sub>2</sub> additive compared to other additives. When considering that two characteristic peaks in the precursor solution affect the photovoltaic performance, MgCl<sub>2</sub> additive is expected to be better in performance than other additives, which will be further evaluated. Fig. 1 shows a schematic illustration of perovskite deposition, where the precursor solution with and without additive is spin-coated on a SnO<sub>2</sub> coated FTO (fluorine-doped tin oxide) substrate. To control the crystal growth, an intermediate is formed by dripping diethyl ether during the spin-coating procedure.<sup>23</sup> The thickness of the 150 °C-annealed perovskite film is about 440 nm as confirmed from cross-sectional scanning electron microscopy (SEM) (images not shown).

The effects of the concentration of the additives on the photovoltaic parameters are investigated. As shown in Fig. S2 (ESI<sup>†</sup>), the photovoltaic parameters are strongly dependent on the additive concentration (note that the final concentration may be different because the solution was filtered prior to use), from which an optimal concentration is determined to be 5 mol% for MgCl<sub>2</sub>, 1 mol% for CaCl<sub>2</sub> and 9 mol% for BaCl<sub>2</sub>. In contrast to the Mg, Ca and Ba cases, the addition of SrCl<sub>2</sub> additive lowers the photovoltaic performance. Despite the negative effect of SrCl<sub>2</sub>, 10 mol% shows better performance among the tested concentrations from 5 mol% to 15 mol%. Fig. 2 shows the statistical short-circuit photocurrent density ( $J_{sc}$ ), open-circuit voltage ( $V_{oc}$ ), fill factor (FF) and power conversion efficiency (PCE) for the optimal concentration of BCl<sub>2</sub> additives. Unlike the BI<sub>2</sub> additives doped in MAPbI<sub>3</sub>,<sup>24,25</sup> 5 mol% MgCl<sub>2</sub> improves substantially  $V_{oc}$  and FF, while a negligible or slight enhancement is observed for CaCl<sub>2</sub> and BaCl<sub>2</sub>. Mean values are listed in Table 1, where the average PCE estimated from the



**Fig. 1** A schematic illustration of the perovskite deposition procedure. The precursor solution was prepared by mixing the pre-synthesized FAPbI<sub>3</sub> powder with BCl<sub>2</sub> additive (B = Mg, Ca, Sr and Ba), which was spin-coated. Diethyl ether was dripped for 20 s after rotating the substrate. The film was annealed at 150 °C in an air atmosphere.



Fig. 2 Statistical photovoltaic parameters of (a)  $J_{sc}$ , (b)  $V_{oc}$ , (c) FF and (d) PCE measured at reverse scan for the BCl<sub>2</sub> additives (B = Mg, Ca, Sr and Ba). Values in parentheses are the optimal mol% of the additive with respect to FAPbI<sub>3</sub>.

Table 1 Mean photovoltaic parameters of PSCs employing FAPbI<sub>3</sub> perovskite films with and without (Ref) BCl<sub>2</sub> additives (B = Mg, Ca, Sr and Ba). FS and RS stand for forward scan and reverse scan, respectively

Additive (mol%)		$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (V)	FF	PCE (%)
Ref (w/o)	FS	21.84 ± 0.42	1.07 ± 0.01	0.72 ± 0.03	16.66 ± 1.06
	RS	21.97 ± 0.68	1.05 ± 0.03	0.71 ± 0.03	16.38 ± 1.02
MgCl <sub>2</sub> (5%)	FS	22.72 ± 0.41	1.11 ± 0.02	0.77 ± 0.02	19.36 ± 0.98
	RS	22.76 ± 0.31	1.11 ± 0.02	0.78 ± 0.03	19.67 ± 1.23
CaCl <sub>2</sub> (1%)	FS	22.37 ± 0.33	1.05 ± 0.01	0.72 ± 0.04	16.86 ± 0.89
	RS	22.11 ± 0.33	1.04 ± 0.01	0.70 ± 0.03	16.09 ± 0.88
SrCl <sub>2</sub> (10%)	FS	21.57 ± 1.12	1.04 ± 0.03	0.57 ± 0.13	12.75 ± 3.70
	RS	21.52 ± 1.12	1.04 ± 0.02	0.62 ± 0.10	13.95 ± 2.69
BaCl <sub>2</sub> (9%)	FS	22.21 ± 0.43	1.07 ± 0.01	0.75 ± 0.01	17.66 ± 0.40
	RS	22.33 ± 0.15	1.07 ± 0.01	0.75 ± 0.01	17.82 ± 0.39

reverse scanned parameters is improved from 16.39% to 19.66% by MgCl<sub>2</sub> addition. A large improvement in  $V_{oc}$  and FF implies that recombination might be reduced by the MgCl<sub>2</sub> additive. In our study, bulk doping in FAPbI<sub>3</sub> with SrCl<sub>2</sub> shows a negative effect leading to deterioration of the photovoltaic performance, which is in contrast to the previous work reporting an improved PCE by the 10–30% doping with SrCl<sub>2</sub> in MAPbI<sub>3</sub> and even the 2% doping with SrI<sub>2</sub> in CsPbI<sub>3</sub>.<sup>26,27</sup>

Surface morphology is not significantly altered by MgCl<sub>2</sub>, while CaCl<sub>2</sub>, SrCl<sub>2</sub> and BaCl<sub>2</sub> change the surface morphology of FAPbI<sub>3</sub> (Fig. 3(a–e)). Cross-sectional SEM images confirm that MgCl<sub>2</sub> results in a pinhole-free interface between SnO<sub>2</sub> and perovskite, whereas large pinholes are formed at the interface for the pristine FAPbI<sub>3</sub>. This indicates that the MgCl<sub>2</sub> additive supports an underlying conformal growth of perovskite on the substrate. The MgCl<sub>2</sub> additive is expected to contribute to the enlargement of the grain size of FAPbI<sub>3</sub> perovskite due to

the higher coordination interaction between FA<sup>+</sup> and Mg<sup>2+</sup> than those of FA<sup>+</sup> and Pb<sup>2+</sup><sup>28,29</sup> and/or retarded crystallization kinetics.<sup>30</sup> The higher  $J_{sc}$  obtained from the MgCl<sub>2</sub> additive is thus probably due to better charge collection owing to the pinhole-free interface. In addition, the crystallinity of  $\alpha$  phase FAPbI<sub>3</sub> is improved in the presence of MgCl<sub>2</sub> as confirmed from the X-ray diffraction (XRD) pattern in Fig. 3(f), which might be associated with higher  $V_{oc}$  and FF because of the long-range ordering of FAPbI<sub>3</sub> and thereby less defects. On the other hand, the addition of CaCl<sub>2</sub>, SrCl<sub>2</sub> and BaCl<sub>2</sub> cannot fully convert the  $\delta$  phase to  $\alpha$  phase because the  $\delta$  phase is still present in the annealed film (Fig. 3(g)). Moreover, the CaCl<sub>2</sub> additive increases the unreacted PbI<sub>2</sub> peak, implying a strong interaction between CaCl<sub>2</sub> and PbI<sub>2</sub> in the precursor solution. Although the ionic radius of Sr<sup>2+</sup> (118 pm) is similar to that of Pb<sup>2+</sup> (119 pm), Sr<sup>2+</sup> is not likely to replace Pb<sup>2+</sup> because unreacted SrCl<sub>2</sub> exists in the annealed film as shown in the XRD peak at around 12.8° in Fig. 3(g) and the lattice constant of cubic FAPbI<sub>3</sub><sup>31</sup> is unchanged by SrCl<sub>2</sub> due to no peak shift in the (100) reflection at  $2\theta = 13.94^\circ$ .

Energy dispersive X-ray spectroscopy (EDS) is carried out to investigate the presence of BCl<sub>2</sub> in the annealed FAPbI<sub>3</sub> film. For the MgCl<sub>2</sub> case in Fig. 4(a), neither Mg nor Cl is detected on the film surface. Similarly, Ca and Cl are not detected on the film surface for FAPbI<sub>3</sub> with CaCl<sub>2</sub> additive (Fig. 4(b)). However, for the SrCl<sub>2</sub> and BaCl<sub>2</sub> cases, Sr, Ba and Cl elements are detected with an atomic ratio of Sr:Cl or Ba:Cl = 1:2 (Fig. 4(c) and (d)). No detection of MgCl<sub>2</sub> and CaCl<sub>2</sub> is probably due to the relatively lower concentration as compared to SrCl<sub>2</sub> and BaCl<sub>2</sub>. The ratio of I to Pb is found to be almost 3 (atomic ratio I:Pb = 18.86:6.16) for the MgCl<sub>2</sub> case, which is indicative of stoichiometric formation of FAPbI<sub>3</sub>. On the other hand, iodide-rich





Fig. 3 (a–e) Top-view and cross-sectional scanning electron microscope (SEM) images and (f, g) X-ray diffraction patterns of FAPbI<sub>3</sub> films with and without (Ref) additives of MgCl<sub>2</sub>, CaCl<sub>2</sub>, SrCl<sub>2</sub> and BaCl<sub>2</sub>.



Fig. 4 Energy dispersive X-ray spectroscopy (EDS) of FAPbI<sub>3</sub> films with additive of (a) MgCl<sub>2</sub> (5%), (b) CaCl<sub>2</sub> (1%), (c) SrCl<sub>2</sub> (10%) and (d) BaCl<sub>2</sub> (9%).

(or Pb-deficient) phase is formed for CaCl<sub>2</sub> and BaCl<sub>2</sub> because of the ratio I/Pb = 3.22 (CaCl<sub>2</sub>) and 3.35 (BaCl<sub>2</sub>). Addition of SrCl<sub>2</sub> results in iodide-deficient (or Pb-rich) phase in the annealed perovskite film. Although excess PbI<sub>2</sub> or organic iodide was reported to passivate the perovskite grain boundary and thereby improve the photovoltaic performance,<sup>32,33</sup> the stoichiometry of the perovskite was also reported to play an important role in photovoltaic performance and stability because defects can be

minimized by stoichiometric composition.<sup>34</sup> Thus, stoichiometric FAPbI<sub>3</sub> formed by MgCl<sub>2</sub> additive is in part responsible for the improved PCE. Since detection of MgCl<sub>2</sub> and CaCl<sub>2</sub> is unavailable by EDS, we further measure surface-sensitive X-ray photoelectron spectroscopy (XPS) to understand the chemical environment of FAPbI<sub>3</sub> films depending on additives.

Fig. 5(a–d) show Mg 1s, Ca 2p, Sr 3d and Ba 3d XPS spectra before and after addition of the additives. The film samples for



Fig. 5 Mg 1s, Ca 2p, Sr 3d and Ba 3d X-ray photoelectron spectroscopy (XPS) spectra of the annealed FAPbI<sub>3</sub> films with and without additives of (a) MgCl<sub>2</sub>, (b) CaCl<sub>2</sub>, (c) SrCl<sub>2</sub> and (d) BaCl<sub>2</sub>. (e) Pb 4f, (f) I 3d and (g) Cl 2p XPS spectra of the FAPbI<sub>3</sub> films before and after adding the MgCl<sub>2</sub> additive.

XPS measurements were prepared on Si wafers. Mg, Ca, Sr and Ba elements are obviously detected. The detection of Cl from the MgCl<sub>2</sub>-treated FAPbI<sub>3</sub> film confirms the existence of MgCl<sub>2</sub> in the film (see Fig. 5(g)). Thus, the additives still exist in the annealed perovskite films. Since addition of MgCl<sub>2</sub> significantly improved the photovoltaic performance among the studied BCl<sub>2</sub> additives, we further investigate Pb 4f and I 3d XPS for the FAPbI<sub>3</sub> films with and without MgCl<sub>2</sub>. In Fig. 5(e), the pristine FAPbI<sub>3</sub> film shows two peaks at binding energies of 143.53 eV and 138.63 eV, which correspond to the Pb 4f<sub>5/2</sub> and 4f<sub>7/2</sub> core levels, respectively, originated from Pb<sup>2+</sup> ions.<sup>35,36</sup> The addition of MgCl<sub>2</sub> in FAPbI<sub>3</sub> shifts the Pb 4f peaks to lower binding energies of 142.93 eV for 4f<sub>5/2</sub> and 138.08 eV for 4f<sub>7/2</sub>. Shift to lower binding energy after adding MgCl<sub>2</sub> is also observed from I 3d XPS (Fig. 5(f)), where the 3d<sub>3/2</sub> peak at 631.13 eV and the 3d<sub>5/2</sub> peak at 619.68 eV shift to 630.63 eV and 619.13 eV. When considering no change in lattice constant by MgCl<sub>2</sub>, Mg or Cl element might not be directly involved in lattice construction. Thus, the shift in binding energy is indicative of a change in chemical environment around Pb and I at the surface. The decrease in binding energy of Pb<sup>2+</sup> and I<sup>-</sup> is probably related to an increase in electron density around Pb<sup>2+</sup> and I<sup>-</sup>.<sup>37–39</sup> In the case that Mg<sup>2+</sup> interacts with iodide at the surface, the (Pb–I) bond is more likely to be ionic due to an increased covalency of the adjacent (Mg–I) bond because of the smaller ionic radius of Mg<sup>2+</sup> (72 pm) than Pb<sup>2+</sup> (119 pm) according to Fajan's rule.<sup>40</sup> Thus, the electron density of iodide in the (Mg–I–Pb) interaction is relatively increased as compared to the (Pb–I–Pb) configuration. In addition, the more covalent character of (Mg–I) will donate electrons to Pb, which increases

the electron density of Pb. Chloride in MgCl<sub>2</sub> can also affect the shift of the Pb 4f and the I 3d peaks by donating lone-pair electrons to the perovskite surface. It was reported that post-treatment with SrCl<sub>2</sub> was found to shift the Pb 4f and the I 3d core levels to lower binding energy.<sup>41</sup>

Modification of the optical bandgap and band position is studied using UV-vis and ultraviolet photoelectron spectroscopy (UPS). Fig. 6(a) shows the UV-vis spectra of the annealed FAPbI<sub>3</sub> with and without additives. The absorbance is slightly enhanced by the additives, which is attributed to a slight increase in  $J_{sc}$ . Despite better absorbance observed from the SrCl<sub>2</sub> case, the lower  $J_{sc}$  than the reference device might be related to the presence of unconverted  $\delta$  phase and/or poor SnO<sub>2</sub>/perovskite interface in the aforementioned Fig. 3. The Tauc plot obtained from the UV-vis spectral data is shown in Fig. 6(b), where a linear fit in the 1.54–1.57 eV range of photon energy reveals that the optical bandgap ( $E_g$ ) is determined to be 1.50 eV for MgCl<sub>2</sub> and CaCl<sub>2</sub> and 1.51 eV for SrCl<sub>2</sub> and BaCl<sub>2</sub>, which are almost unchanged as compared to the pristine FAPbI<sub>3</sub> ( $E_g$  = 1.50 eV). Unaltered  $E_g$  is consistent with the invariable lattice constant as observed in XRD. Our result is different from the doping effect on  $E_g$  of MAPbI<sub>3</sub> or CsPbI<sub>3</sub>, where  $E_g$  was influenced by doping due to the substitution effect.<sup>42–45</sup> Valence band ( $E_{VB}$ ) and conduction band ( $E_{CB}$ ) positions are determined from UPS using He I photon energy ( $h\nu$  = 21.2 eV). In Fig. 6(c), UPS spectra are illustrated, showing the binding energy region of the cut-off energy ( $E_{cutoff}$ ) and the valence band maximum (VBM). Work function (WF) is determined from  $WF = h\nu - E_{cutoff}$  (see Fig. S3 (ESI<sup>†</sup>)) for determining  $E_{cutoff}$  and  $E_{VB}$  is determined using  $E_{VB} = WF + VBM$  (see Fig. S3 (ESI<sup>†</sup>)) for determining VBM.<sup>46</sup> To determine



Fig. 6 (a) UV-vis spectra, (b) Tauc plot, (c) ultraviolet photoelectron spectroscopy (UPS) and (d) band (conduction band (CB) and valence band (VB)) positions for the FAPbI<sub>3</sub> films with and without additives. UPS spectra were measured with He I photon energy (21.2 eV).

**Table 2** Work function (WF), valence band energy ( $E_{VB}$ ) and conduction band energy ( $E_{CB}$ ) estimated from the cut-off energy ( $E_{cutoff}$ ), valence band maximum (VBM) and optical bandgap ( $E_g$ )

Sample	$E_{cutoff}$ (eV)	WF (eV)	VBM (eV)	$E_{VB}$ (eV)	$E_g$ (eV)	$E_{CB}$ (eV)
Ref (w/o)	16.05	5.15	1.23	6.38	1.50	4.88
MgCl <sub>2</sub> (5%)	16.05	5.15	1.55	6.70	1.50	5.20
CaCl <sub>2</sub> (1%)	16.00	5.20	1.55	6.75	1.50	5.25
SrCl <sub>2</sub> (10%)	16.02	5.18	1.45	6.63	1.51	5.12
BaCl <sub>2</sub> (9%)	16.11	5.09	1.47	6.56	1.51	5.05

VBM, we use a logarithmic scale method.<sup>47</sup> The estimated values are listed in Table 2 and plotted in Fig. 6(d).  $E_{VB}$  is determined to be 6.38 eV for the non-additive pristine FAPbI<sub>3</sub>, which is consistent with the reported value obtained from the combined experimental and theoretical data.<sup>48</sup> Upon addition of additives, WF is almost unchanged, which indicates that the additive might not act as a dopant. Unlike the BI<sub>2</sub> additive in MAPbI<sub>3</sub> perovskite, resulting in up-shift of  $E_{VB}$  and  $E_{CB}$ ,<sup>49</sup>  $E_{VB}$  is down-shifted by the BCl<sub>2</sub> additives in FAPbI<sub>3</sub> perovskite films. The chloride seems to play a common effect on down-shifting  $E_{VB}$ . Since the antibonding-nature  $E_{VB}$  for the pristine FAPbI<sub>3</sub> is formed by overlapping the Pb 6s orbital with the I 5p from the viewpoint of molecular orbital theory, the chloride at the surface is likely to lower the  $E_{VB}$  because of overlap with a more electronegative Cl 3p orbital.<sup>50</sup> It was reported that a low concentration of Mg doping

into MAPbI<sub>3</sub> led to down-shift of  $E_{VB}$  and more n-type property.<sup>51</sup> Thus, more n-type FAPbI<sub>3</sub> might be induced by addition of MgCl<sub>2</sub>.

#### Effect of MgCl<sub>2</sub> additive on carrier mobility and trap density of FAPbI<sub>3</sub>

The improved  $V_{oc}$  by MgCl<sub>2</sub> additive in spite of the unchanged  $E_g$  underlines that carrier lifetime, associated with trap density, is probably improved. To verify this hypothesis, we measure time-resolved photoluminescence (TRPL) along with steady-state PL. In Fig. 7(a), the PL intensity of the bulk perovskite film is increased by MgCl<sub>2</sub>, which is indicative of reduction of non-radiative recombination. Upon contacting the perovskite film with SnO<sub>2</sub>, the PL intensity is similarly decreased by 90.4% (pristine) and 89.5% (MgCl<sub>2</sub>). Despite a similar degree of PL quenching, a lower  $J_{sc}$  for the pristine FAPbI<sub>3</sub> is due to the presence of pinholes at the SnO<sub>2</sub>/perovskite interface (see Fig. 3). The TRPL spectrum in Fig. 7(b) is fit with the bi-exponential decay equation,  $f(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ , where  $\tau_1$  and  $\tau_2$  are time constants and  $A_1$  and  $A_2$  are amplitude.<sup>33</sup> Table 3 lists the fit results of pristine perovskite and perovskite film with MgCl<sub>2</sub> additive on the glass substrate. The addition of MgCl<sub>2</sub> increases  $\tau_1$  from 1.9 ns to 3.9 ns and  $\tau_2$  from 201.2 ns to 376.5 ns. In addition, the amplitude ratio ( $A_1/A_2$ ) decreases significantly from 447.9 to 30.3 after addition of MgCl<sub>2</sub>. This decrease in  $A_1/A_2$  indicates that the contribution of the





Fig. 7 (a) Steady-state photoluminescence (PL) of the FAPbI<sub>3</sub> film with and without MgCl<sub>2</sub> deposited on a glass substrate and SnO<sub>2</sub>-coated FTO substrate. (b) Time-resolved PL (TRPL) for the FAPbI<sub>3</sub> film with and without MgCl<sub>2</sub> on a glass substrate. Dark current density ( $J$ )–voltage ( $V$ ) curves for (c) the FTO/SnO<sub>2</sub>/FAPbI<sub>3</sub> (with or without MgCl<sub>2</sub>)/PCBM/Au electron-only device and (d) the full solar cell device.

**Table 3** Parameters for fitting TRPL data with a bi-exponential decay equation of  $f(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ . Average lifetime ( $\tau_{\text{ave}}$ ) was calculated by the weighted average of  $(A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$

Samples	$A_1$	$\tau_1$ (ns)	$A_2$	$\tau_2$ (ns)	$\tau_{\text{ave}}$ (ns)
Glass/perovskite w/o MgCl <sub>2</sub>	29111.5	1.9	65.0	201.2	40.1
Glass/perovskite w/MgCl <sub>2</sub>	4545.8	3.9	150.2	376.5	287.6

recombination pathway associated with  $\tau_1$  decreases or in other words is mostly suppressed by the additive. Since  $\tau_1$  is the one related to the surface defects, whereas  $\tau_2$  is linked to bulk traps,<sup>52</sup> MgCl<sub>2</sub> appears to not only slow down the recombination process but suppress especially the presence of surface traps (*i.e.* the higher the number of surface traps, the larger the contribution ( $A_1$ )). As a result, average carrier lifetime ( $\tau_{\text{ave}}$ ) increases significantly from 40.1 ns to 287.6 ns after addition of MgCl<sub>2</sub>. Trap density ( $n_t$ ) is also evaluated from the space charge-limited current (SCLC) of a device with an electron-only configuration of FTO/SnO<sub>2</sub>/perovskite/PCBM/Au<sup>53</sup> as shown in Fig. 7(c).  $n_t$  is

calculated based on the trap-filled-limit voltage ( $V_{\text{TFL}}$ ) obtained from dark  $J$ - $V$  curves in Fig. 7(c).<sup>15</sup>  $V_{\text{TFL}}$  is estimated to be 0.702 V for the pristine FAPbI<sub>3</sub>, which is significantly lowered to 0.186 V after the addition of MgCl<sub>2</sub>. As a result,  $n_t$  decreases from  $1.08 \times 10^{16} \text{ cm}^{-3}$ , which is consistent with the reported value,<sup>54</sup> to  $3.19 \times 10^{15} \text{ cm}^{-3}$  after the addition of MgCl<sub>2</sub>. The prolonged  $\tau_{\text{ave}}$  is thus attributed to the decreased  $n_t$ . The reverse saturation current density ( $J_0$ ) and the ideality factor ( $m$ ) are also estimated from the full solar cell device structure in the dark. The dark  $J$ - $V$  data shown in Fig. 7(d) result in  $J_0 = 2.64 \times 10^{-4} \text{ mA cm}^{-2}$  for the PSC employing the FAPbI<sub>3</sub> without additive, which is more than two orders of magnitude lowered after MgCl<sub>2</sub> ( $J_0 = 4.87 \times 10^{-6} \text{ mA cm}^{-2}$ ). In addition, the addition of MgCl<sub>2</sub> lowers  $m$  from 1.82 to 1.42. The lower  $J_0$  supports that the MgCl<sub>2</sub> additive in FAPbI<sub>3</sub> decreases shallow trap states. The reduced  $m$  is indicative of a suppression of the trap-assisted (mono molecular) recombination by the presence of MgCl<sub>2</sub> since the ideality factor correlates with the bimolecular band-to-band recombination ( $m = 1$ ) and the Shockley-Read-Hall (SRH)

recombination ( $m = 2$ ) in photoelectric devices.<sup>55</sup> The change in  $J_0$  and  $m$  is also responsible for the improved  $V_{oc}$  and FF.<sup>56,57</sup>

### Efficiency and stability of PSCs employing the FAPbI<sub>3</sub> film with MgCl<sub>2</sub> additive

Fig. 8(a) shows the  $J$ - $V$  curves for the best performing PSCs employing the FAPbI<sub>3</sub> films with and without 5 mol% MgCl<sub>2</sub>. The relevant photovoltaic parameters obtained from RS and FS are listed in Table 4. The PCE estimated from RS is enhanced from 17.27% to 21.11% after addition of 5 mol% MgCl<sub>2</sub> in the FAPbI<sub>3</sub> precursor solution due to the increment of  $V_{oc}$  from 1.06 V to 1.15 V, FF from 0.73 to 0.79 and  $J_{sc}$  from 22.39 mA cm<sup>-2</sup> to 23.33 mA cm<sup>-2</sup>. The integrated  $J_{sc}$ s from the EQE data in Fig. 8(b) show a slight deviation from the measured  $J_{sc}$  values but the same tendency (20.07 mA cm<sup>-2</sup> without additive vs. 22.32 mA cm<sup>-2</sup> with MgCl<sub>2</sub> additive). It is found from the steady-state  $J_{sc}$  and PCE measured at the maximum power point (MPP) that  $J_{sc}$  and PCE remain almost unchanged after 1500 s (Fig. 8(c)). This indicates that the MgCl<sub>2</sub>

**Table 4** Photovoltaic parameters of the best performing PSCs employing FAPbI<sub>3</sub> with and without 5 mol% MgCl<sub>2</sub> additive. FS and RS stand for forward scan and reverse scan, respectively

		$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (V)	FF	PCE (%)
Ref (w/o)	FS	22.41	1.07	0.74	17.74
	RS	22.39	1.06	0.73	17.27
MgCl <sub>2</sub> (5%)	FS	23.33	1.13	0.78	20.58
	RS	23.33	1.15	0.79	21.11

additive improves not only the efficiency but also the stability due to reduced bulk and surface defects simultaneously.

## Conclusions

We have demonstrated that the addition of MgCl<sub>2</sub> in the FAPbI<sub>3</sub> precursor solution substantially improved the photovoltaic performance without altering the bandgap and lattice constant. It was also found that the concentration of the additive played an important role in determining the photovoltaic



**Fig. 8** (a)  $J$ - $V$  curves and (b) external quantum efficiency (EQE) of PSCs employing FAPbI<sub>3</sub> with and without MgCl<sub>2</sub> additive. (c) Steady-state  $J_{sc}$  and PCE for the PSCs employing FAPbI<sub>3</sub> with and without the MgCl<sub>2</sub> additive, measured at the maximum power point (MPP) for 1500 s under continuous 1 sun illumination.



performance.  $\text{CaCl}_2$  and  $\text{BaCl}_2$  were found to increase the photovoltaic performance but the increment was marginal. For  $\text{SrCl}_2$ , the addition of  $\text{SrCl}_2$  showed a negative effect due to poor morphology and incomplete  $\delta \rightarrow \alpha$  phase transition. Using a nominal concentration of 5 mol% of  $\text{MgCl}_2$ , a photo-stable and 21.11% efficient PSC was achieved.

## Experimental details

### Materials

*N,N*-Dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.9%), diethyl ether (99.7%), chlorobenzene (CB, 99.8%), formamidinium acetate (FAAc, 99%), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 99.8%), 4-*tert*-butylpyridine (*t*BP, 98%), acetonitrile (ACN, 99.999%), hydroiodic acid (HI, 57 wt% in water), magnesium chloride ( $\text{MgCl}_2$ , 99.99%), calcium chloride ( $\text{CaCl}_2$ , 99.9%), strontium chloride ( $\text{SrCl}_2$ , 99.99%) and barium chloride ( $\text{BaCl}_2$ , 99.999%) were purchased from Sigma-Aldrich. Aqueous colloidal tin(IV) oxide solution ( $\text{SnO}_2$ , 15% in  $\text{H}_2\text{O}$ ) was purchased from Alfa Aesar. 2,2',7,7'-tetrakis(*N,N'*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-MeOTAD) was purchased from Share-Chem. Lead(II) iodide ( $\text{PbI}_2$ , 95%) was purchased from Kanto Chemical Co., Inc. All the chemicals were used as-received without further purification. Fluorine doped tin oxide (FTO) glass (Pilkington, TEC-8,  $8 \Omega \text{ sq}^{-1}$ ) was used as a transparent electrode.

### Synthesis of formamidinium iodide (FAI)

FAI was synthesized by reacting FAAc with HI. HI was slowly dropped into a round-bottom flask filled with FAAc, which was stirred for 2 h at  $0^\circ\text{C}$ . The product was recovered by evaporating the solvent at  $60^\circ\text{C}$  using a rotary evaporator, which was washed with diethyl ether and recrystallized from ethanol. Finally, the white precipitate was dried in a vacuum oven at  $65^\circ\text{C}$  for 24 h and then stored in a glove box filled with argon prior to use.

### Synthesis of $\text{FAPbI}_3$ powder

$\text{FAPbI}_3$  powder was synthesized by reacting FAI (2.236 g) with  $\text{PbI}_2$  (4.61 g) (molar ratio FAI :  $\text{PbI}_2$  = 1.3 : 1) in 60 ml ACN under stirring for 2 days at room temperature.<sup>20</sup> The product was dried in a vacuum oven for 2 days at room-temperature and then stored in a glove box filled with argon.

### Device fabrication

FTO-coated glass was cleaned with solvents (water and ethanol), and was further treated with ultraviolet-ozone (UVO) for 40 min. A  $\text{SnO}_2$  thin layer was prepared by spin-coating the diluted  $\text{SnO}_2$  solution on the cleaned FTO substrate at 4000 rpm for 20 s and then annealed at  $185^\circ\text{C}$  for 30 min. The  $\text{SnO}_2$ -coated FTO substrate was treated with UVO for 20 min prior to deposition of the perovskite precursor. The perovskite precursor solution was prepared by dissolving the pre-synthesized  $\text{FAPbI}_3$  powder (concentration was 1.4 M) in a mixed solvent of DMF and DMSO (DMF : DMSO = 8 : 1 v/v). To study the effect of the additives, a certain amount of additive ( $\text{MgCl}_2$  (5%): 0.0033 g,  $\text{CaCl}_2$

(1%): 0.0008 g,  $\text{SrCl}_2$  (10%): 0.0111 g, and  $\text{CaCl}_2$  (9%): 0.0131 g) was mixed with 0.4431 g of  $\text{FAPbI}_3$  powder in 0.5 ml of DMF/DMSO mixed solvent, which was stirred for over 12 h. It should be noted that  $\text{MgCl}_2$  itself was dissolved well in the mixed DMF/DMSO solvent but a precipitate was partially formed when it was mixed with  $\text{FAPbI}_3$ . Thus filtration was required especially for the  $\text{MgCl}_2$  case. For the perovskite deposition, the spin-coating condition was as follows. The precursor solution was filtered and 25  $\mu\text{l}$  of precursor solution was spread on a  $\text{SnO}_2$ /FTO substrate, which was spun at 1000 rpm for 5 s and 5000 rpm for 20 s. Diethyl ether (1 ml) was dripped 20 s after spinning. The as-spun film was annealed at  $150^\circ\text{C}$  for 30 min. A spiro-MeOTAD hole transporting layer was formed on the perovskite film by spin coating 20  $\mu\text{l}$  of the spiro-MeOTAD solution (72.3 mg of spiro-MeOTAD, 28.8  $\mu\text{l}$  of *t*BP, and 17.5  $\mu\text{l}$  of LiTFSI solution (520 mg LiTFSI in 1 ml ACN in 1 mL of CB)) at 4000 rpm for 20 s. On top of the spiro-MeOTAD layer, a ca. 65 nm-thick Au electrode was formed by a thermal evaporation method at an evaporation rate of  $0.3 \text{ \AA s}^{-1}$  under ca.  $3.8 \times 10^{-7}$  Torr.

### Characterization

Current density–voltage (*J*–*V*) curves were obtained by a solar simulator with a 450 W xenon lamp (Newport 6279 NS) and a Keithley 2400 source meter. The AM 1.5G one sun ( $100 \text{ mW cm}^{-2}$ ) was adjusted by the NREL-calibrated silicon reference solar cell with a KG-5 filter. The external quantum efficiency (EQE) was measured using an EQE system equipped with a 75 W xenon lamp (USHIO) as a white light source, where the monochromatic beam was generated by chopping the white light. Scanning electron microscopy (SEM) images were observed with field-emission scanning electron microscopy (JSM7000F). UV-vis spectra were recorded using a UV-vis spectrophotometer (Lambda 45, PerkinElmer). Steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra were measured using a fluorescence spectrometer (QuantaTau C11367-12, Hamamatsu) with excitation of a 464 nm laser (PLP-10, Hamamatsu) pulsed at a frequency of 10 MHz for steady-state PL and 200 kHz for TRPL. X-ray diffraction (XRD) patterns were obtained by the diffractometer (Rigaku Smart lab SE) with monochromatic  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) at a scan rate of  $4^\circ \text{ min}^{-1}$ . X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) measurements were carried out on an ESCALAB 250 XPS system (Thermo Fisher Scientific) with Al  $\text{K}\alpha$  X-ray radiation (1486.6 eV) for XPS and He I (21.2 eV) for UPS.

## Conflicts of interest

The authors declare no conflict of interest.

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