11th International Conference on Green Energy & Environmental Engineering (GEEE-2025) Proceedings of Engineering & Technology – PET-Vol 94, pp. 217-231

Enhancing the Stability of CsPbI3 for Photovoltaic Applications via Formamidinium Iodide Incorporation in ambient air

Rania Boudaya^{#1}, Fayçal Kouki^{#1}, Philippe Lang *²

^{#1} Laboratoire de Matériaux Avancés et Phénomènes Quantiques (LMAPQ), Faculté des Sciences de Tunis, Université Tunis El-Manar, 2092 Tunis, Tunisia

¹ boudaya.rania11@gmail.com

¹ faycal_kouki@yahoo.fr

^{*2} ITODYS, Université Paris-Cité, CNRS UMR 7086, 15 rue Jean-Antoine de Baïf, 75205, Paris, CEDEX 13, France

² Philippe Lang lang@u-paris.fr

Abstract

Perovskite materials exhibit tremendous promise for next-generation photovoltaic technologies due to their outstanding optoelectronic properties, involving high absorption coefficients, adjustable bandgaps, and long carrier diffusion lengths. Among them, lead halide perovskite has more advanced, achieving power conversion efficiencies (PCE) surpassing 25.2% in single-junction solar cells. However, challenges related to stability, scalability, and environmental impact continue to limit their commercialization. Cesium lead triiodide (CsPbI3) perovskites have great potential for photovoltaic applications but suffer from phase instability. Under ambient conditions, they undergo a rapid transition from the desirable black-phase (α -phase) to the non-perovskite yellow-phase (δ -phase), resulting in significant optical degradation and reduced solar cell efficiency and durability. To address this issue, we incorporated Formamidinium iodide (FAI) as a stabilizing agent for CsPbI₃. The formation of a mixed A-site perovskite (Cs_{0.5} FA_{0.5}) PbI3 via equal cation substitution promotes the obtaining of the black phase, improving crystallinity, reducing defect density, and improving the long-term stability of the material, making it more efficient for photovoltaic devices. This study highlights an effective strategy for stabilizing CsPbI₃-based perovskites, bringing them closer to large-scale deployment in high-performance solar cells.

Keywords: CsPbI₃, equimolar substitution, mixed cation, photoactive phase, perovskite solar cells

I. Introduction

Lead halide perovskites, particularly organic-inorganic hybrid perovskites have revealed previously unheardof levels of efficiency, increasing quickly from 9.7% to more than 25.7% [1-4]. Methylammonium lead triiodide (CH3NH3PbI₃ or MAPbI₃) and formamidinium lead triiodide (NH2CHNH2PbI3 or FAPbI3) are the most widely studied researched materials) with the chemical formula ABX₃, in which A typically represents a monovalent cation such as methylammonium (MA⁺), formamidinium (FA⁺), and cesium (Cs⁺) cations, B is a divalent cation like lead (Pb^{2+}) and tin (Sn^{2+}) cations, and X is anions in the form of halides like iodide (I^{-}), bromide (Br), and chloride (Cl) [5-7]. However, due to their hygroscopicity and volatility, organic components (like methylammonium [MA⁺] and formamidinium [FA⁺]) will chemically degrades in extreme conditions such as high temperatures, moisture, oxygen, and light. As a result, hybrid PSCs have low longterm stability, which significantly limits their commercialization [8,9]. Therefore, an appropriate replacement of the organic components with inorganic cation, producing perovskite that is entirely inorganic and devoid of volatile substances. The most useful all-inorganic lead halide perovskites are $CsPbX_3$ (X = I, Br, Cl), among which CsPbI3 is the most fascinating material in this field. It has outstanding excellent properties such as a narrow band gap approximately 1.73 eV, a high absorption coefficient, long carrier diffusion lengths, low exciton binding energy, and high photoluminescence quantum yields [10-12]. Nonetheless, the photo active CsPbI₃ perovskite phase (cubic α , tetragonal β and orthorhombic γ phases) is unstable and tends to convert into a non-perovskite phase at ambient conditions, which undergoes into an optically inactive yellow phase (δ orthorhombic phase, $E_g = 2.82$ eV), thus significantly affecting the device performance. To enhance the phase stability of CsPbI₃ perovskite for high-efficiency PVs, many strategies and research efforts have been adopted. A high thermodynamically stable CsPbI₃ perovskite was successfully synthesized by Wang et al and obtained a device with a champion PCE of 18.4% [13]. Yuqi Cui, his coworkers reported the CsPbI₃ PSCs achieved PCEs of more than 21% by using a multifunctional room-temperature molten salt, dimethylamine acetate (DMAAc), to control the phase conversion process [14]. Jungang and his co-workers obtained a PCE of 21.15% which is one of the highest PCE among all the reported CsPbI₃ PSCs to date by fabricating γ -CsPbI₃ (photo active phase) by developing an acyloin ligand (1,2-di(thiophen-2-yl) ethane-1,2-dione (DED)) as a phase stabilizer and defect passivator [15]. It should be noted that several studies have demonstrated the effectiveness of aqueous HI as a stabilizer for the cubic CsPbI₃ perovskite phase. The HI additive can significantly lower the crystallization temperature of black perovskite phase. Luo et al. reported a modified HI additive method to prepare black-phase CsPbI₃, in which the as-prepared film was first immersed into hot IPA solution and then annealed at 100 °C [16]. Goldsmith (or tolerance) factor, one of the stability factors of perovskite, helps to determine stability. The ionic radius of formamidinium (2.79 Å) is considerably large, which gives rise to a Goldsmith factor close to 1.01, therefore favoring the hexagonal phase. For cesium, this radius equals 1.81 Å; the tolerance factor corresponds to the orthorhombic CsPbI₃ phase. A straightforward combination of FA⁺ and Cs⁺ cations has the potential to regulate the tolerance factor, achieving values indicative of a stable mixed perovskite phase [17,18]. In this work, we used Formamidinium iodide (FAI) as a stabilizer with equimolar as CsI in the precursor solution to obtain a stable perovskite phase in ambient air because the CsPbI₃ perovskite cannot maintain the cubic octahedral cage and more easily forms an orthorhombic phase at RT. Furthermore, through promoting the formation of compact and homogeneous layers (due to decreased moisture adsorption), ethyl acetate, a low-toxic anti-solvent, has allowed for higher conversion yields. Ethyl acetate and DMSO slow down the photoactive phase transition by inhibiting fast evaporation and increasing conversion yields through hydrogen bonding. By stabilizing CsPbI3 perovskite, these approaches provide absorber material with lower structural dimensionality which improved their performance in perovskite solar cells

II. Experimental Section

2.1. Perovskite precursor solutions: The CsPbI₃ precursor solution was prepared by dissolving a stoichiometric mixture of PbI₂ (1M) and CsI (1M) in anhydrous N, N-dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) mixed solvents (V/V, 8:2). The final solution was stirred and heated at 70 °C for about 15 min then filtered through a 0.45 μ m PVDF syringe filter before deposition. The perovskite solution was applied in two steps, with spin-coating at 1000 and 3000 rpm for 10 and 30 s, respectively. Anti-solvent Ethyl acetate has been purchased from Sigma Aldrich with high purity (>99%) ensuring fabrication of good quality thin films (100 μ L) was added to the substrate 10 s before the end of the second program. The CsPbI3 layers were then annealed on a hot plate at 180 °C for 10 min in ambient air to induce crystallization. The Cs_{0.5} FA_{0.5} PbI₃ precursor solutions were prepared by dissolving PbI2 (1M), CsI (0.5) and FAI (0.5) in anhydrous N, N-dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) mixed solvents (V/V, 8:2). The final solution was stirred and heated at 70 °C for about 15 min and filtered through a 0.45 μ m PVDF syringe filter before

deposition. The perovskite solution was applied in two steps, with spin-coating at 1000 and 3000 rpm for 10 and 30 s, respectively. 100 μ L of ethyl acetate was added to the substrate 10 s before the end of the second program. The films immediately turned brown after spin-coating, indicating perovskite crystallization. Finally, the substrates were annealed at 180 °C for 10 and 13 minutes on a hot plate in ambient air to complete the crystallization process.

2.2. Preparation and characterization of the pure CsPbI₃ and Cs_{0.5} FA_{0.5} PbI₃ thin films: the FTO/Compact-TiO₂ were cleaned sequentially with deionized water, isopropanol and acetone. The perovskite CsPbI₃ and Cs_{0.5} FA_{0.5} PbI₃ thin films were deposited onto FTO/Compact-TiO₂ using two steps, with spin-coating at 1000 and 3000 rpm for 10 and 30 s, respectively. The thin films were annealed at 180 °C in ambient air.

The UV–vis absorption spectra of the films were obtained using UV-visible spectra ranging from 175 to 900 nm were acquired with a Varian Cary 4000 spectrometer. The X-ray diffraction measurements were conducted before and after film aging using a Pananalytical X'PERT PRO X-ray diffractometer equipped with a Co-K α tube ($\lambda = 1.7902$ Å) and an X-ray detector.

III. Results and Discussion

At room temprature, CsPbI₃ crystallizes in the yellow orthorhombic phase (Pnma space group) with wide bandgap, unsuitable for solar cell applications as shown in Figure 1.a [19,20]. Cs⁺ and I⁻ atoms are bonded in a 9-coordinate geometry. Cs-I bond distances varied from 3.93- 4.29 Å. In order to form edge-sharing PbI₆ octahedra, Pb²⁺ is bonded to six I⁻ atoms. The estimated range of Pb-I bond distances ranging from 3.09-3.43 Å [21,22]. This symmetry features three I⁻ sites that are not equivalent. In the first I⁻ site, I⁻ is associated with a 5-coordinate geometry, linked to three Cs⁺ atoms and two Pb²⁺ atoms. In the second site I⁻, I⁻ is linked to two Cs⁺ atoms and three Pb²⁺ atoms to form distorted trigonal bipyramids ICs₂Pb₃ that share corners with three square pyramids ICs₄Pb , as well as corners with four equivalent ICs₂Pb₃ trigonal pyramids, edges with four ICs₄Pb square pyramids and edges with two ICs₂Pb₃ trigonal pyramids. In the third I⁻ site, I⁻ is bonded to four equivalent Cs⁺ and one Pb²⁺ atom to form distorted ICs4Pb square pyramids that share corners with four equivalent ICs4Pb square pyramids, corners with three equivalent ICs2Pb3 trigonal bipyramids, edges with four equivalent ICs4Pb square pyramids, and edges with four equivalent ICs2Pb3 trigonal bipyramids. CsPbI₃ is (Cubic) Perovskite structured and crystallizes in the cubic $P\bar{m}3m$ space group as shown in Figure 1.b. Cs⁺ is bonded to twelve equivalent I⁻ atoms to form CsI₁₂ cuboctahedra that share corners with twelve equivalent CsI₁₂ cuboctahedra, faces with six equivalent CsI₁₂ cuboctahedra, and faces with eight equivalent PbI₆ octahedra. All Cs-I bond lengths are 4.44 Å. Pb²⁺ is bonded to six equivalent I⁻ atoms to form PbI₆ octahedra that share corners with six equivalent PbI₆ octahedra and faces with eight equivalent CsI₁₂ cuboctahedra. The corner-sharing octahedra are not tilted. All Pb-I bond lengths are 3.14 Å. I⁻ is joined to four equivalent Cs¹⁺ and two equivalent Pb²⁺ atoms to form a mixture of distorted corner, edge, and face-sharing ICs₄Pb₂ octahedra [23,24].



Figure 1: a) the orthorhombic phase of CsPbI3 (δ, Pnma), b) the cubic phase of CsPbI3 (α, Pm3m)

We firstly fabricated CsPbI₃ perovskite by one step anti-solvent spin coating on an FTO substrate covered with a layer of compact TiO₂ in ambient air. To identify and assign the different peaks in the diffractogram, XRD spectra of the stack FTO/Compact-TiO₂/Pure CsPbI₃ were taken concurrently before and after the perovskite layer was deposited. These perovskite thin films turned into brown during the spin-coating process, a signal of the black phase perovskite formation. The CsPbI₃ pure film shows a rapid change from cubic phase to orthorhombic phase when annealing time is extended to room temperature. The results obtained indicate that the pure CsPbI₃ is dominated by the yellow phase as shown in the XRD pattern in Fig. 2a. Although, the presence of secondary phases, the photoactive black phase was detected at around 14°, 19.8° and 28.2° respectively associated with the reticular planes: (110), (211) and (220) [20,25]. However, the "black" photoactive phases (cubic α , tetragonal β and orthorhombic γ phases) of CsPbI₃ are formed at high temperatures (e.g. > 350 °C for α -CsPbI₃) it is not easy to obtain this phase with annealing at only 180°C and it undergoes the "yellow" orthorhombic polymorph δ -CsPbI₃ even after we obtain these photoactive phases of CsPbI₃ [26-28].

To address these issues of stability, incorporation of FA^+ into CsPbI₃ has been investigated. Additionally, it was demonstrated that formamidinium iodide (FAI) was an effective surface ligand for the CsPbI₃ quantum dots, enhancing their functionality in perovskite solar cells [29,30]. By adding 0.5 of FAI in the precursor solution of 0.5 CsI-PbI₂ in DMSO and DMF., the resulting perovskite composition is Cs_{0.5} FA_{0.5} PbI₃. Figure 2.b shows the evolution of the XRD patterns of the is Cs_{0.5} FA_{0.5} PbI₃ DRX analyses have revealed the formation of the perovskite phase. This shows that we have succeeded in stabilizing the photoactive (α) phase under atmospheric conditions using simple, effective technological approaches. We can also observe the absence of the PbI_2 peak (hexagonal phase). This could possibly correspond to a complete conversion of PbI_2 to perovskite [31]. Notably, the monotonic shift of the (100) reflection from 14.4° observed in the XRD patterns of Cs_{0.5} FA_{0.5} PbI₃(10 min of annealing) to 14.8° for Cs_{0.5} FA_{0.5} PbI₃ annealed for 13 minutes. The preferred crystallite growth orientation of $Cs_{0.5}$ FA_{0.5} PbI₃(10 min of annealing) perovskite phase. This observation suggests that Cs⁺ and FA⁺ cations are mixed in the crystal lattice. Cationic engineering considerably improves the material's thermal stability with respect to humidity. Additional peaks appearing at 20.2°, 24.8°, 32.8 associated respectively with the reticular planes (110) (111) and (210) that correspond to the α -FACsPbI₃ phase. These peaks shifted to a larger angle as the annealing temperature increases, indicating distortion of the CsPbI₃ crystal lattice due to the incorporation of larger formamidinium ions in place of cesium cations [32]. This can be explained by the inclined position of the octahedra $[PbI_6]^4$ -caused by the difference in ionized radiation between cesium (1,67Å) and formamidinium (2,53Å), as the size of the cation at site A significantly affects the length of the Pb=I liaison [33]. Furthermore, the absence of the yellow δ phase in the film with 13 min annealing confirms the significance of the formamidinium 's incorporation in this film. Given that FAI was introduced in significant quantities to CsPbI₃ instead, the formation of Ruddlesden-Popper layered phases should be expected. Indeed, the low-intensity diffraction peak at 11.11° observed for both films indicates the presence of the broadened interplane spacing characteristic of perovskitelike layered phases [34,35,36] An increase in the intensity of this peak was observed for samples with 13

minutes annealing time. The absence of this peak in the pure $CsPbI_3$ film confirms that added FAI has been incorporated into the perovskite lattice, leading to the stabilization of the photoactive phase and the formation of 2D materials. This prediction is further supported by the fact that similar 2D structures with other organic cations have previously been described in the literature [34, 35,37,38].



Figure 2: X-ray diffraction patterns of a) pure CsPbI₃ annealed for 10 minutes, b) Cs_{0.5} FA_{0.5} PbI₃: 10 min of annealing and Cs_{0.5} FA_{0.5} PbI₃: 13 min of annealing

In this study, the structural parameters of the synthesized materials, including crystallite size, dislocation density, microstrain, and lattice defects, were thoroughly evaluated to understand the impact of introducing FAI on the crystal structure of the CsPbI₃. These parameters were calculated using both the Debye Scherrer method and the Williamson–Hall (W–H) analysis. The Debye–Scherrer equation provided an initial estimation of the average crystallite size based on peak broadening observed in the X-ray diffraction (XRD) patterns.

The crystallites size of the samples was calculated using Debye-Scherrer equation, the following formula is:

$$\mathbf{D} = \frac{\mathbf{K} \cdot \boldsymbol{\lambda}}{\boldsymbol{\beta} \cdot \boldsymbol{\cos} \boldsymbol{\Theta}}$$

while D represents the average crystallite size; K the Scherer's constant (k=0.9)

 λ the wavelength of the X-ray beam (, $\lambda = 1.79$ Å the wavelength of the Co K α), Θ is the Bragg angle and β is the width at half height of the maximum peak (FWHM) of the diffracted line with angle 2 Θ .

11th International Conference on Green Energy & Environmental Engineering (GEEE-2025) Proceedings of Engineering & Technology – PET-Vol 94, pp. 217-231

The average crystallite sizes obtained for samples, pure CsPbI₃ annealed for 10 minutes and Cs_{0.5} FA_{0.5} PbI₃ annealed for 10 min and 13 min as shown in Figure 3 were 32 nm, 36.3 nm and 39.95 nm respectively. When FAI is added to the crystal structure of CsPbI₃, grain size increases dramatically and increases with annealing time. Based on grain size values, the dislocation density (δ) and the micro strain (ϵ) were determined using these following equations:

$$\delta = \frac{1}{D^2}$$
$$\varepsilon = \frac{\beta \cos(\theta)}{4}$$



Figure 3: Crystallite size, microstrain and dislocation of pure CsPbI₃, Cs_{0.5} FA_{0.5} PbI₃: 10 min and 13 min of annealing calculated using the Scherer equation

However, to gain deeper insights into the contribution of lattice strain and to more accurately separate size and strain-induced broadening effects, the Williamson–Hall method was employed.

In Uniform Deformation Model (UDM), the microstrain ε is assumed to be uniform in all crystalline directions and the W-H equation can be written as:

$$\beta Cos(\theta) = \frac{k\lambda}{D} + 4\varepsilon \sin(\theta)$$

Using the results of linear fit, the microstrain is estimated from the slope of the linear fit and the crystallite size from the intersection of the linear fit with the Y-axis. Assuming spherical particles (K=1), the ratio of wavelength to Y-intercept gives the crystallite size. W-H plots of the samples are shown in Fig 4. and the results are shown in Table 1.

Table 1: Results of Debye Scherrer and	W-H analysis: Crystallite size,	microstrain and dislocation density(δ)
--	---------------------------------	---

	Debye Scherrer		W-H analysis		
Samples	Average crystallite size (nm)	Microstrain ε	Average crystallite size (nm)	Microstrain ε	Dislocation density(δ) (line/m2)
Pure CsPbI3	32	0.945	31.81	0.875	9,21622× 10 ¹⁴
Cs _{0.5} FA _{0.5} PbI ₃ : 10 min of annealing	36.3	0.978	35.47	0.895	7,58904× 10 ¹⁴
Cs _{0.5} FA _{0.5} PbI ₃ : 13 min of annealing	39.95	0.838	45.33	0.84	6,26565× 10 ¹⁴



11th International Conference on Green Energy & Environmental Engineering (GEEE-2025) Proceedings of Engineering & Technology – PET-Vol 94, pp. 217-231

Figure 4: W-H plot of pure CsPbI₃, Cs_{0.5} FA_{0.5} PbI₃: 10 min and 13 min of annealing

The crystallite sizes calculated using the Debye–Scherrer and Williamson–Hall methods are closely aligned, indicating consistency between the two approaches. The slight variation between them is due to the Williamson-Hall method accounting for both microstrain and crystallite size, whereas the Debye-Scherrer method considers only size broadening. After incorporating formamidinium iodide (FAI) into the CsPbI3 system, the crystallite size increased slightly from 32 nm to 33 nm, suggesting a modest improvement in crystal growth. Further enhancement was observed when the annealing time of the doped CsPbI3 was extended to 13 minutes, resulting in a significant increase in crystallite size to 39 nm. This growth was accompanied by a decrease in dislocation density, indicating fewer crystal defects. Such improvements are highly beneficial for solar cell performance, as larger crystallite sizes Studying the optical properties of materials is essential in solar cell applications, as they directly influence the device's ability to absorb sunlight and convert it into electrical energy. In this study, we analyzed the absorbance spectra of pure CsPbI3 annealed for 10 minutes, and Cs_{0.5} FA_{0.5} PbI₃ annealed for both 10 and 13 minutes, across the 400–800 nm wavelength range. The results revealed a clear trend: the absorbance increased from the pure CsPbI3 sample to the Cs_{0.5} FA_{0.5} PbI₃ annealed for 10 minutes, with a further enhancement observed in the 13-minute annealed doped sample. This progressive increase can be attributed to improved crystallinity, reduced defect density, and enhanced phase stability introduced by FAI doping and extended annealing. The incorporation of FAI likely facilitates better film formation and promotes the formation of a more photoactive perovskite phase, which contributes to stronger light absorption, an essential factor for boosting solar cell efficiency.





samples

The extinction coefficient (k) represents how strongly a material absorbs or attenuates light as it travels through it. A higher extinction coefficient indicates that more light is being absorbed within the material, which is highly desirable for solar cell applications, as it enhances the generation of charge carriers from incident light. The extinction coefficient is calculated using the following formula: $\kappa = \frac{\alpha \Lambda}{4\pi}$

As shown in Figure 5.b, the sample of $Cs_{0.5}$ FA_{0.5} PbI₃ annealed for 13 minutes exhibited the highest extinction coefficient across the measured wavelength range, indicating superior light absorption capability. This increase in k suggests improved optical density and more effective harvesting of solar energy, both of which are critical for enhancing the overall power conversion efficiency of the solar cell.

IV. conclusion:

In this study, we have successfully developed high-purity α-phase CsPbI3 without the presence of secondary phases under ambient conditions by incorporating equal molar of FAI into CsPbI3. Introducing FAI is an effective method for improving the stability of CsPbI3 perovskite in ambient air and promoting the development of the photoactive black phase by reducing the dimensionality of the CsPbI3 perovskite structure and results in the formation of layered 2D compounds. The development of a precursor that contains an antisolvent during the deposition of the perovskite layer, along with the adjustment of annealing time and temperature, have proven the high quality and stability of the resultant perovskite. According to the study, FAI-incorporated materials with a ratio as CsI have better optical and structural qualities, which makes them more appropriate for photovoltaic applications. Better crystal growth, larger Crystallites and improve optical characteristics are the results of 13 minutes of annealing Cs 0.5 FA 0.5 PbI3, which may improve solar cell performance.

[1] YAO, Xinpeng, HE, Benlin, ZHU, Jingwei, *et al.* Adaptation d'une interface enterrée tout-en-un de type II pour cellules solaires à pérovskite CsPbBr3 entièrement inorganiques de tension 1,635 V. *Nano Energy*, 2022, vol. 96, p. 107138.

[2] YOO, Jason J., SEO, Gabkyung, CHUA, Matthew R., *et al.* Efficient perovskite solar cells via improved carrier management. *Nature*, 2021, vol. 590, no 7847, p. 587-593.

[3] NREL chart (2019) <u>https://www.nrel.gov/pv/cell-efficiency.html</u>

[4] KOJIMA, Akihiro, TESHIMA, Kenjiro, SHIRAI, Yasuo, *et al.* Organometal halide perovskites as visiblelight sensitizers for photovoltaic cells. *Journal of the american chemical society*, 2009, vol. 131, no 17, p. 6050-6051.

[5] LI, Mingya, YUE, Ziyao, YE, Zecong, *et al.* Improving the efficiency and stability of MAPbI3 perovskite solar cells by dipeptide molecules. *Small*, 2024, vol. 20, no 25, p. 2311400.

[6] LU, Ruixue, LIU, Yang, ZHANG, Jiafeng, *et al.* Highly efficient (200) oriented MAPbI3 perovskite solar cells. *Chemical Engineering Journal*, 2022, vol. 433, p. 133845.

[7] TANG, Yan, GU, Zhenkun, FU, Chunpeng, *et al.* FAPbI3 perovskite solar cells: from film morphology regulation to device optimization. *Solar RRL*, 2022, vol. 6, no 6, p. 2200120.

[8] Park, N.G., Grätzel, M., Miyasaka, T., Zhu, K. and Emery, K., Towards stable and commercially available perovskite solar cells. *Nature Energy*, 2016 *1*(11), pp.1-8.

[9] Conings, B., Drijkoningen, J., Gauquelin, N., Babayigit, A., D'Haen, J., D'Olieslaeger, L., Ethirajan, A., Verbeeck, J., Manca, J., Mosconi, E. and Angelis, F.D., Intrinsic thermal instability of methylammonium lead trihalide perovskite. *Advanced Energy Materials*, 2015, *5*(15), p.1500477.

[10] SUTTON, Rebecca J., EPERON, Giles E., MIRANDA, Laura, *et al.* Bandgap-tunable cesium lead halide perovskites with high thermal stability for efficient solar cells. *Advanced Energy Materials*, 2016, vol. 6, no 8, p. 1502458.

[11] JING, Qiang, ZHANG, Mian, HUANG, Xiang, *et al.* Surface passivation of mixed-halide perovskite CsPb (Br x I 1-x) 3 nanocrystals by selective etching for improved stability. *Nanoscale*, 2017, vol. 9, no 22, p. 7391-7396.

[12] DASTIDAR, Subham, LI, Siming, SMOLIN, Sergey Y., *et al.* Slow electron–hole recombination in lead iodide perovskites does not require a molecular dipole. *ACS energy letters*, 2017, vol. 2, no 10, p. 2239-2244.

[13] WANG, Yong, DAR, M. Ibrahim, ONO, Luis K., *et al.* Thermodynamically stabilized β -CsPbI3–based perovskite solar cells with efficiencies> 18%. *Science*, 2019, vol. 365, no 6453, p. 591-595.

[14] CUI, Yuqi, SHI, Jiangjian, MENG, Fanqi, *et al.* A versatile molten-salt induction strategy to achieve efficient CsPbI3 perovskite solar cells with a high open-circuit voltage> 1.2 V. *Advanced Materials*, 2022, vol. 34, no 45, p. 2205028.

[15] WANG, Jungang, CHE, Yuhang, DUAN, Yuwei, *et al.* 21.15%-efficiency and stable γ -CsPbI3 perovskite solar cells enabled by an acyloin ligand. *Advanced Materials*, 2023, vol. 35, no 12, p. 2210223.

[16] Luo, Paifeng, Wei Xia, Shengwen Zhou, Lin Sun, Jigui Cheng, Chenxi Xu, and Yingwei Lu. "Solvent engineering for ambient-air-processed, phase-stable CsPbI3 in perovskite solar cells." *The journal of physical chemistry letters* 7, no. 18 (2016): 3603-3608.

[17] BOZIKI, Ariadni, KUBICKI, Dominik J., MISHRA, Aditya, *et al.* Atomistic Origins of the Limited Phase Stability of Cs+-Rich FA x Cs (1–x) PbI3 Mixtures. *Chemistry of Materials*, 2020, vol. 32, no 6, p. 2605-2614.

[18] YAO, Zhun, ZHAO, Wangen, et LIU, Shengzhong Frank. Stability of the CsPbI 3 perovskite: From fundamentals to improvements. *Journal of Materials Chemistry A*, 2021, vol. 9, no 18, p. 11124-11144.

[19] STOUMPOS, Constantinos C., MALLIAKAS, Christos D., et KANATZIDIS, Mercouri G. Semiconducting tin and lead iodide perovskites with organic cations: phase transitions, high mobilities, and near-infrared photoluminescent properties. *Inorganic chemistry*, 2013, vol. 52, no 15, p. 9019-9038.

[20] EPERON, Giles E., PATERNÒ, Giuseppe M., SUTTON, Rebecca J., *et al.* Inorganic caesium lead iodide perovskite solar cells. *Journal of Materials Chemistry A*, 2015, vol. 3, no 39, p. 19688-19695.

[21] WELLER, Mark T., WEBER, Oliver J., HENRY, Paul F., *et al.* Complete structure and cation orientation in the perovskite photovoltaic methylammonium lead iodide between 100 and 352 K. *Chemical communications*, 2015, vol. 51, no 20, p. 4180-4183.

[22] DENG, Jianping, LI, Jinglei, YANG, Zhi, *et al.* All-inorganic lead halide perovskites: a promising choice for photovoltaics and detectors. *Journal of Materials Chemistry C*, 2019, vol. 7, no 40, p. 12415-12440.

[23] Marronnier, A., Roma, G., Boyer-Richard, S., Pedesseau, L., Jancu, J.M., Bonnassieux, Y., Katan, C., Stoumpos, C.C., Kanatzidis, M.G. and Even, J., 2018. Anharmonicity and disorder in the black phases of cesium lead iodide used for stable inorganic perovskite solar cells. *ACS nano*, *12*(4), pp.3477-3486.

[24] MOIN, Mehrunisa, QADOOS, A., MOIN, Muhammad, *et al.* Pressure-induced modifications in the electronic, mechanical, optical, and thermodynamic properties of CsPbI3 for advanced optoelectronic applications: A DFT study. *Results in Physics*, 2025, p. 108150.

[25] SWARNKAR, Abhishek, MARSHALL, Ashley R., SANEHIRA, Erin M., *et al.* Quantum dot–induced phase stabilization of α-CsPbI3 perovskite for high-efficiency photovoltaics. *Science*, 2016, vol. 354, no 6308, p. 92-95.

[26] A. Marronnier, G. Roma, S. Boyer-Richard, L. Pedesseau, J.-M. Jancu, Y. Bonnassieux, C. Katan, C.C. Stoumpos, M.G. Kanatzidis, J. Even, Anharmonicity and Disorder in the Black Phases of Cesium Lead Iodide Used for Stable Inorganic Perovskite Solar Cells, ACS Nano 12 (4) (2018) 3477–3486

[27] B. Zhao, S.-F. Jin, S. Huang, N. Liu, J.-Y. Ma, D.-J. Xue, Q. Han, J. Ding, Q.-Q. Ge, Y. Feng, J.-S. Hu, Thermodynamically Stable Orthorhombic γ -CsPbI3 Thin Films for High-Performance Photovoltaics, J. Am. Chem. Soc. 140 (37) (2018) 11716–11725

[28] R.J. Sutton, M.R. Filip, A.A. Haghighirad, N. Sakai, B. Wenger, F. Giustino, H. J. Snaith, Cubic or Orthorhombic? Revealing the Crystal Structure of Metastable Black-Phase CsPbI3 by Theory and Experiment, J. ACS Energy Lett. 3 (8) (2018) 1787–1794

[29] S.B. Shivarudraiah, M. Ng, C.-H.A. Li, J.E. Halpert, All-Inorganic, SolutionProcessed, Inverted CsPbI3 Quantum Dot Solar Cells with a PCE of 13.1% Achieved via a Layer-by-Layer FAI Treatment, ACS Appl. Energy Mater. 3 (2020) 5620–5627,

[30] LI, Yong, DUAN, Yuwei, FENG, Jiangshan, *et al.* 25.71%-Efficiency FACsPbI3 Perovskite Solar Cells Enabled by A Thiourea-based Isomer. *Angewandte Chemie International Edition*, 2024, vol. 63, no 49, p. e202410378.

[31] TUMEN-ULZII, Ganbaatar, QIN, Chuanjiang, KLOTZ, Dino, *et al.* Detrimental effect of unreacted PbI2 on the long-term stability of perovskite solar cells. *Advanced Materials*, 2020, vol. 32, no 16, p. 1905035.

[32] Y. Wang, X. Yuan, H. Zhang, et al., "Stabilizing the α -Phase of CsPbI₃ Perovskite by FA Cation Incorporation for Efficient Photovoltaic Applications," *ACS Applied Materials & Interfaces*, **2018**, *10*(32), 26876–26884.

[33] GAO, Caiyun, SHAO, Z]hipeng, SUN, Xiuhong, *et al.* Fabrication and Characterization of FA x Cs1- x PbI3 Polycrystal Perovskite Solar Cells. *Solar RRL*, 2021, vol. 5, no 7, p. 2100166.

[34] J.-F. Liao, H.-S. Rao, B.-X. Chen, D.-B. Kuang, C.-Y. Su, Dimension engineering on cesium lead iodide for efficient and stable perovskite solar cells, J. Mater. Chem. A. 5 (5) (2017) 2066–2072

[35] G. Yang, X. Liu, Y. Sun, C. Teng, Y. Wang, S. Zhang, H. Zhou, Improved current efficiency of quasi-2D multi-cation perovskite light-emitting diodes: the effect of Cs and K, Nanoscale. 12 (3) (2020) 1571–1579

[36] C. Qin, T. Matsushima, A.S.D. Sandanayaka, Y. Tsuchiya, C. Adachi, CentrifugalCoated Quasi-Two-Dimensional Perovskite CsPb2Br 5 Films for Efficient and Stable Light-Emitting Diodes, J. Phys. Chem. Lett. 8 (2017) 5415–5421

[37] Y. Jiang, J. Yuan, Y. Ni, J. Yang, Y. Wang, T. Jiu, M. Yuan, J. Chen, ReducedDimensional α -CsPbX3 Perovskites for Efficient and Stable Photovoltaics, Joule. 2 (7) (2018) 1356–1368

[38] Z. Zhou, S. Yang, K. Xu, H.W. Qiao, J. Xie, Z. Lin, B. Ge, J. He, M. Chen, J. Zhang, Y. Hou, H.G. Yang, Diammonium-Cesium Lead Halide Perovskite with PhaseSegregated Interpenetrating Morphology for Photovoltaics, J. Phys. Chem. Lett. 11 (3) (2020) 747–754