Engineering bandgap of CsPbI$_3$ over 1.7 eV with enhanced stability and transport properties

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HIGHLIGHTS
Perspectives of applying structural distortion to improve the band gap
Perovskites with high band gap over 1.7 eV for potential multijunction application
Enhancing phase stability and transport property without instinct phase separation
The introduction of organic cation of EA with the optimum amount below 0.15
Engineering bandgap of CsPbI₃ over 1.7 eV with enhanced stability and transport properties

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SUMMARY
Potential multijunction application of CsPbI₃ perovskite with silicon solar cells to reach efficiencies beyond the Shockley-Queisser limit motivates tremendous efforts to improve its phase stability and further enlarge its band gap between 1.7 and 1.8 eV. Current strategies to increase band gap via conventional mixed halide engineering are accompanied by detrimental phase segregation under illumination. Here, ethylammonium (EA) in a relatively small fraction (x < 0.15) is first investigated to fit into three-dimensional CsPbI₃ framework to form pure-phase hybrid perovskites with enlarged band gap over 1.7 eV. The increase of band gap is closely associated with the distortion of Pb-I octahedra and the variation of the average Pb-I-Pb angle. Meanwhile, the introduction of EA can retard the crystallization of perovskite and tune the perovskite structure with enhanced phase stability and transport properties.

INTRODUCTION
Generating electricity from solar radiation is a compelling pathway that could lead to a sustainable energy future for the world (Chen, et al., 2016; Zhang et al., 2016; Zheng et al., 2015; Zhang, et al., 2020; Chen, et al., 2017). Inorganic CsPbI₃ perovskite has triggered worldwide interest owing to its relatively large band gap of 1.68 eV to potentially serve as the top cell in tandem devices with silicon solar cell (Yu et al., 2016) and rapid improvement in power conversion efficiency (PCE) from the initial PCE of 0.09% in 2013 to 19.03% in 2019 (Stoumpos et al., 2013; Wang et al., 2019a, 2019b). Despite these clear advantages, cubic black CsPbI₃ is unstable at room temperature and tends to transform into the orthorhombic yellow (d) phase without photovoltaic activity (Straus et al., 2020; Marronnier et al., 2018), largely hampering its further commercialization. Several strategies have been extensively developed to improve the phase stability of CsPbI₃ including composition engineering (Tian et al., 2020; Lau et al., 2019; Lu et al., 2020), crystallization regulation by introducing Lewis acid-base adducts (Li et al., 2020a; Nenon et al., 2018) or polymers (Li et al., 2018a; Jeong et al., 2020; Chen et al., 2019) into the CsPbI₃ precursor, surface capping treatments (Wu et al., 2019; Wang et al., 2018), and dimension reduction by scaling down to quantum dots (Bai et al., 2019; Sadeghi et al., 2020), nanocrystals (Ghosh et al., 2018), or quasi two-dimensional (2D) films (Qing et al., 2019; Zhang et al., 2017; Mauck and Tisdale, 2019; Liu et al., 2018). Among them, composition engineering by partly replacing Cs⁺ with large organic cations can regulate the structural tolerance factor to improve the intrinsic phase stability of CsPbI₃ (Xu et al., 2017, 2019; Lee et al., 2021). The soft lattice of CsPbI₃ induced by its ionic bonding is favorable for a facile cation exchange to regulate the perovskite composition (Deng et al., 2019). Meanwhile, compared with reducing dimension of perovskites exhibiting insufficient charge transport properties (Wheeler et al., 2018; Li et al., 2020b), alloying organic cations is favorable for the formation of sufficient photocarriers to improve the transport properties in photovoltaic devices (Egger et al., 2020). Therefore, composition regulation to form hybrid perovskites is an ideal strategy for structure engineering to adjust the photoelectric properties. However, engineering CsPbI₃ perovskite with organic cations to improve its intrinsic stability is limited to only a few organic cations such as formamidinium (FA) (Hazarika et al., 2018) and methylammonium (MA) (Wang and Chen, 2016). MA and FA cations are inherently unstable in thermal and UV conditions, leading to the degradation of perovskite and the poor lifetime of the photovoltaic devices (Chen et al., 2020b; Juarez-Perez et al., 2016; Yang et al., 2019).

Theoretically, a perovskite-silicon tandem solar cell composed of a silicon bottom cell with a band gap of 1.12–1.2 eV and a perovskite top solar cell with a band gap of 1.7–1.8 eV can achieve a potential PCE over...
CsPbI3 at 500 K exhibits low symmetry structure with distinct tilting of the PbI6 octahedra. The Pb-I distance with EA fractions between 0.1 and 0.5 can regulate the tolerance factor of EAxCs1-xPbI3. The Pb-I distance in EA0.1Cs0.9PbI3 is longer than that in CsPbI3 at 500 K. The structure of EA0.1Cs0.9PbI3 can be retained at 500 K. This approach of alloying large organic EA cations into CsPbI3 perovskite opens up a new avenue to tune the structures of CsPbI3 perovskite with enhanced phase stability and transport properties for potential multijunction applications.

RESULTS AND DISCUSSION
Structure engineering
A prerequisite for a stable three-dimensional (3D) cubic perovskite structure is having a suitable tolerance factor, t, value ranging from 0.8 to 1.0. The t value is defined by the equation $t = (r_M + r_X) / \sqrt{2(r_a + r_e)}$, where $r_M$, $r_X$, and $r_a$ represent the ionic sizes of a univalent cation, an octahedrally coordinated bivalent metal ion, and a halide ion, respectively (Miyazawa et al., 2018). The t value should be close to 1 for a high-symmetry cubic structure. Owing to the small radius of Cs to generate a stable PbI6 octahedral framework (Figures 1A–1C and see Figure S1). Moreover, introducing a certain amount of EA can interact with I by Lewis base N–I hydrogen bonding (Binek et al., 2015), which can inhibit the phase degradation from halide migration (Lin et al., 2020). With the increase of EA fractions from 0.1 to 0.3, distinct structure distortion with a decrease of the average Pb-I-Pb angle can be observed in EA0.3Cs0.7PbI3 (Figure 1C). Theoretically, the decrease of the average Pb-I-Pb angle with a corresponding variation of the Pb-s/p and I-p antibonding overlap will change the band gap of the hybrid perovskite. The band gap variation upon mixing will be further discussed by band structure calculation. The thermal stability of the perovskite upon mixing can be simulated by dynamic calculation as shown in the bottom row of Figures 1A–1C. CsPbI3 at 500 K exhibits low symmetry structure with distinct tilting of the PbI6 octahedra. The Pb-I distance in EA0.1Cs0.9PbI3 is longer than that in CsPbI3 at 500 K. The structure of EA0.1Cs0.9PbI3 can be retained at 500 K, whereas the structure of EA0.3Cs0.7PbI3 collapses completely under the same conditions. These simulation results reveal the deteriorated thermal stability upon EA incorporation. In experiment, when heating at 210°C, it took ~10 min for pure CsPbI3 black film to completely turn yellow, whereas this change for EA0.1Cs0.9PbI3 and EA0.3Cs0.7PbI3 took ~7 min and ~3 min, respectively, indicating poor thermal stability in EA0.3Cs0.7PbI3 hybrid perovskites. The relatively poor thermal stability of organic-inorganic perovskite is mainly induced by the configuration-increased entropy and protons-induced side reactions (Aristidou et al., 2015; Ripalda et al., 2020). After exposing chlorobenzene-submersed films to light, the degradation of EA0.1Cs0.9PbI3 and EA0.3Cs0.7PbI3 films (Figures 1D and 1E) with I2 release was slower than that of CsPbI3 film (Figure 1F), indicating better structural stability upon EA incorporation. The inhibition of I2 release during light soaking might be induced by strain engineering (Li et al., 2018b) and enhanced N-I interaction upon introducing large-sized EA (Figures 1B and 1C). Alloying EA+ in CsPbI3 to form hybrid perovskites with EA fractions between 0.1 and 0.5 can regulate the tolerance factor of EA0.1Cs0.9PbI3 ranging from 0.82 to 0.87 (Figure 1G). The transport properties and the energy band structure of pure CsPbI3 and EA0.1Cs0.9PbI3 perovskites were explored by the calculated partial density of states (PDOS) (Figures 1H and 1I). The transport properties of...
the perovskite solar cells mainly refer to the intrinsic electron transport properties from ion migration/accumulation, the light-induced charge carrier numbers, and the charge carrier recombination lifetime. The conduction bands of pure CsPbI$_3$ were mainly composed of Pb 6p, whereas the valence bands were mainly composed of I 5p (Figure 1H). The negligible density of state (DOS) at the Fermi level of CsPbI$_3$ indicated its relatively poor electron transport property. When incorporating EA, the Fermi energy level moved down to the valence band maximum (VBM), indicating a p-type doping property of EA incorporation (Figure 1I). The band gap of EA$_{0.1}$Cs$_{0.9}$PbI$_3$ was 1.8 eV, slightly larger than that of CsPbI$_3$, resulting from the increase of the antibonding interaction between I-5p and Pb-6p orbitals. Meanwhile, the incorporation of EA with lattice expansion increases the DOS at the Fermi level suggesting enhanced electron transport properties. EA incorporation contributes mainly to the DOS in the region below the VBM instead of the band gap beneficial for more carriers hopping without trap state recombination (Figure 1I).

**Structural characterizations**

Figure 2A shows photographs of the EA$_x$Cs$_{1-x}$PbI$_3$ (0 ≤ x ≤ 0.5) perovskite thin films prepared with different colors. The CsPbI$_3$ inorganic perovskite films with alloyed EA fractions below 0.3 are black purple. The film gradually changed to black brown as the EA concentration increased over 0.3. Further observation by scanning electron microscopy (SEM) revealed the differences in the film morphologies upon introducing different fractions of EA in the films (Figures 2B–2D and see Figure S2). The pure CsPbI$_3$ perovskite film consisted of closely packed crystals with size 300–400 nm (Figure 2B). The CsPbI$_3$ films with EA fractions 0.05 and 0.1 showed a relatively uniform surface with few pinholes, similar to the pure CsPbI$_3$ film. In the EA$_x$Cs$_{1-x}$PbI$_3$ (x = 0.3, 0.4 and 0.5) samples, the perovskite films are coarse with a noticeable number of pinholes. The thickness of EA$_{0.1}$Cs$_{0.9}$PbI$_3$ film was ~520 nm (Figure 2C). As shown in Figure 2E, the main
diffraction peaks in the X-ray diffraction (XRD) patterns of these mixed mixed-cation EAxCs1-xPbI3 perovskites could be attributed to the tetragonal perovskite phase (Wang et al., 2019a). The emerging diffraction peaks at 11.6° and 12.6° could be attributed to \( \delta \) perovskite and PbI\(_2\) (Akkerman et al., 2017), respectively, when EA content increased over 0.15, suggesting the deterioration of perovskites. No diffraction peaks related to EAI, PbI\(_2\), or \( \delta \) perovskite could be found in the XRD patterns of the EA0.1Cs0.9PbI3 films, indicating the pure tetragonal perovskite phase. Tauc plots revealed that the band gaps of pure CsPbI\(_3\) and EA0.1Cs0.9PbI3 perovskites are 1.68 eV and 1.71 eV, respectively (Figure 2F).

Crystallization and intermediates

The effect of the addition of EAI on the perovskite crystallization was further investigated by UV-visible (UV-vis) and XRD measurements. The shape and the increased intensity of UV-vis spectrum of CsPbI\(_3\) after annealing at 210°C for 1 min revealed the appearance of optical activity (Figure 3A). In contrast, EA0.1Cs0.9PbI3 remained optically inactive after annealing for 1 min (Figure 3B). After annealing for 3 min, the UV-vis intensity of CsPbI3 remains basically unchanged, whereas the intensity of EA0.1Cs0.9PbI3 at 5 min was stronger than that at 3 min, indicative of the retarding crystallization of perovskite upon introducing EAI into precursor. The diffraction peak at 11.6° in XRD patterns of EA0.1Cs0.9PbI3 could be ascribed to DMAPbI3 (Figures 3C and 3D). This characteristic peak of DMAPbI3 can also be found in the XRD patterns of EA0.1Cs0.9PbI3 and CsPbI3 after annealing at 210°C for 2 min (Figure 3C and see Figure S3). The addition of dimethylammonium iodide (DMAI) in the precursor solution could form DMAPbI3 intermediate. The relative ratio of DMAPbI3/perovskite is very low after annealing at 210°C for 3 min providing the proof of the volatile additive of DMAI in the crystallization process (Pei et al., 2019; Bian et al., 2020). In experiment, we found that the introduction of EAI in the precursor solution could retard the crystallization of perovskite with a longer...
annealing time to form the black phase (see Table S1). In particular, the film with EA fraction of 0.3 after annealing at 210°C for 10 s appeared orange. This orange intermediate film could be kept in dry air at room temperature for several days. XRD pattern of this orange intermediate showed distinct characteristic diffraction peaks at 10.3° and 15.7°. To further explore the effect of the addition of EAI on the intermediate phases, the precursors with PbI2 + DMAI and PbI2 + DMAI + EAI (Figure 3D) annealing at 210°C for 10 s were further characterized by XRD measurements. The emerging peak at 10.3° is induced by the addition of EAI. The color and the diffraction peaks of the orange intermediate film of EA0.3Cs0.7PbI3 intermediate resemble the previously reported 2D (CH3(CH2)3NH3)2(MA)2Pb3I10 (Cao et al., 2015). Analysis by UV spectra further reveals the quasi-2D absorption nature of this intermediate film (Zhang et al., 2017) (see Figure S4). EAPbI3 with a tolerance factor close to the upper limit had been previously reported to crystallize in a 2D structure with a large orthorhombic unit cell (Peng et al., 2017). XRD patterns of EA0.3Cs0.7PbI3 and pure CsPbI3 annealing at 210°C for 10 s revealed the presence of DMAPbI3 intermediates (Figure 3D). For
EA\textsubscript{0.15}Cs\textsubscript{0.85}PbI\textsubscript{3} and EA\textsubscript{0.2}Cs\textsubscript{0.8}PbI\textsubscript{3}. XRD patterns revealed the coexistence of EAPb\textsubscript{i3}n+1 and DMAPbI\textsubscript{3} intermediates at the start of annealing. No characteristic diffraction peaks of DMAPbI\textsubscript{3} can be found in the XRD pattern of EA\textsubscript{0.3}Cs\textsubscript{0.7}PbI\textsubscript{3} intermediate film.

In low EA content, DMAI and PbI\textsubscript{2} first formed DMAPbI\textsubscript{3} intermediate. The sublimation of DMAI during the annealing process, concomitant with the incorporation of Cs\textsuperscript{+} and EA\textsuperscript{+} cations into the crystal lattice, generated the EA-Cs hybrid perovskite. When the EA\textsubscript{i} fractions increased to 0.15 and 0.2, EA\textsubscript{i} reacted with PbI\textsubscript{2} to form EAPb\textsubscript{i3}n+1, alongside forming the DMAPbI\textsubscript{3} intermediate. Further sublimation of DMAI and transformation of EAPb\textsubscript{i3}n+1 to perovskite was accompanied with Cs entering into the lattice. EA\textsubscript{i} with fractions over 0.3 would interact with DMAI to form quasi-2D intermediates, which then transformed into EA\textsubscript{0.3}Cs\textsubscript{0.7}PbI\textsubscript{3} perovskites during the crystallization. The distribution of C and Cs throughout the EA\textsubscript{0.1}Cs\textsubscript{0.9}PbI\textsubscript{3} perovskite films prepared from HPbI\textsubscript{3+x}-containing precursors was investigated using time-of-flight secondary ion mass spectrometry (TOF-SIMS). The depth profiles and the mapping images revealed that C was homogeneously distributed in the EA\textsubscript{0.1}Cs\textsubscript{0.9}PbI\textsubscript{3} perovskite film, indicating the successful incorporation of EA into CsPbI\textsubscript{3} (Figures 3E and 3F). Further analysis by the cross-sectional element profiling of the EA\textsubscript{0.1}Cs\textsubscript{0.9}PbI\textsubscript{3} revealed the homogeneous distribution of C and Cs (see Figure S5).

Photovoltaic performance and transport properties
EA\textsubscript{0.1}Cs\textsubscript{0.9}PbI\textsubscript{3} perovskites were utilized as light harvesters for perovskite solar cells to evaluate the impact of alloyed EA on the photovoltaic performance of Cs-EA hybrid perovskites (Figure 4A). Overall, the PCE of EA\textsubscript{0.1}Cs\textsubscript{0.9}PbI\textsubscript{3} perovskite solar cells was inversely proportional to the EA contents (Figure 4B). EA\textsubscript{0.1}Cs\textsubscript{0.9}PbI\textsubscript{3}-based solar cell delivered a PCE of 16.01\% with a V\textsubscript{oc} of 1.026\,V, a short-circuit current density (J\textsubscript{sc}) of 20.21\,mA\,cm\textsuperscript{-2}, and a fill factor (FF) of 77.20\% (Figure 4B and see Table S2). The short-circuit current density of EA\textsubscript{0.1}Cs\textsubscript{0.9}PbI\textsubscript{3} was slightly higher than that of pure CsPbI\textsubscript{3}-based devices. With the increase of EA\textsubscript{i} fractions from 0.1 to 0.3, the V\textsubscript{oc} did not change considerably, whereas the J\textsubscript{sc} and FF values declined greatly (Figures 4C and 4D). Further increase of EA\textsubscript{i} content to 0.5 had a primary negative effect on the J\textsubscript{oc}. The integrated current densities in typical external quantum efficiency (EQE) plots of the EA\textsubscript{0.1}Cs\textsubscript{0.9}PbI\textsubscript{3} solar cells were close to the J\textsubscript{oc} values obtained from the current density-voltage (J-V) measurements (Figure 4E).

The carrier transit time of the EA-alloyed perovskites solar cells was investigated by the transient photocurrent decay (TPC) measurements (Figure 4F). TPC under short-circuit condition illustrates the photocarrier transit time across the bulk perovskite and the electrode interface (Ji et al., 2021; Zuo et al., 2017). The photocarrier transit time in pure CsPbI\textsubscript{3} was estimated to be ~2.7\,\mu s, and little decrease was observed for EA\textsubscript{0.1}Cs\textsubscript{0.9}PbI\textsubscript{3} (~2.4\,\mu s), indicating the enhanced charge transport in the EA\textsubscript{0.1}Cs\textsubscript{0.9}PbI\textsubscript{3}-based devices. However, when EA\textsubscript{i} fraction increased to 0.3, the transit time becomes longer (~3.5\,\mu s), indicating an increased charge trap and reduced charge carrier lifetime in the EA\textsubscript{0.3}Cs\textsubscript{0.7}PbI\textsubscript{3}-based devices. Space-charge limited current (SCLC) measurements were performed with an electron-only FTO/TiO\textsubscript{2}/perovskite/phenyl-C\textsubscript{61}-butyric acid methyl ester (PCBM)/Ag device and utilized to estimate the charge trap densities (Figure 4G). In low applied voltages, a linear relationship of the current density and the bias voltage indicates an ohmic response. With the increase of the bias voltage, a kink point voltage could be observed in the SCLC plots reflecting a transition to the trap-filled limit (TFL) stage (Liu et al., 2017; Ji et al., 2017). The density of trap states (n\textsubscript{T}) is proportional to V\textsubscript{TFL} according to the equation (Bube, 1962): 

\[ V_{TFL} = \frac{e\eta L^2}{2\epsilon_0\epsilon} \]

where e is the elementary charge, \eta is the trap density, L is the thickness of the crystal between two Ag electrodes, \epsilon is the relative dielectric constant of perovskite absorber (~5.3), and \epsilon_0 is the dielectric constant of vacuum (Peng et al., 2017; Chen et al., 2020a). The measured V\textsubscript{TFL} for the pristine CsPbI\textsubscript{3} film was ~0.35\,V, whereas the value decreased to 0.24\,V for EA\textsubscript{0.1}Cs\textsubscript{0.9}PbI\textsubscript{3}. Accordingly, a decrease of n\textsubscript{T} of ~3.0\times10\textsuperscript{15} cm\textsuperscript{-3} for the EA\textsubscript{0.1}Cs\textsubscript{0.9}PbI\textsubscript{3}-based devices was observed, compared with the control CsPbI\textsubscript{3} devices (4.5\times10\textsuperscript{15} cm\textsuperscript{-3}), indicating the suppression of the non-radiative recombination in the EA\textsubscript{0.1}Cs\textsubscript{0.9}PbI\textsubscript{3}-based devices. At higher voltage for the child region, the carrier mobility (\mu) could be assessed with the equation: 

\[ \mu = \frac{9\epsilon_0 S V}{8L^3} \]

where S is the area of the electrodes and \mu is the mobility (Chen et al., 2017; Chen and Wang, 2017). The electron mobility of EA\textsubscript{0.1}Cs\textsubscript{0.9}PbI\textsubscript{3} was higher than that of pure CsPbI\textsubscript{3}. The dark current density of the EA\textsubscript{0.1}Cs\textsubscript{0.9}PbI\textsubscript{3}-based devices was lower than that of the pure CsPbI\textsubscript{3}-based devices by one order of magnitude (Figure 5A).

The low leakage current density in EA\textsubscript{0.1}Cs\textsubscript{0.9}PbI\textsubscript{3}-based devices suggested the suppressed charge recombination, which was further characterized by carrier transport measurements under illumination from electrochemical impedance spectroscopy (EIS) (Figure 5B). The middle frequency zone of EIS semicircle was closely associated with the interfacial recombination resistance between transport materials and perovskite (Chen et al., 2020c). Compared with EA\textsubscript{0.3}Cs\textsubscript{0.7}PbI\textsubscript{3} and pure CsPbI\textsubscript{3} devices, the EA\textsubscript{0.1}Cs\textsubscript{0.9}PbI\textsubscript{3}-based...
devices had the largest impedance (largest circle arc), indicating a suppressed recombination in EA$_{0.1}$Cs$_{0.9}$PbI$_3$ (Zheng et al., 2018). The results reveal improved charge transport and suppressed charge recombination in EA$_{0.1}$Cs$_{0.9}$PbI$_3$ compared with CsPbI$_3$.

**Conclusion**

In summary, besides the generally used MA and FA organic cations to form hybrid perovskites, EA cation has been investigated for the first time as an alternative cation with which to fabricate hybrid perovskites by balancing lattice strain. Different from FA incorporation with distinct adsorption redshift, i.e., decrease of band gap, and the pure-phase FA-Cs mixed-cation perovskites at higher FA fractions, the EA incorporation would lead to a slight increase of the band gap, and a pure-phase EA-Cs hybrid perovskites could be obtained in a relatively small EA fraction ($x < 0.15$). The EA cation is presented as a potential replacement for Cs$^+$ in lead iodide perovskites, owing to the slightly increased band gap, enhanced phase stability, and improved transport properties of EA$_{0.1}$Cs$_{0.9}$PbI$_3$. The increased band gap was closely associated with a decrease of the average Pb-I-Pb angle. Meanwhile, the average Pb-I band distance was revealed to reflect the thermal stability of perovskites from DFT calculation. However, the incorporation of high fractions of EA

![Figure 4. Photovoltaic performance](image)
(x ≥ 0.3) would deteriorate the perovskite films with abundant pinholes and grain boundaries, which is unfavorable for the carrier’s separation in solar cells owing to the nonradiative combination. Engineering large organic EA cations into CsPbI3 perovskite is promising to tune the structure of CsPbI3 perovskite with enhanced phase stability and transport properties for multijunction applications.

Limitations of the study

Here, a new A-site engineering approach based on structural distortion with different bond mixing is demonstrated to enlarge the band gap of CsPbI3 from 1.68 eV to over 1.7 eV for potential multijunction application. Compared with traditional mixed halides engineering, this method can inherently eliminate the structural degradation of high-band-gap perovskites under illumination. The optimum amount of EA is revealed to be below 0.15 based on the pure phase of perovskite, structural stability, and transport property. EA0.7Cs0.3PbI3 cannot reach the instant efficiency as high as CsPbI3. However, the increase of the band gap of perovskite in the range of 1.7–1.8 eV will achieve the maximum efficiency of tandem solar cell. From 1.68 to 1.71 eV, the tandem solar cells’ efficiency can improve ~4%. The light stability instead of thermal stability is revealed to reflect the instinct phase stability. It therefore demonstrates a proof-of-concept of applying structural distortion to improve the band gap and the structural stability of perovskite.

Resource availability

Lead contact
Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Jun Chen (jun.chen@ucla.edu).

Materials availability
All chemicals were obtained from commercial resources and used as received.

Data and code availability
Data and all results are available on request from the authors. Calculated structure cif files can be found in https://doi.org/10.1016/j.isci.2021.102235.

METHODS

All methods can be found in the accompanying transparent methods supplemental file.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.isci.2021.102235.

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AUTHOR CONTRIBUTIONS

J.C. designed and developed the concept and supervised the project. S.X. conducted the experiments, performed the analysis, and wrote the manuscript, and all authors discussed the results and commented on the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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Supplemental information

Engineering bandgap of CsPbI₃ over 1.7 eV with enhanced stability and transport properties

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Figure S1. Crystal structure of CsPbI$_3$, EA$_{0.1}$Cs$_{0.9}$PbI$_3$ and EA$_{0.3}$Cs$_{0.7}$PbI$_3$. Related to Figure 1.
Figure S2. SEM images of EA$_{0.15}$Cs$_{0.85}$PbI$_3$, EA$_{0.2}$Cs$_{0.8}$PbI$_3$, EA$_{0.4}$Cs$_{0.6}$PbI$_3$ and EA$_{0.5}$Cs$_{0.5}$PbI$_3$.

Related to Figure 2.
Figure S3. XRD patterns of CsPbI\textsubscript{3} perovskites after annealing at 210 °C for different time. 
Related to Figure 3.
Figure S4. UV-spectra of the $\text{EA}_{0.3}\text{Cs}_{0.7}\text{PbI}_3$ and $\text{CsPbI}_3$ intermediates annealing at 210 °C for 10 s.

Related to Figure 3.
Figure S5. Cross-sectional SEM image and EDS line scanning of $\text{EA}_{0.1}\text{Cs}_{0.9}\text{PbI}_3$. Related to Figure 3.
Figure S6. J-V characteristics of EA\textsubscript{x}Cs\textsubscript{1-x}PbI\textsubscript{3} based device under simulated AM 1.5 G solar illumination of 100 mW cm\textsuperscript{-2} in reverse and forward scans. Related to Figure 4.
Supplemental Tables

Table S1. The recorded annealing time for EA$_x$Cs$_{1-x}$PbI$_3$ during crystallization. Related to Figure 3.

|                | Crystallization beginning (Black phase emerging) | Complete crystallization (Black film) | Glossy Film | Turning Yellow |
|----------------|-----------------------------------------------|--------------------------------------|-------------|----------------|
| CsPbI$_3$      | -80 s                                         | 120 s                                |             |                |
| EA$_{0.1}$Cs$_{0.9}$PbI$_3$ | 94 s                                         | 161 s                                | 218 s       |                |
| EA$_{0.2}$Cs$_{0.8}$PbI$_3$ | 109 s                                         | 173 s                                | 228 s       |                |
| EA$_{0.3}$Cs$_{0.7}$PbI$_3$ | 120 s                                         | 240 s                                | 378 s       | 557 s          |
| EA$_{0.4}$Cs$_{0.6}$PbI$_3$, EA$_{0.5}$Cs$_{0.5}$PbI$_3$ | 150 s                                         | 378 s                                |             |                |
Table S2. Photovoltaic parameters of EA$_{x}$Cs$_{1-x}$PbI$_{3}$ solar cells under 1 sun (AM 1.5 illumination).

Related to Figure 4.

|                  | PCE (%) | FF  | Jsc (mA cm$^{-2}$) | Voc (V) |
|------------------|---------|-----|--------------------|---------|
| CsPbI$_{3}$      | 16.649  | 0.785 | 19.876             | 1.067   |
| EA$_{0.1}$Cs$_{0.9}$PbI$_{3}$ | 16.008  | 0.772 | 20.206             | 1.026   |
| EA$_{0.2}$Cs$_{0.8}$PbI$_{3}$ | 12.760  | 0.661 | 19.575             | 0.987   |
| EA$_{0.3}$Cs$_{0.7}$PbI$_{3}$ | 12.610  | 0.641 | 19.479             | 1.009   |
| EA$_{0.4}$Cs$_{0.6}$PbI$_{3}$ | 11.385  | 0.648 | 18.852             | 0.932   |
| EA$_{0.5}$Cs$_{0.5}$PbI$_{3}$ | 10.995  | 0.623 | 17.753             | 0.994   |
**Transparent Methods**

**Materials and Chemicals.**

CsI and PbI$_2$ were purchased from Alfa Aesar. Dimethylammonium iodine (DMAI) were purchased from J&K Ltd. Ethylamine iodine (EAI), anhydrous dimethylformamide (DMF) and bis(trifluoromethane) sulfonamide lithium salt (LiTFSI) were purchased from Sigma-Aldrich. 4-tert-butylpyridine (TBP) was purchased from TCL Co., Ltd.

**Device Fabrication.**

A compact TiO$_2$ layer was deposited on the laser patterned FTO substrate by spraying pyrolysis of 0.2 M Ti$^{IV}$ bis(ethyl acetatoacetate)-diisopropoxide in butanol solution at 450 °C, and then annealed at 450 °C for 1 h. 0.7 M EA$_x$Cs$_{1-x}$PbI$_3$ perovskite precursor was prepared by dissolving stoichiometric EAI, CsI, PbI$_2$ and DMAI with $x$: 1-$x$: 1: 1.2 molar ratio in DMF ($x = 0.1-0.5$). 0.6 M EA$_x$Cs$_{1-x}$PbI$_3$ perovskite precursor was prepared by dissolving stoichiometric EAI, CsI and HPbI$_{3+x}$ with $x$: 1-$x$: 1 molar ratio in DMF ($x = 0.1-0.5$). Then, the CsPbI$_3$ active layer was spin-coated on the pre-warmed TiO$_2$/FTO substrate at 70 °C (3000 rpm, 30 s). Further annealing the substrates at 210 °C for 6 min fabricated the EA$_x$Cs$_{1-x}$PbI$_3$ perovskite films. The devices were assembled in a dry box (10~20% RH). A layer of hole transport material (HTM) composed of 0.1 M spiro-MeOTAD, 0.035 M bis(trifluoromethane) sulfonamide lithium salt (LiTFSI), and 0.12 M 4-tert-butylpyridine (TBP) in chlorobenzene/acetonitrile (10:1, v/v) solution was spin-coated onto top of the above annealed films at 4000 rpm for 25 s. Finally, thermal evaporation was utilized to deposit a 100-nm thick Ag layer at the evaporation rate of ~0.2 Å s$^{-1}$ from 0-300 Å, and ~0.6 Å s$^{-1}$ from 300-1000 Å. All the process for the metal evaporation was processed in N$_2$ atmosphere with < 10% R.H.

**Characterization and Measurements.**

UV-vis spectra were detected by a spectrophotometer (DR6000 HACH, USA). XRD patterns were performed on Shimadzu XRD-6100 diffractometer with Cu Kα radiation for crystal structural characterization. The morphology of the films was assessed using a FESEM (FEI NOVA Nano SEM 230, USA). TOF-SIMS and TOF-SEM were carried out on a TESCAN Gaia3 FESEM. The J-V characteristics were measured with a Keithley 2401 source meter at a scan rate of 0.05 V s$^{-1}$ under a simulated AM 1.5 G illumination (100 mW cm$^{-2}$) using Enlitech’s 3A light source. EQE was measured on a QE-3011 system (Enlitech). The TPC measurements were carried out by a microsecond pulse of a white light incident on solar cells under short circuit conditions with a very
low resistor at 20 Ω in the dark.

**DFT Calculations.**

First-principles electronic structure calculations were carried out using the Vienna ab initio simulation package (VASP) code\(^1,2\) within the generalized gradient approximation (GGA) approach\(^3\). The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was used to describe the electronic exchange and correlation effects. Uniform G-centered k-points meshes with a resolution of \(2\pi \times 0.04 \, \text{Å}^{-1}\) and Methfessel-Paxton electronic smearing were adopted for the integration in the Brillouin zone for geometric optimization. The simulation was run with a cutoff energy of 500 eV throughout the computations. These settings ensured convergence of the total energies to within 1 meV per atom. Structure relaxation proceeded until all forces on atoms were less than 1 meV Å\(^{-1}\) and the total stress tensor was within 0.01 GPa of the target value. The simulation cells were adopted by supercells of CsPbI\(_3\), i.e., Cs\(_{20}\)Pb\(_{20}\)I\(_{60}\), EA\(_2\)Cs\(_{18}\)Pb\(_{20}\)I\(_{60}\). In order to keep the temperature and volume constant, we used the NVT ensemble during the MD simulation and the Nosé-Hoover thermostat was used in the NVT ensemble to keep the temperature. The melting process was calculated by MD simulation of the movements of the Cs, Pb, I, C, N and H atoms with 2000 steps (3 fs \(^{-1}\)).
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