Bication lead iodide 2D perovskite component to stabilize inorganic α-CsPbI3 perovskite phase for high-efficiency solar cells

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Among various all-inorganic halide perovskites exhibiting better stability than organic-inorganic halide perovskites, α-CsPbI3 with the most suitable band gap for tandem solar cell application faces an issue of phase instability under ambient conditions. We discovered that a small amount of two-dimensional (2D) EDAPbI4 perovskite containing the ethylenediamine (EDA) cation stabilizes the α-CsPbI3 to avoid the undesirable formation of the nonperovskite δ phase. Moreover, not only the 2D perovskite of EDAPbI4 facilitate the formation of α-CsPbI3 perovskite films exhibiting high phase stability at room temperature for months and at 100°C for >150 hours but also the α-CsPbI3 perovskite solar cells (PSCs) display highly reproducible efficiency of 11.8%, a record for all-inorganic lead halide PSCs. Therefore, using the bication EDA presents a novel and promising strategy to design all-inorganic lead halide PSCs with high performance and reliability.

INTRODUCTION

In past years, the organic-inorganic hybrid lead halide perovskite solar cells (PSCs) have progressed in an impressive manner approaching commercialization (1–5). However, the instability of organic-inorganic hybrid perovskite, such as CH3NH3PbI3 under thermal stress, might stem from the volatility of the organic cation and has become a challenge for long-term practical deployment. Although organic-inorganic mixed-cation PSCs demonstrating improved efficiency and stabilities have been documented (6–8), all-inorganic lead halide perovskite absorbers are much desired, specifically because the issues related to the release or decomposition of the organic component can be avoided. The most suitable all-inorganic structure could be based on CsPbX3 perovskite because only the Cs is large enough to occupy the A sites with a suitable tolerance factor to fit the ABX3 perovskite (B = Pb, X = halide) configuration. The phase-stable CsPbX3 perovskite is usually based on bromide with a suitable tolerance factor, but the CsPbBr3 perovskite has a too wide band gap to realize the fabrication of high-efficiency solar cells. Unfortunately, the α-CsPbI3 perovskite with a band gap of 1.73 eV, which is suitable for tandem solar cells, is structurally unstable and transforms spontaneously into the unwanted δ-CsPbI3 phase under ambient conditions at room temperature. Currently, cesium has been successfully used as A cation along with formamidinium in high-efficiency PSCs, but at concentrations above 20%, it leads to the formation of non-perovskite δ-CsPbI3 (7–12). Previous reports have suggested that the phase stability of α-CsPbI3 strongly depends on the crystallite size because stability improves by trimming the dimensions of the α-CsPbI3 grains toward the nanoregime (13, 14). Size-dependent phase or thermal stability has been reported in nanomaterials, especially when surfactants were used as growth-controlling agents (15, 16). However, conventional deposition strategies, which do not involve surfactants, mostly yield large-sized CsPbI3 crystallites. Recently, α-CsPbI3 quantum dots with well-controlled size synthesized by hot injection have been fashioned into stable PSCs exhibiting an efficiency of up to 10% (17). In addition, a two-dimensional (2D) interface has been demonstrated as an effective strategy to stabilize the organic-inorganic hybrid perovskite or to increase the thermal stability of CH3NH3PbI3 (18, 19). However, a 2D segment of these structures may impair the electron transport across the device, lowering their efficiency (18). Therefore, it becomes imperative to judiciously design the bication 2D architecture.

Here, we report a new and facile one-step deposition method to obtain highly efficient and stable α-CsPbI3 PSCs (2). We stabilize the α-CsPbI3 perovskite films by introducing ethylenediamine cations (EDA2-), whose terminal NH2+ groups are expected to cross-link the CsPbI3 perovskite crystal units, rendering them less prone to unwanted phase transition to the δ structure. Stable α-CsPbI3 films have been deposited by introducing a small amount of bication 2D perovskite of EDAPbI4 into the CsPbI3 precursor solution. This cross-links the α-CsPbI3 films without impairing the charge-carrier transport. The resulting α-CsPbI3 structures are highly robust at room temperature for months and can retain their phase even after annealing at 100°C for a week. In addition to the high stability, PSCs based on the α-CsPbI3 films showed highly reproducible photoconversion efficiency (PCE) of 11.8%, a record for α-CsPbI3 devices.

RESULTS

We used a typical one-step method to deposit CsPbI3 films using a regular precursor containing stoichiometric CsI and PbI2 dissolved in N,N′-dimethylformamide (DMF). A rough yellowish film was obtained after annealing the precursor film at 150°C. As shown in Fig. 1 (A and B), the absorbance peak located at 414 nm and a strong x-ray diffraction (XRD) peak at 9.78° suggest the formation of the unwanted nonperovskite δ-CsPbI3 phase. This is quite expected because the yellow-to-black phase transformation occurs at 350°C (13, 20). Toward the formation of α-CsPbI3, we develop a low-temperature fabrication method using PbI2·xHI (x > 1.3) and CsI as precursors. The XRD pattern of PbI2·xHI is shown in Fig. S1, which exhibits no signature corresponding to the PbI2 phase and is different from the previous reports on HPbI3 (21). The brown perovskite CsPbI3 film was obtained via one-step deposition using the PbI2·xHI + CsI precursor, followed by the low-temperature annealing at 100° to 150°C. It seems that the HI in the PbI2·xHI adduct decreases the crystallization energy barrier for the α-CsPbI3 phase. The as-prepared film shows an absorbance onset at ~718 nm in Fig. 1A,
indicating a band gap of 1.73 eV, consistent with the previous reports on α-CsPbI3 (13, 22). The XRD pattern (Fig. 1B) obtained from the brown CsPbI3 film could be indexed to a phase-pure cubic α-CsPbI3 perovskite structure (12, 13). However, the PSC based on this α-CsPbI3 film revealed a modest PCE of 5.59% (Fig. 1C), which is comparable to previous reports (10, 13, 23). Unfortunately, this phase-pure α-CsPbI3 film also suffers from phase instability issues. As shown in Fig. 1D, the brown α-CsPbI3 film transforms into a yellow δ-CsPbI3 film within 12 hours.

In organic-inorganic or inorganic lead halide perovskite, the cation usually occupies one A site in either 3D ABX3 or 2D A2BX4 perovskites. Here, the two NH3+ groups of EDA can occupy two A sites and cross-link these 2D layers. This bication 2D perovskite has been theoretically predicted, and the copper halide perovskite based on EDA has been prepared from PbI2·xHI + CsI. a.u., arbitrary units.

Previously, some reports suggested that the bication 2D perovskite can be either a regular 2D/3D perovskite of CsPbI3·0.05EDAPbI4 or to the decrease in crystallite size. Such a confinement effect was further manifested by the blueshift of absorption onset (Fig. 2D), which is quite evident for the CsPbI3·0.05EDAPbI4 sample. The photoluminescence (PL) spectra of CsPbI3·xEDAPbI4 (fig. S6A) also exhibited blueshift when the content of EDAPbI4 is increased. Moreover, their PL lifetimes also increased with the content of EDAPbI4 (fig. S5B). Such a blueshift has been observed in CsPbI3 quantum dots synthesized using hot-injection solution-based method and other hybrid lead halide perovskite films with the incorporation of 2D perovskite (34). The blueshift in both UV-vis and PL spectra can be ascribed either to the formation of 2D/3D perovskite of CsPbI3·0.05EDAPbI4 or to the decrease in crystal size. In the plausible 2D/3D configuration, we hypothesize that the (110) layered 2D EDAPbI4 component can also function as an interface to separate small CsPbI3 crystal units, as in the regular 2D/3D perovskite. The 2D EDAPbI4 might also work as a blocking layer similar to the surfactant, which can eventually reduce the crystallite size of the CsPbI3·xEDAPbI4 perovskite structures. Previous reports have suggested that the reduced crystal size can lead to the blueshift of optical spectrum even when the crystal size is larger than the Bohr radius (35).
Furthermore, the addition of a small amount of EDAPbI₄ also helps reduce the pinholes in the deposited CsPbI₃ perovskite films and passivates their surface, similar to a previously reported regular 2D/3D or cross-linked 2D/3D perovskite (18, 28). Figure S6B shows that the PL lifetime of the CsPbI₃-xEDAPbI₄ film increases with its EDAPbI₄ content, suggesting a suppression of radiation-recombination. The scanning electron microscopy (SEM) and AFM images (Fig. 3, A and B) show that the grain size of CsPbI₃-xEDAPbI₄ decreases markedly from ~300 nm (x = 0) to ~35 nm (x = 0.025) with increasing EDAPbI₄ content. This is consistent with the XRD peak broadening observed in Fig. 2. Note that the pinholes became much less with the addition of EDAPbI₄, which is favorable for high-performance PSC fabrication.

All these results reveal that the addition of a small content of EDAPbI₄ has strongly affected the properties of CsPbI₃. To rationalize this observation, we first exclude the possibility of Cs⁺ substitution by EDA on a single A site of CsPbI₃ to form an EDA-Cs₁₋ₓPbI₃ mixed-cation perovskites on the basis of the large size of EDA (r = 0.31 nm). Moreover, replacing Cs⁺ by larger cations, such as EDA, should narrow the band gap and induce an XRD peak shift, although we observe a widening of the band gap and no shift in the XRD peak position.

We adopted a planar configuration to fabricate PSCs based on these CsPbI₃-xEDAPbI₄ perovskites. The photovoltaic parameters extracted from the J-V curves (Fig. 4A) are listed in Table 1. We found that CsPbI₃-xEDAPbI₄ (x = 0.0125 to 0.05) devices show a much better performance than those based on the pure CsPbI₃. The enhancement in all the photovoltaic parameters, that is, J_{SC}, V_{OC}, and FF, can be attributed to less pinholes, desired charge-carrier dynamics, and surface passivation by EDAPbI₄. For x ≤ 0.025, the transient photovoltage decay curves (fig. S7) exhibit monotonic increase in the lifetime with the EDAPbI₄ incorporation, which is consistent with the PL decay dynamics (fig. S6B). Furthermore, the 2D EDAPbI₄ in these CsPbI₃-xEDAPbI₄ (x = 0.0125 to 0.05) compositions seem to have less impact on the charge transfer because this can be significantly hindered in regular 2D/3D PSCs (18). The best performing cell used the CsPbI₃-0.025E-DAPbI₄ perovskite formulation showing a remarkable PCE of 11.8% under reverse scan. To the best of our knowledge, this is a record for CsPbI₃-based PSCs. Hysteresis between different scan directions is also found in our planar cell structure (fig. S8), and the scan rate-independent maximum power tracking (Fig. 4B) indicates an efficiency of 10.5%. The integrated J_{SC} obtained from the incident photon-to-electron conversion efficiency (IPCE) is consistent with the values extracted from the J-V curves. Note that the IPCE value of the champion cell has reached 86% over a wide wavelength range. Device performance was also highly reproducible, as shown in Fig. 4D. The improved reproducibility demonstrated by the CsPbI₃-xEDAPbI₄ solar cells can be ascribed to the better control on the film formation (less pinholes) (36, 37).

The best solar cell based on the CsPbI₃-0.025EDAPbI₄ perovskite showed good stability because it retained ~10% efficiency after storing in a dark dry box for 1 month without any encapsulation (Fig. 5A). All the above results establish that the formation of CsPbI₃-xEDAPbI₄ perovskite significantly improves the performance of the devices. Besides the high efficiency, the thermal stability of CsPbI₃-xEDAPbI₄ films markedly improved as compared to the pure CsPbI₃ (fig. S9). The α-CsPbI₃ perovskite phase of the CsPbI₃-0.025EDAPbI₄ sample can be retained for months at room temperature (fig. S10) and after heating the CsPbI₃-0.025EDAPbI₄ film at 100°C for 1 week, as shown in Fig. 5B.

**DISCUSSION**

All of the above results demonstrate the superior photovoltaic performance of CsPbI₃-xEDAPbI₄ over pure α-CsPbI₃-based PSCs. It appears that the hypothesized EDAPbI₄ 2D perovskite component not only stabilizes the α-CsPbI₃ perovskite phase but also reduces the deterioration of charge-carrier transport across the perovskite film caused by the “insulating” long alkyl spacing layers (18, 38). This improvement in both efficiency and stability is closely related to this unique bifunctional cation perovskite component. We cannot obtain the efficient and stable α-CsPbI₃ perovskite films if we merely add EDAI₂ instead of EDAI₂ + PbI₂ into the CsPbI₃ precursor solution. In addition, if the EDA is replaced by the monofunctional ethylamine (EA) in the regular 2D/3D CsPbI₃-xEA₂PbI₄ samples, the perovskite phase of CsPbI₃-xEA₂PbI₄ (x = 0.025) deteriorated markedly as observed in the pure CsPbI₃. As shown in fig. S11, the typical sample of brown CsPbI₃-0.025EA₂PbI₄ turns into a yellow phase within a day at room temperature. In contrast, the bication EDA with CH₂–CH₂ can effectively assemble the CsPbI₃ crystal units. Furthermore, all the CsPbI₃–xEA₂PbI₄ perovskite film-based solar cells exhibited poor photovoltaic performance, and the best J-V curve obtained from the PSCs based on CsPbI₃-0.025EA₂PbI₄ is listed in fig. S12. The efficiency is only ~4.4%, which is way too low than that of CsPbI₃ PSCs. Such low stability could be due to either the weak

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**Fig. 3.** Effect of EDAPbI₄ on the evolution of morphology of CsPbI₃-xEDAPbI₄. (A) AFM and (B) SEM images of perovskite films obtained from the CsPbI₃-xEDAPbI₄ additive precursor (x = 0, 0.0125, 0.025, and 0.05).

**Fig. 4.** Device characteristics for CsPbI₃-xEDAPbI₄ films. (A) Typical J-V curves of CsPbI₃-xEDAPbI₄ PSCs. (B) Stable current output at the maximum point of the champion CsPbI₃-0.025EDAPbI₄ PSC. (C) IPCE of the best solar cell based on the CsPbI₃-0.025EDAPbI₄ perovskite. (D) Histogram of device efficiencies of CsPbI₃-0.025EDAPbI₄ PSCs based on 32 cells from three batches.
Like CsPbI$_3$$\cdot$0.025EDAPbI$_4$, the CsPbI$_3$$\cdot$0.025BDAPbI$_4$ samples are of the champion PSC fabricated from CsPbI$_3$$\cdot$0.025EDAPbI$_4$ as a function of storage time in a dark dry box. The CsPbI$_3$$\cdot$0.025BA$_2$PbI$_4$ sample with the (110) layered EDBEPbI$_4$ shows enhanced thermal stability of CsPbI$_3$$\cdot$0.025EDAPbI$_4$ could be ascribed to the unique (110) layered perovskite structure of EDAPbI$_4$. The CsPbI$_3$$\cdot$0.025EDBEPbI$_4$ (fig. S15A) has been shown to be a (110) layered 2D perovskite (\textsuperscript{33}). This result suggested that both the steric effect and bication enhance the overall phase stability of CsPbI$_3$-xEDAPbI$_4$ particulate materials.

To further understand the mechanism behind the high phase stability of CsPbI$_3$$\cdot$xEDAPbI$_4$, we used other two bications, that is, 1,4-diaminobutane (BDA) and 2,2'-[(ethylenedioxy)bis(ethylammonium)] (EDBE)\textsuperscript{2+}, which are similar to EDA. The BDA$_2$PbI$_4$ perovskite has been demonstrated to be a (100) layered bication 2D perovskite, whereas the EDBEPbI$_4$ has been shown to be a (110) layered 2D perovskite (29–31, 33). Like CsPbI$_3$$\cdot$0.025EDAPbI$_4$, the CsPbI$_3$$\cdot$0.025BDAPbI$_4$ samples are composed of smaller perovskite crystallites (fig. S14), exhibiting significantly enhanced thermal stability than pristine CsPbI$_3$. However, after holding at 100°C for 3 days, the CsPbI$_3$$\cdot$0.025EDAPbI$_4$ film turns into the yellow δ phase, suggesting that its phase stability is lower than that of CsPbI$_3$$\cdot$0.025EDAPbI$_4$ (fig. S15A). The main difference between EDAPbI$_4$ and BDAPbI$_4$ is that the former is a (110) layered 2D perovskite, whereas the latter is a (100) layered 2D perovskite. It is likely that the higher phase stability of CsPbI$_3$$\cdot$0.025EDAPbI$_4$ could be ascribed to the unique (110) layered perovskite structure of EDAPbI$_4$. The CsPbI$_3$$\cdot$0.025EDBEPbI$_4$ sample with the (110) layered EDBEPbI$_4$ shows enhanced thermal stability than CsPbI$_3$; however, as compared to CsPbI$_3$$\cdot$0.025BDAPbI$_4$, its thermal stability is even poorer, as shown in fig. S15B. It is found that the CsPbI$_3$$\cdot$0.025EDBEPbI$_4$ perovskite sample shows a larger crystal size than CsPbI$_3$$\cdot$0.025BDAPbI$_4$ and CsPbI$_3$$\cdot$0.025EDAPbI$_4$, suggesting that the lower thermal stability of CsPbI$_3$$\cdot$0.025EDBEPbI$_4$ sample might be due to the presence of large crystallites. All these findings demonstrate that the confluence of reduced crystal size and the unique (110) layered bication 2D perovskite structure enhance the overall phase stability of α-CsPbI$_3$. Specifically, we ascribe the enhanced phase stability of CsPbI$_3$$\cdot$xEDAPbI$_4$ to the reduced crystallite size and the EDAPbI$_4$ component’s unique (110) layered structure.

In summary, we report a phase-stable α-CsPbI$_3$ film with an EDAPbI$_4$ 2D perovskite component prepared via a novel and facile single-step method under ambient conditions for high-efficiency all-inorganic PSCs. By introducing the 2D perovskite of EDAPbI$_4$, the structurally robust α-CsPbI$_3$ perovskite films were obtained even at temperatures several hundred°C below the phase transition point. The addition of a small amount of EDAPbI$_4$ stabilizes the α-CsPbI$_3$. Moreover, these perovskite films can retain the α-CsPbI$_3$ phase even after annealing at 100°C for >150 hours and are also stable at room temperature for months. The EDAPbI$_4$ (x = 0 to 0.05) not only enhances the phase stability of α-CsPbI$_3$ crystallites significantly but also connects them for effective electron transfer and passivates the surface defects. Finally, a champion α-CsPbI$_3$ PSC based on CsPbI$_3$$\cdot$0.025EDAPbI$_4$ perovskite films showing a PCE of 11.8%, a record for all-inorganic PSCs, was realized. Therefore, the concept of using bication presents a novel and promising strategy for designing all-inorganic lead halide PSCs yielding high performance and reliability. Such a bication 2D perovskite with different oriented layer structure concepts could also be extended to balance high performance and high stability in organic-inorganic hybrid lead halide perovskites with the incorporation of a 2D component for their use in optoelectronic applications.

### MATERIALS AND METHODS

#### Materials

EDA$_2$I$_2$ was synthesized by reacting EDA and hydroiodic acid with a molar ratio of 1:2.2 in an ice bath for 2 hours. The precipitate was collected by rotary evaporation, washed three times with diethyl ether, and then vacuum-dried. 1,4-Diaminobutane dihydroiodide (BDA$_2$I$_2$), 2,2'-[(ethylenedioxy)bis(ethylammonium)] dihydroiodide (EDBE$_2$I$_2$), ethylammonium iodide (EAI), and butylammonium iodide (BAI) were synthesized following the similar procedure. The Pb$_2$-xHI sample was synthesized as follows: 1 M PbI$_2$ in DMF solution was reacted with 1.5 molar ratio of hydroiodic acid for 1 hour, followed by rotary evaporation, washed three times with diethyl ether, and then vacuum-dried; the concentration of Pb$_2$ in the final product should be within the range of 62 to 65 weight %. All the other materials were purchased from Sigma-Aldrich and used as received without any purification.

The CsPbI$_3$$\cdot$xEDAPbI$_4$ precursor solution was prepared by dissolving 1 mmol of PbI$_2$-xHI and 1 mmol of CsI (1 mM) in 2 ml of DMF to form a 0.5 M precursor solution mixed with different x ratios of...
0.5 M EDAPbI₄ solution. The 0.5 M EDAPbI₄ solution was obtained by dissolving 0.5 mmol of EDAL₃ and 0.5 mmol of PbI₂ in 1 ml of DMF.

**Device fabrication**

A 20-nm-thick compact TiO₂ layer was first deposited on the patterned fluorine-doped tin oxide using 0.2 M Ti(IV) bis(ethyl acetoacetato) disopropoxide in 1-butanol solution at 450°C, followed by annealing at 450°C for 1 h. The CsPbI₂:EDAL₃ precursor solutions were then spin-coated onto the prewarmed c-TiO₂-coated substrate (50°C) at 3500 rpm for 30 s, followed by annealing at 150°C for 2 min. After the films were cooled down to room temperature, a layer of hole transport material of 0.1 M spiro-MeOTAD, 0.035 M bis(trifluoromethane)sulfonic acid (HFSA) and 0.1 M LiTFSI, spin-coated onto the prewarmed c-TiO₂ substrate, was spin-coated at 3500 rpm for 30 s, followed by annealing at 150°C for 2 min. An indium-tin-oxide (ITO) thin film of 400-nm thickness was then deposited onto the CsPbI₂:EDAL₃ films as a top contact layer by radio-frequency sputtering. The AFM images of the CsPbI₂:EDAL₃ films were examined by a Nanosurf SmartNano AFM (Nanosurf AG, Switzerland) using a 4 μm cantilever in contact mode. The XPS spectra were acquired with a Kratos Axis Ultra DLD spectrometer (Kratos Analytical-A Shimadzu Group Company) using a mono-chromatic Al K source (1486.6 eV). Time-integrated PL and time-resolved PL experiments were performed by exciting the samples deposited onto a nonconductive glass using the second harmonic of a picosecond mode-locked Ti:sapphire laser (80.5 MHz) at 420 nm under ambient conditions. The average power was kept around 0.05 mW/cm² per pulse. Using a 32-cm focal length monochromator equipped with a charge-coupled device, which has a spectral resolution of >1 meV, and a streak camera with a temporal resolution of >2 ps, the PL data were spectrally and temporally analyzed. The J-V curves of the PSCs were measured by a Keithley 2401 SourceMeter under simulated air mass 1.5 global illumination with a scan rate of 0.05 V/S (100 mW/cm²) (Enlitex SS-F5-3A Class AAA Solar Simulator; the light intensity was calibrated by a stand Si cell before test), equipped with a nonreflective metal mask with an aperture area of 0.12 cm²; the IPCE was measured on a QE-3011 system from Enlitex. All the J-V and IPCE tests were performed in atmosphere with a relative humidity of 30 to 45%.

**Supplementary Materials**

For further information, please visit: http://advances.sciencemag.org/
T. Zhang, L. Xie, L. Chen, N. Guo, G. Li, Z. Tian, B. Mao, Y. Zhao, In situ fabrication of highly emissive bifunctional amino acid cross-linked 2D/3D NH3(CH3)2COI(CH3)NH3PbBr3\textsubscript{1-x} perovskite films. Adv. Funct. Mater. 27, 1603568 (2017).


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