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Pushing the limit of Cs incorporation into FAPbBr₃ perovskite to enhance solar cells performances

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ABSTRACT

Cation compositional engineering has revealed a powerful design tool to manipulate the perovskite structural and optoelectronic characteristics with a tremendous impact on device performances. Tuning the bandgap by cation and anion compositional mixing, for instance, is paramount to target different optoelectronic segments, from light emitting applications to tandem solar cells. However, structural and photo instabilities, and phase segregation come along, imposing a severe control on the material composition and structure. Here we develop highly uniform alloy of mixed cation $FA_{(1-x)}Cs_xPbBr_3$ perovskite thin films pushing for the first time the Cs content up to 30%. In contrast to what has been reported so far, this composition leads to a high quality crystalline film, maintaining a single cubic phase arrangement. In addition, a remarkably high robustness against moisture and phase purity is observed. The experimental finding is also supported by density functional theory simulations, demonstrating at the atomistic level Cs segregation starting from Cs concentration around 37.5%. Beyond that, phase segregation happens, leading to formation of an unstable pure Cs-rich region. Low temperature photoluminescence (PL) measurements reveal that the addition of Cs eliminates the non-radiative channel into mid-gap traps, as evident by the lack of the broad emission band, often associated with recombination of self-trapped exciton, present for 0% Cs. This, in turn, reduces the non-radiative recombination losses which manifests as high performance solar cells. Indeed, when embodied in solar devices, Cs incorporation leads to enhanced device performances, with an open circuit voltage beyond 1.33 V.

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In recent years, we have witnessed the enormous increase in interest for metal halide perovskite for optoelectronic applications, ranging from photovoltaics (PVs) to light emitting diodes (LEDs) and photodetectors.^{1–6} Their unique attributes, such as high extinction coefficients,⁷ long charge carrier diffusion lengths,^{8–10} tunable bandgaps,^{11–15} and high charge carrier mobilities,^{16–18} along with the ease of processes, sustained such rapid expansion. Hybrid perovskites generally arrange into the ABX₃ structure, which includes

the A cation such as methylammonium (MA), formamidinium (FA), or cesium (Cs); the metal cation B (Pb²⁺, Sn²⁺, Bi⁺, or Ge²⁺); and a halide anion X (Cl⁻, Br⁻, I⁻).^{1,19-23} Controlling the A-site cations and halide anions enabled the fine tuning of the optoelectronic and structural properties, such as the material bandgap, which triggered a large variety of optoelectronic applications. The MA-based hybrid perovskite has been the pioneer for this class of materials; however, despite state-of-the art performances, MA-cation-based

perovskites suffer from inherently high instability. When exposed to heat or moisture, MAPbX3 can decompose to gaseous methylamine and hydrogen iodide.²⁴ In search for a stable perovskite crystal structure, A cations such as FA⁺ and Cs⁺ have been used in combination/or in replacement of MA⁺. FAPbI₃, for instance, demonstrated superior thermal stability, along with a reduced bandgap, and longer carrier lifetime. At room temperature, however, this material spontaneously forms a non-perovskite yellow δ-phase.^{25,26} In contrast to FAPbI₃, FAPbBr₃ has a relatively stable pseudocubic structure,²⁷ higher charge-carrier mobility [62 cm²/Vs in single crystals with respect to MAPbBr₃ (24 cm²/Vs)], at comparable trap density (around 10^{10} cm⁻³ in single crystals).^{28,29} Alternatively, the use of Cs cations has recently attracted an enormous interest: CsPbBr₃ perovskites, for instance, have demonstrated high thermal stability (~580 $^\circ C$ for CsPbBr3, compared to ~220 $^\circ C$ for MAPbBr3.) 30 In addition, these materials have excellent optoelectronic properties such as the high charge-carrier mobility (1000 cm²/Vs), long exciton lifetime (2.5 μ s),³¹ and reduced exciton binding energy (40 meV).³² In particular, when mixed with the organic A site cations, the smaller ionic radius of Cs (1.81 Å), compared to MA (2.70 Å) and FA (2.79 Å), can effectively assist the crystallization of a stable FA perovskite, by the concomitant effects of lattice contraction and entropy stabilization.^{33,34} As a result, Cs doping stabilizes the FAPbI3 or FAPbI3-xBrx perovskite with consequent benefit for material and device stability.³⁴ Importantly, the intrinsic entropy favors a stable crystal phase with the Cs addition. However, it has been so far experimentally proven to be able to modulate the Cs/FA stoichiometry range only up to 10%-20%.⁵ Beyond this, intrinsic instability happens and unwanted phase segregation occurs.

In this work, we have carefully modulated the perovskite composition and deposition process, enabling to boost the crystallinity by pushing the limit of Cs incorporation to 30% in FA_{0.7}Cs_{0.3}PbBr₃. The perovskite films exhibit outstanding structural stability tested for 28 days, with no evidence of phase segregation, as well as improved physical-chemical properties, in terms of suppressed nonradiative recombination associated with reduced trap density, as proven by temperature dependent photoluminescence (PL) studies. Our experimental findings have been supported by density functional theory (DFT) calculations, which predict the Cs segregation at high Cs concentrations.

In addition, to demonstrate the practical importance of this material, we have tested it as an active layer in solar cells. Perovskite solar cells have been developed showing a remarkably high Voc, beyond 1.3 V, and enhanced PV performances, providing a step further in the research towards high open circuit voltage (Voc) perovskite materials, a hot topic for tandem perovskite solar cell applications (see Table 1).

TABLE I. Photovoltaic parameters of best performing $FA_{(1-x)}Cs_xPbBr_3$ perovskite solar cells (x = 0, 0.3, 0.5) measured under 1 sun illumination.

Composition	Voc (V)	Jsc (mA/cm ²)	FF (%)	PCE (%)
FA _{0.7} Cs _{0.3} PbBr ₃	1.338	7.06	0.788	7.45
FA0.9Cs0.1PbBr3	1.234	7.07	0.711	6.21
FAPbBr ₃	1.181	7.06	0.731	6.10

Perovskite thin films have been prepared from a perovskite solution (1.2M) obtained by mixing FABr, CsBr, and PbBr₂ in DMSO. Various percentages of CsBr from x = 0, 0.1, 0.3, 0.5, 0.7,0.9, and 1 have been tested to form $FA_{(1-x)}Cs_xPbBr_3$ thin films. Note that for Cs% > 50% the solutions present partial aggregation due to scarce insolubility of the CsBr in DMSO. This causes the formation of aggregates which prevents the deposition of a uniform film (see Fig. S1). The prepared perovskite precursors are spin-coated on the fluorine-doped tin oxide (FTO)/compact layer TiO₂ (c-TiO₂)/mesoporus layer TiO₂ (mp-TiO₂)/SnO₂ substrates at 1000 rpm for 10 s and 4000 rpm for 30 s. Instead of using the $FA_{(1-x)}Cs_xPbBr_3$ nanocrystal pinching method by using additives in the antisolvent as reported by Cho *et al.* for LED applications,⁵ we use a simple anti-solvent dropping process to wash out the DMSO and to induce an instantaneous crystallization of the perovskite film by adding chlorobenzene 6 s before the end of the spin-coating process. The films are finally annealed at 100 °C for 60 min. This results in a compact, pinhole-free thin film of $FA_{(1-x)}Cs_xPbBr_3$. The FA_{0.7}Cs_{0.3}PbBr₃ film shows closely packed grains with an average size of 315 nm (as shown in the supplementary material, Fig. S2).

First, we verified, both experimentally and theoretically, how the chemical composition of $FA_{(1-x)}Cs_xPbBr_3$ impacts on the optoelectronic properties of the film in terms of bandgap.

Figures 1(a) and 1(b) show the ultraviolet-visible (UV-VIS) absorption and PL spectra for the different FA(1-x)CsxPbBr3 at 0 < x < 1, along with a picture of the perovskite thin films on glass [see the inset of Fig. 1(a)] and the calculated bandgap. The FAPbBr₃ shows an absorbance edge at 2.273 eV, as retrieved from the Tauc plot in Fig. S3a. As we increase the fraction of Cs, the absorption band experiences a clear blue shift up to 2.311 eV, when x = 1 (see Fig. S3). The corresponding bandgap of the perovskite is gradually shifted to the higher energy from 2.27 to 2.31 eV. In fair matching, the normalized PL spectra [Fig. 1(b)] show a continuous shift upon varying the Cs/FA ratio. In Fig. 1(c), the theoretical predictions of the bandgap evolution are given for the structures relaxed with Perdew-Burke-Ernzerhof for solids (PBEsol) [and Perdew-Burke-Ernzerhof (PBE) in Fig. S4] density functionals. The overall trend is the increase in the bandgap upon Cs substitution into FAPbBr₃, which nicely agrees with the experimental data.^{4,5} The fluctuations observed for PBE at 12%-20% of Cs are small and comparable with those induced by different orientations of the FA cation, demonstrating how the bandgap is sensitive to geometrical changes. Such a gradual shift is attributed to a fine geometrical effect influencing the crystal structure: Cs doping of the FAPbBr₃ structure reduces the Pb-Br-Pb angles [Fig. 1(d)], in line with the observed bandgap increase. The reduction in the Pb-Br orbital overlap due to the angle Pb-Br-Pb decrease pushes the valence band maximum and conduction band minimum toward lower energies and thereby increases the optical bandgap.^{35,36} Notably, such widening of the bandgap is potentially highly beneficial for the construction of perovskite tandem solar cells.^{37,38} Moreover, the introduction of Cs decreases crystallographic cell parameters and homogenizes the distribution of Pb–Br bond lengths, favoring structure stabilization [see Fig. 1(d) and Fig. S5].

To identify the effect of Cs cations on the crystallization of the $FA_{(1-x)}Cs_xPbBr_3$ perovskite, we performed X-ray diffraction (XRD) analysis, as shown in Fig. 2(a). The (100) and (200) reflections are clearly visible near $2\theta \sim 14^{\circ}-15^{\circ}$ and $28^{\circ}-30^{\circ}$. The XRD shows that



FIG. 1. (a) UV-Vis absorption of FA1-xCsxPbBr3 (inset: pictures of the $FA_{1-x}Cs_xPbBr_3$ films going from x = 1 to x = 0, left to right); (b) photoluminescence (PL) spectra (normalized) upon excitation at 400 nm for the $FA_{1-x}Cs_xPbBr_3$ deposited on glass/FTO/c-TiO2/mp-TiO2/SnO2 substrate; (c) bandgaps of FA1-xCsxPbBr3 as a function of Cs concentration (PBEsol-relaxed structures, GLLBSC gaps + PBE-SOC correction); (d) structural changes in FAPbBr3 upon Cs doping: comparison of FAPbBr3 (left) with FA0.5Cs0.5PbBr3 (right): change in the tilting angles.

even for a high Cs content, a single-phase $FA_{(1-x)}Cs_xPbBr_3$ crystal is present, and the peaks corresponding to the hexagonal FAPbBr₃ phase are absent. In the literature, one often observes an XRD peak at ~12.5° (assigned to PbBr₂), which is usually ascribed to incomplete reaction between FABr/CsBr and PbBr₂ at Cs = 30%. Going

from Cs = 10% to Cs = 30%, the peak shifts to higher 2 θ positions [from 14.92° for x = 0 to 14.94° for x = 0.1 and to 15.08° for x = 0.3; see the enlarged XRD pattern in Fig. 2(a)]; this trend indicates that the lattice constant gradually decreased because of the much lower ionic radius of Cs⁺ cations (1.81 Å) than of FA⁺ cations (2.79 Å), in



FIG. 2. (a) X-ray diffraction (XRD) pattern of the FA_(1-x)CsxPbBr₃ perovskite film (x = 0, 0.1, 0.3, 0.5) on glass/FTO/c-TiO₂/mp-TiO₂/SnO₂ substrates (left) and enlarged XRD pattern on (100) reflections (right). (b) XRD pattern of the FA_{0.7}Cs_{0.3}PbBr₃ film measured after 0, 2, and 4 weeks and stored in dark in a dry box.

agreement with the literature.⁴ The gradual shift in XRD peak position also implies the formation of single-phase FA_(1-x)Cs_xPbBr₃ crystals without phase segregation. This trend not only implies the formation of single-phase FA(1-x)CsxPbBr3 crystals without phase segregation but also indicates that in our case the lattice constant is unaffected by Cs doping (at least up to 30%, within the instrument resolution). To confirm the integration of Cs % in the film, we performed elemental mapping and energy dispersive X-ray spectroscopy (EDS), as shown in Fig. S6. Results confirm that Cs is well distributed in the thin film. Upon the addition of 50% Cs, the 100 intensity decreases indicating that above this threshold the increase in Cs molar proportion decreases the crystal quality of $FA_{(1-x)}Cs_{x}PbBr_{3}$ films. Figure 2(b) compares the XRD pattern of the representative $FA_{(1-x)}Cs_xPbBr_3$ (x = 0.3) film measured after 2 and 4 weeks upon aging in dry atmosphere. Note that we chose this percentage because, as explained later on, it is the most relevant for devices. No visible change in the XRD spectra is observed, neither the rise of additional peaks related to the formation of phases associated with degradation nor phase separation. Thus, the incorporation of inorganic Cs cations in the A-site in the perovskite could suppress its instability in air.

Mixing Cs^+ and FA^+ allows us to improve the tolerance factor (t) in the mixed compounds $FA_{(1-x)}Cs_xPbBr_3$, enhancing the stability of the perovskite phase,

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$$

Computing the tolerance factor either for crystal or ionic radii of constituent elements leads to the optimum Cs concentration of 20%–30%. At the same time, this does not exclude the possibility of Cs phase segregation leading to the appearance of other phases. To verify this hypothesis, we examine the relative energies of structures with different patterns of Cs distribution (depicted in Fig. 3), ranging from the segregated to homogeneous ones, taking as a reference the energy of the most stable structure: $E_{rel} = E - E_{min}$.

The sum of all Cs–Cs distances $a_{Cs^i-Cs^j}$ in the sample is taken as a homogeneity criterion

$$\sum_{i=1}^n \sum_{j>i}^n a_{Cs^i - Cs^j}$$

The smaller is this sum, the more inhomogeneous, or segregated, is the distribution of Cs, and vice versa, the biggest sums correspond to the most homogeneous Cs distributions. At small Cs concentrations (~25%), the energy difference between the structures with Cs-segregated (6 Å) and homogeneous Cs (10 Å) distribution is only 0.05–0.10 eV, implying that homogeneous Cs distribution can take place. With increasing Cs concentration (\geq 37.5%) segregated structures become more stabilized compared to homogeneous ones (Fig. 3). Indeed, at Cs concentrations as high as 37.5%–50%, segregated configuration is stabilized with respect to the homogeneous ones by ca. 0.25 eV per unit cell.

It means that admixing high amounts of Cs leads to structural inhomogeneities, which can result in defects, crystal cleavages, and phase segregation, which is also observed experimentally in the form of additional CsPbBr₃ and Cs₄PbBr₆ phases.⁴ These inhomogeneities, either in the form of additional phases or simply as Cs accumulations, can be detrimental for device performances and potentially serve as recombination centers.



FIG. 3. Energy distribution of homogeneous and segregated Cs-doped $FA_{(1-x)}Cs_xPbBr_3$ structures as a function of Cs concentration: [(a)-(c)] structure of $FA_{(1-x)}Cs_xPbBr_3$ models and [(d)-(f)] dependence of relative energy on the sum of Cs-Cs distances.

To gain deeper insight into the optoelectronic properties, we measured the PL spectra as a function of temperature. Results are shown in Fig. 4.

Figure 4 compared the PL spectra as a function of temperature for the $FA_{(1-x)}Cs_xPbBr_3$, where x = 0.3 and x = 0 [Figs. 4(a) and 4(b), respectively). Upon reducing temperature, PL spectra get narrower due to reduced broadening. Interestingly, if no Cs is incorporated, at low T (100 K), an additional band is observed around 600 nm, red shifted with respect to the main band edge emission. This band has been already observed in hybrid perovskites and generally attributed to mid gap defect-induced emission or self-trapped exciton.³⁹ If 30% of Cs is incorporated, we note the absence of this band, which implies that the incorporation of Cs = 30% eliminates the non-radiative trapping channel, favoring the radiative recombination. Note that for an unbalanced Cs/FS ratio (such as 0:1 or 1:0) this band is also detectable at room temperature [Fig. 1(b)], as a further confirmation that mixing with Cs% between 10% and 30% is beneficial, reducing trap-mediated recombination. This effect is also visible in total PL (see Fig. S7) as it shows a higher intensity for the Cs = 30% sample.



FIG. 4. PL spectra of $FA_{(1-x)}Cs_xPbBr_3$ on the glass-SnO₂ substrate from 300 K to 100 K upon excitation at 400 nm for (a) x = 0.3 and (b) x = 0. Inset: a comparison of the two compositions at 100 K (normalized PL).

Given the structural stability of the material, we explore the application of the $FA_{(1-x)}Cs_xPbBr_3$, with x = 30% in high bandgap solar cells which have recently attracted enormous interest for tandem solar cell applications. Devices were prepared according to a standard deposition protocol. Details can be found in the experimental part, and following the protocol in the previous reports, ^{40,41} the $FA_{(1-x)}Cs_xPbBr_3$ perovskite layer is deposited on top of an FTO glass substrate coated with a thin compact layer of TiO₂ as an electron transporting layer, mesoporous TiO₂ layer, and passivating SnO₂ layer. PTAA as the hole-transporting materials (HTMs) and gold counter electrode are deposited on top of the perovskite layer.

Devices show improved performances with the addition of 30% Cs, delivering Voc = 1.338 V and PCE = 7.45% for the champion cell [see Fig. 5(a) and Table 1], which is among the highest value reported so far in the literature for Br-based high bandgap

perovskite solar cells. Hysteresis is observed for the device employing $FA_{0.7}Cs_{0.3}PbBr_3$ perovskite and reported in Fig. S8. Device statistics and external quantum efficiency (EQE) measurement are reported in Table S1 and Fig. S9, respectively. Figure 5(b) shows the J-V characteristics of the same device measured after 11 weeks upon being stored in a dry box. It is remarkable that the device shows nearly the same behavior without any relevant sign of degradation of the device performances.

Our study demonstrated that the Cs% can be pushed up to 30% for the fabrication of uniform polycrystalline $FA_{(1-x)}Cs_xPbBr_3$ films with the optimal structural properties and reduced defect density. The Cs doping imparts beneficial structural properties to the perovskite, improving the single-phase crystal quality for the Cs content up to 30% which results in polycrystalline films with the optimal structural properties and reduced defect density. Employed in solar



FIG. 5. (a) J-V characteristics of FA_(1-x)Cs_xPbBr₃ perovskite solar cells measured at 1 sun intensity. (b) J-V characteristics of FA_{0.7}Cs_{0.3}PbBr₃ perovskite solar cells: comparison between the fresh sample and the aged sample after 11 weeks (stored in a dry environment).

cells, the perovskite delivers high open circuit voltage approaching 1.4 V, which is highly desirable for tandem application. Our work provides compelling evidence that careful cation engineering with such a large Cs amount can be an interesting route toward high bandgap efficient perovskite solar cells. In addition, we envisage that our material can also be an interesting testbed for efficient light emitting applications, owing to the reduced trap-mediated recombination and wide bandgap.

Additional data, including material characterization, experimental details, and additional information on the computational results, have been included in the supplementary material.

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