Structural Properties and Stability of Inorganic CsPbI$_3$ Perovskites

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All inorganic lead halide perovskites (ILHPs) have recently become one of the research hotspots in the field of photovoltaics. Due to the absence of weakly bonded organic components, ILHPs exhibit excellent thermal stability compared with the hybrid organic–inorganic perovskites. However, the low structural stability against ambient conditions still limits their practical applications. Herein, the phase stability and structural properties of the inorganic CsPbI$_3$ are discussed, followed by a comprehensive review of strategies to improve the performance and stability of CsPbI$_3$ perovskite solar cells (PSCs) with respect to material engineering and device configuration engineering. Finally, the challenges of inorganic PSCs and the promising directions to further improve their efficiency and stability are discussed.

1. Introduction

Hybrid organic–inorganic lead perovskites (HOILPs) have attracted extensive attention in the field of photovoltaics (PV) in recent years. Over the past decade, the power conversion efficiency (PCE) of perovskite solar cells (PSCs) has rapidly increased from 3.8% to 25.5% due to their excellent photoelectric properties, including appropriate and adjustable bandgaps, ultralong carrier diffusion length, and high absorption coefficient. Despite the high PCE, HOILPs suffer from stability issues especially under heat stress due to the volatile and weakly bonded organic components, which limit their practical applications. Compared with HOILPs, cesium (Cs)-based inorganic lead halide perovskites (ILHPs) show enhanced thermostability because of the existing of strong ionic bonding, which provides a possible pathway for simultaneously fulfilling both high efficiency and high stability of PSCs.

ILHPs and solar cells have experienced a rapid development. In 2014, the first cesium lead triiodide (CsPbI$_3$) PSCs with the device configuration of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS)/CsPbI$_3$/phenyl-C$_6$1-butyric acid methyl ester (PCBM)/Al exhibits a PCE of only 0.09%. In subsequent years, enormous efforts were made which successfully resulted in improved device performance of ILHP based PSCs. Very recently, Wang and coworkers used dimethylamine iodide (DMAI) as an additive to regulate the crystallization of CsPbI$_3$, which led to a record PCE of 19.03% that has been reported to now. In addition, ILHPs based on other composition such as CsPbI$_2$Br, CsPbBr$_2$, and CsPbBr$_3$ have also experienced fast development, with PCEs increasing from 9.84% in 2016, 4.7% in 2016, 5.95% in 2015 to 17.16% in 2020, 11.53% in 2019, 10.85% in 2020, respectively. To further improve the performance of ILHP-based PSCs, there are two main issues that need to be dealt with. One is the preferred phase transformation from perovskite phase to nonperovskite phase at room temperature caused by the low tolerance factor (t). The low t values of ILHPs compared with those of HOILPs are attributed to the smaller ionic size of Cs cations. To solve this problem, strategies like ion doping, dimension engineering, and device configuration engineering are often used to stabilize the ideal perovskite phase for solar cell applications. The second is the energy loss caused by unavoidable defects and energy-level mismatch, which limits the PCE of PSCs. In this regard, additive engineering, interface engineering, and charge transfer layer (CTL) modifications are commonly studied and optimized.

Herein, we mainly discuss the structural stability of ILHPs and the strategies to improve device efficiency and stability. First, the structural stability, crystal structure, electronic structure, and optical properties of CsPbI$_3$ are introduced. Then the research progresses of material engineering are reviewed in detail, including nanocrystals (NCs), surface engineering, and compositional tuning. Next, further improvements to enhance the performance and stability of ILHP-based PSCs are reviewed as well. Finally, a perspective about challenges and opportunities in ILHP-based PSCs is given.
2. Structure and Properties of Inorganic Perovskite Materials

2.1. Thermal Stability and Light Stability

ILHPs have drawn much attention due to their superior stabilities under heat and light stresses compared with HOILPs.\(^{[33,44,45]}\) The low thermostability of HOILPs has been investigated, and many efforts have been made to reveal the degradation mechanism both experimentally and theoretically.\(^{[46–49]}\) Although the detected decomposition species varies, which is likely due to the limitation of detection accuracy of different methods, a general recognition is that HOILPs irreversibly dissociate to lead halides, organic halides, and other organic species under heat stress.\(^{[47,50–52]}\) The organic species may further decompose to other volatile species with elevated temperatures.\(^{[47,53]}\) The dissociation and release of these organic compounds induce the collapse of the 3D perovskite structure which is detrimental to the device performance. Unlike the high vapor pressure methylammonium (MA) and formamidine (FA) have, alkali metal Cs usually has a much lower volatility which makes the ILHPs more endurable against heat stress. Akbulatov et al. compared the thermal stabilities of MAPbX\(_3\), FAPbX\(_3\), and CsPbX\(_3\) (X = I and Br) by aging these thin films at 90 °C for 20 h.\(^{[54]}\) It was found the FA- and MA-based samples experienced a more severe decomposition compared with the Cs-based ones.\(^{[54]}\) From a typical comparison of CsPbI\(_3\) and MAPbI\(_3\) films before and after aging, as shown in Figure 1, we can observe that the morphology of the CsPbI\(_3\) film after aging is highly preserved, with no obvious change on the film composition. The distinct changes of the X-ray diffraction (XRD) patterns of CsPbI\(_3\) film after aging somehow indicate a phase transition, and it will be discussed later. They correlated the increased thermal stability of MAPbI\(_3\) < FAPbI\(_3\) < CsPbI\(_3\) to the decreased volatility of univalent cation halides (MAX < FAX < CsX). Using first-principles calculations, Zhang et al. predicted that even without applying external heat stress at room temperature, MAPbI\(_3\) was already intrinsically unstable and was readily decomposes to MAI and PbI\(_2\).\(^{[55]}\) By substituting MA\(^+\) with Cs\(^+\), the formation enthalpy of CsPbI\(_3\) decomposition was increased to ≈0.1 eV, which indicated that CsPbI\(_3\) is intrinsically stable at 0 K.

Photodegradation is another issue limiting the long-term stability of PSCs.\(^{[52,53–57]}\) Abdelmageed et al. found that light exposure of MAPbI\(_3\) in the presence of oxygen induces iodide anions oxidization and releases electrons.\(^{[58]}\) The electrons further form free radicals which react with MA\(^+\) cations and release MA gaseous species by capturing protons from MA\(^+\). It was found under illumination stress, high energetic photons can generate hot electrons with long lifetime and migration distance.\(^{[59]}\) The hot electrons then readily deprotonate MA cations via Columbic coupling and then release MA gaseous species. Other than that, the released free photons can also pair with undercoordinated I\(^–\), promoting the formation of HI gas and iodine vacancies. The continuous loss of HI and organic gas species tilt the [PbI\(_6\)]\(^4–\) octahedra from a corner-sharing configuration to face-sharing and break the homogeneity of phase equilibrium, which result in the decomposition of MAPbI\(_3\) to lower-dimensional materials such as PbI\(_2\). Unlike MA and FA in HOILPs, alkali metal Cs has no proton, thus the deprotonation by free electrons and hot carriers will be prohibited, which preserves the monovalent Cs cations and locks iodine atoms in the perovskite structure.\(^{[59]}\) As we discussed earlier, benefiting from the alkali metal nature of Cs, CsPbI\(_3\) is more intrinsically stable against light and heat stresses which makes it more promising for the practical application under working conditions.

2.2. Crystal Structure

Despite the excellent compositional stability that has been discussed earlier, the 3D perovskite phase CsPbI\(_3\) possesses three metastable crystal structures and undergoes invertible phase transitions at different temperatures.\(^{[60,61]}\) As perovskite crystals favor 3D structures when the tolerance factor (t) ranges from

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**Figure 1.** a–c) Atomic force microscopy (AFM) images, scanning electron microscopy (SEM) images, and XRD pattern of MAPbI\(_3\) and CsPbI\(_3\) d–e) films before and after aging at 90 °C for 20 h. Reproduced with permission.\(^{[54]}\) Copyright 2020, Elsevier.
0.8 to 1, the metastable property of CsPbI₃ is likely due to the small ionic radius of Cs⁺, which leads to a low t of 0.8. The metastable phases of CsPbI₃ show different structural, electronic, and optical properties, which as a result determine the PV performance. Thus, a comprehensive understanding of the metastable 3D perovskite polymorphs of CsPbI₃ as well as its nonperovskite yellow phase is necessary.

Starting from the nonperovskite δ-phase (lattice constant \(a = 10.4342 \text{ Å}, b = 4.7905 \text{ Å}, c = 17.7610 \text{ Å}) CsPbI₃ at room temperature (293 K), it transforms to a more thermodynamically stable cubic α-phase (lattice constant \(a = b = c = 6.297 \text{ Å}) when the temperature is ramped up to 593 K. The δ- to α-phase transition is accompanied by an abrupt expansion of the cell volume and a dynamic tilting of the PbI₆ octahedra from edge-sharing to symmetric corner-sharing configuration in the presence of a high thermal energy. Upon cooling down, instead of a direct transition to the nonperovskite δ-phase, the α-phase CsPbI₃ polymorph goes through a continuous phase transition, first to the tetragonal β-phase (lattice constant \(a = b = 6.241 \text{ Å}, c = 6.299 \text{ Å}) and then to the orthorhombic γ-phase (\(a = 6.095 \text{ Å}, b = 6.259 \text{ Å}, c = 6.250 \text{ Å}) at, as shown in Figure 2a. The detailed crystal structure parameters are shown in Table 1. We can also observe from Figure 2a that among the three polymorphs, α-phase shows the most ideal cubic archetype structure with a 180° Pb—I–Pb angle. This highly symmetric phase then responds to the reduction of temperature by tilting the PbI₆ octahedra and lowering the Pb—I–Pb angle for β-phase and then γ-phase polymorphs.

Sutton et al. calculated the formation energies with respect to the precursors of CsI and PbI₂ following the equation of

\[ E_f = E[\text{CsPbI}_3] - E[\text{CsI}] - E[\text{PbI}_2] \]  

where \(E_f\) is the formation energy and \(E\) is the total energy. As shown in Figure 2b, the formation of α- and β-phases are endothermic, therefore, these two polymorphs are unstable and willing to transform to other more energetically favorable phases. While the formation of γ-phase is exothermic, indicating it is more thermodynamically stable compared with the other two metastable states. Although the γ-phase polymorph is intrinsically stable, it transfers to the nonperovskite δ-phase upon the exposure to humidity. Incorporating Br and Cl to form mixed halide perovskites can effectively improve the stability against humidity. However, the incorporation of smaller anions inevitably increases the bandgap from the optima value of \(≈1.3\) eV according to the Shockley—Queisser limit. Also, the incorporation of Br can cause phase segregation, which is harmful to the long-term stability. Other strategies such as A and B sites doping, 2D material passivation and applying encapsulation layers are all effective ways to suppress the phase transformation, but they are outside the scope of this section and will be discussed later.

### 2.3. Electronic Structure

ABX₃ perovskites are a family of direct bandgap semiconductors with efficient electron-hole pairs generation and light absorption. Considering CsPbI₃ as an example, its bandgap is defined by the overlap between p-orbitals of I atoms and the hybrid s and p orbitals of the Pb atoms. In this case with the identical PbI₆ octahedra, the bandgap should have no substantial change when only changing A-site cations. However, due to the “soft” nature of perovskites, the A-site cation is expected to squeeze the flexible Pb—I–Pb moiety and deform

![Figure 2](image-url)

Figure 2. a) Phase transition of CsPbI₃ polymorphs with heating and cooling. Reproduced with permission. Copyright 2018, American Chemical Society. b) Formation energies of CsPbI₃ polymorphs. Reproduced with permission. Copyright 2018, American Chemical Society.

| Polymorph | Space group | Crystal system | A[Å] | B[Å] | C[Å] |
|-----------|-------------|----------------|------|------|------|
| δ-phase   | Pnma (no.62)| orthorhombic   | 10.4 | 4.79 | 17.8 |
| α-phase   | Pm-3 m (no.221)| cubic     | 6.3  | 6.3  | 6.3  |
| β-phase   | P4/mbm (no.127)| tetragonal | 6.24 | 6.24 | 6.3  |
| γ-phase   | Pbnm/Pnma (no.62)| orthorhombic | 6.1  | 6.26 | 6.25 |

Table 1. Crystal parameters of CsPbI₃ polymorphs.
the perovskite lattice by Coulombic interactions, which as a result tilt the PbI$_6$ octahedra and contribute to the change of electronic structure close to the band edges. This explains why MA-, FA-, and Cs-based lead triiodide perovskites are having different bandgaps when using the same PbI$_6$ framework. The phase transition of CsPbI$_3$ also induces the change of bandgap through the way of tilting PbI$_6$ octahedra. As we discussed earlier, the α-phase CsPbI$_3$ at high temperature adopts a highly symmetric cubic archetype with a 180° Pb–I–Pb angle. The bandgap continuously increases with the increase in the octahedral tilting when the temperature cools down for β-CsPbI$_3$ and γ-CsPbI$_3$ polymorphs. Fadla et al. characterized the band structure of the three CsPbI$_3$ polymorphs along the principal high-symmetry directions in the Brillouin zone using the Perdew–Burke–Ernzerhof generalized gradient approximation (GGA-PBE) function, as shown in Figure 3. The bandgap of CsPbI$_3$ originally locates at the R point of the Brillouin zone for the cubic α-phase then shifts to Z and G points for the β- and γ-phases. The folding of the band edges from R to Z to G points for the α-, β-, and γ-phases narrows the bandwidth and widens the bandgap. In the theory of density-of-states, the ideal undistorted crystal structure of the α-phase CsPbI$_3$ has the optimal axial orbital overlap and thus results in the broadening of valence band which increases the bandwidth and narrows the bandgap. The tilting of the octahedra weakens the axial orbital mixing and thus leads to a decrease in the bandwidth of conduction band and an increase in bandgap. There are many works theoretically calculated the bandgap of the three metastable phases using different methods, however due to the limitation of the models and the different conditions that are considered, the calculated bandgap values are different. We here conclude these values and their corresponding calculation methods in Table 2. Although the values may have deviation from the experimentally measured values, the increased trend of bandgap from α- to β- and to γ-phase is in good agreement with our discussion earlier.

### 2.4. Optical Properties

Perovskite materials are also promising light harvest layers due to their excellent optical properties. The dielectric response of a semiconductor to the perturbation of an external electric field is very essential to the understanding of its optical properties. The response can be described by the dielectric function of $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, in which $\varepsilon_2(\omega)$ represents the imaginary part and is related to the absorption properties, and $\varepsilon_1(\omega)$ represents the real part and is related to the refractive properties. Once we know the real and imaginary parts of the dielectric function, we can derive the optical constants using the following equations summarized by Soni et al.

\[
n(\omega) = \sqrt{\frac{|\varepsilon(\omega)| + \text{Re}(\varepsilon(\omega))}{2}} \tag{2}
\]

\[
k(\omega) = \sqrt{\frac{|\varepsilon(\omega)| - \text{Re}(\varepsilon(\omega))}{2}} \tag{3}
\]

\[
R(\omega) = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2} \tag{4}
\]

### Table 2. Bandgaps of CsPbI$_3$ polymorphs.

| Method                  | Polymorphs |
|-------------------------|------------|
|                         | α [eV]     | β [eV] | γ [eV] |
| Ta$^{[72]}$             | 1.61       | 1.83   | 2.25   |
| scGW + SOC$^{[63]}$     | 1.48       | 1.89   | 2.53   |
| GGA-PBE CASTEP$^{[72]}$ | 1.88       | 1.96   | 2.17   |
| GGA-PBE ABINIT$^{[72]}$ | 1.78       | 1.94   | 1.78   |
| GGA-PBE + SOC ABINIT$^{[72]}$ | 0.63 | 1.3   | 0.83   |

Figure 3. Band structure of CsPbI$_3$ polymorphs. Reproduced with permission.$^{[72]}$ Copyright 2020, Elsevier.
\[ \alpha(\omega) = \frac{4\pi k(\omega)}{\lambda} \quad (5) \]
\[ \sigma(\omega) = \frac{2 W_{CV} h \omega}{2\pi E_0^2} \quad (6) \]
\[ L(\omega) = -\text{Im} \left( \frac{1}{\varepsilon_1(\omega)} \right) \quad (7) \]

In which \( n(\omega), k(\omega), R(\omega), \alpha(\omega), \sigma(\omega), \) and \( L(\omega) \) represent the refractive index, extinction coefficient, reflection, absorption, conductivity, and energy loss function, respectively, and \( \lambda, h, W_{CV}, \) and \( E_0 \) are wavelength, Planck constant, transition probability per unit time, and ground state energy, respectively.\(^{[78]}\)

Ahmad et al. calculated the frequency-dependent dielectric function, refractive index \( n(\omega) \), electron loss function \( L(\omega) \), and the sum rule \( \sigma(\omega) \) of CsPbI\(_3\) polymorphs, as shown in Figure 4.\(^{[79]}\) As the tetragonal \( \beta \)- and orthorhombic \( \gamma \)-polymorphs have different lattice constants, the calculation is along [100], [001] and [100], [010], and [001] planes, respectively.

The imaginary part \( \varepsilon_2(\omega) \) represents the absorption of free electrons.\(^{[78]}\) All the three polymorphs show similar absorption edge at \( \approx 1.7 \) eV which is related to their optical bandgaps. And the peaks after the absorption edge of the three polymorphs indicate electron transitions at certain energies. What should be noted here is there shows a slightly increase trend of the peak intensity from \( \alpha \)- to \( \beta \)-phase and a distinct increase from \( \beta \)- to \( \gamma \)-phase, which is an evidence of the enhanced absorption of the \( \gamma \)-CsPbI\(_3\) polymorph. The real part \( \varepsilon_1(\omega) \) of the dielectric function on the other hand is related to the refractive properties.

The zero-frequency limit \( \varepsilon_1(0) \) describes the electronic polarizability, which is how an electron dipole in the material would dynamically distorted by an external electric field.\(^{[79]}\) As shown in Figure 4, \( \varepsilon_1(0) \) increases when the polymorph transfers from \( \alpha \)- to \( \beta \)- and to \( \gamma \)-phase, which indicates their increasing dielectric properties. The real part \( \varepsilon_1(\omega) \) of these three polymorphs start to increase from \( \varepsilon_1(0) \) to the maximum and afterward decrease to 0. \( \varepsilon_1(\omega) \) even show negative values at certain points for the \( \alpha \)- and \( \beta \)-phases, implying the blocking and refraction of the corresponding photons into the bulk. However, the negative value does not show for the \( \gamma \)-phase, which indicates a wide range of photon absorption. Both of the improved imaginary and real parts of the dielectric function of \( \gamma \)-phase polymorph prove its wide range electron absorption and strong ability of retaining the absorbed energies, indicating the ideality of \( \gamma \)-phase as a light absorber material for solar cells.

Photons polarize and reduce speed when transmitting into materials. The refractive index \( n(\omega) \) describes how fast photons travel through a medium and is an important parameter to determine the absorption property.\(^{[79]}\) As shown in Figure 4, \( n(\omega) \) show similar trend for the three polymorphs, first increase to a maximum and then decrease at different energies. The electron loss function \( L(\omega) \) describes the energy loss of an electron when transporting into materials and characterizes the inelastic scattering property.\(^{[79]}\) Figure 4 shows that there is no peak when the energy is below the bandgap, and above the bandgap, all the three polymorphs show similar peaks, which indicate their similar energy loss. The sum rule \( \sigma(\omega) \) is another important factor which

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**Figure 4.** Dielectric function, refractive index \( n(\omega) \), electron loss function \( L(\omega) \), and the sum rule \( \sigma(\omega) \) of CsPbI\(_3\) polymorphs. Reproduced with permission.\(^{[79]}\) Copyright 2017, Elsevier.
relates to the strength or number of electrons involved in the transition from valence band to conduction band.\(^{[79]}\) The \(\alpha\)- and \(\beta\)-phases show similar trend in the range, whereas for the \(\gamma\)-phase it shows a rapid increase and high intensity.

By the comparison of the dielectric function and optical parameters, we can conclude that all the three metastable phases of \(\text{CsPbI}_3\) show proper properties as light absorbers, with reasonable optical band gap and strong light absorption ability. Especially, the \(\gamma\)-phase \(\text{CsPbI}_3\) has stronger absorption and faster photoresponse, which make it an ideal candidate for PV applications and needs to pay more attention.

3. Fabrication and Stabilization of \(\text{CsPbI}_3\)

The high-temperature method has become a universal way to fabricate the \(\gamma\)-\(\text{CsPbI}_3\) perovskite through cooling the \(\alpha\)-\(\text{CsPbI}_3\).\(^{[80,81]}\) Wang et al. optimized the high-temperature fabrication process through a solvent-controlled growth (SCG) of inorganic perovskite films (Figure 5a), promoting the PCE of \(\text{CsPbI}_3\) solar cells to 15.7\%, and the devices exhibit a high light-soaking stability over 500 h (Figure 5b,c).\(^{[68]}\) Template-assisted fabrication, or in other words, cation exchange method, is a more effective high-temperature way to prepare the \(\gamma\)-\(\text{CsPbI}_3\) films. By adding ammonium iodide (AI, \(A = \text{MA}\), dimethylamine (DMA), (adamantan-1-yl) methanammonium (ADMA), or other amines) act as sacrificial additive, this method not only produce a well-crystalized pin-hole free film, but also passivate defects through functionalized additive design.\(^{[82,83]}\) The MAI additive was first reported in the fabrication of \(\text{CsPbI}_3\)Br and achieved remarkable effect.\(^{[12]}\) Then Lau et al. studied the MAI additive in the fabrication of \(\text{CsPbI}_3\). It was found that the MAPbI\(_3\) perovskite was first formed and acted as a structure template for the subsequent ion exchange, whereby the \(\text{MA}^+\) were replaced by \(\text{Cs}^+\) to gradually form the \(\text{CsPbI}_3\) perovskite at 330 °C (Figure 5d).\(^{[84]}\)

As discussed earlier, the main drawback of the \(\text{CsPbI}_3\) is the phase instability at room temperature, which greatly limits its fabrication and application. There are various strategies, which have been developed to enhance the stability of \(\text{CsPbI}_3\) perovskite, which can be summarized into three types: \(\text{CsPbI}_3\) NCs, surface engineering, and compositional tuning.

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Figure 5. a) Schematic illustration SCG method for \(\text{CsPbI}_3\). b) \(J-V\) curve of the devices with and without the SCG process. c) Photostability of the devices under continuous illumination (100 mW cm\(^{-2}\), with 420 nm UV filter) in \(\text{N}_2\). a–c) Reproduced under the terms of the CC-BY 4.0 license.\(^{[68]}\) Copyright 2018, The Authors, published by Springer Nature. d) Schematic illustration cation exchange method for \(\text{CsPbI}_3\) film. Reproduced with permission.\(^{[84]}\) Copyright 2019, Wiley-VCH.
3.1. CsPbI₃ NCs—Reducing the Surface Energy

Reducing the size of CsPbI₃ crystals to the nanoscale has been demonstrated to be a promising method to stabilize the perovskite polymorphs at room temperature. The surface energy plays the key factor in perovskite NCs with a high surface/volume ratio (Figure 6a). Theoretical calculations show that γ-CsPbI₃ with a lower surface free energy becomes thermodynamically preferred over δ-CsPbI₃ at larger surface areas above 8600 m² mol⁻¹.[65] This fact decreases the phase transition temperature from nonperovskite to perovskite phase. The total energy per formula unit in a NC consist of two parts, the bulk part $E_{\text{bulk}}$ and the surface part $E_{\text{surf}}$

$$E_{\text{NC}} = E_{\text{bulk}} + E_{\text{surf}}$$  

Estimated by density functional theory (DFT) calculations, α- and γ-CsPbI₃ present a smaller $E_{\text{surf}}$ values of 1.2 and 4.0 meV Å⁻², respectively, whereas this value of δ-CsPbI₃ is around 7.5 meV Å⁻².[85] At the bulk limit, the total energy converges to the formation energies of the bulk (α > γ > δ), as the surface energy is negligible for large NCs. As the diameter decreases, the total energy starts to increase as surfaces cost energy to form. The transition starts at the diameter decreased to 5.6 nm where perovskite-phase γ-CsPbI₃ is more stable than the nonperovskite-phase δ-CsPbI₃, and further decreasing the diameter to 2.7 nm, α-CsPbI₃ is thermodynamically stable (Figure 6b). In addition to surface area, surface composition also makes a critical effect on surface energy. Calculation results also indicate a Cs-rich film presents improved perovskite-phase stability (Figure 6c).[85] The superior stability of Cs-rich perovskite film has been also demonstrated both in solution process and coevaporation process (Figure 6d).[86,87]

Normally there are two strategies to regulate the perovskite grain size. The first way is to synthesis CsPbI₃ NCs directly in ex situ, the other way is in situ regulating the grain size of perovskite through additives during the formation of perovskite film.

CsPbI₃ NCs have been well studied in photovoltaic. Swarnkar et al. demonstrated the formation of CsPbI₃ NC films that were phase-stable for months in ambient air.[14] The NCs exhibit a cubic phase, with tunable bandgap from 1.82 to 2.07 eV via controlling size from 3.4 to 12.5 nm. The optimized device showed an efficiency of 10.77% with $V_{\text{OC}}$ up to 1.23 V.

It is generally assumed that in the NCs film the current density could be limited due to the long-chain ligands capping layer of NCs. Surface engineering of the CsPbI₃ has been adopted to enhance the packing states of NC solids and to passivate the surface defects. Sanehira et al.[88] enhanced carrier mobility using AX post treatment (A = FA⁺, MA⁺, or Cs⁺ and X = I⁻ or Br⁻) to enhance the electronic coupling between NCs, and the PCE was improved from 10% to 13%. Pb(NO₃)₂, MeOAc, or GA⁺ treatment are also used to remove the long organic oleic acid and oleylamine ligands to improve the charge transport.

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**Figure 6.** a) Calculated Gibbs free energy of CsPbI₃ polymorphs as a function of surface area through molecular dynamics simulations. Reproduced with permission.[85] Copyright 2018, American Chemical Society. b) Total energy of nanocrystal for α-, γ-, and δ-phases as a function of diameter. c) Phase diagram of α-, γ-, and δ-phases, as a function of the chemical potential $\Delta\mu_{\text{CsI}}$ and the nanocrystal size. b,c) Reproduced with permission.[85] Copyright 2020, American Institute of Physics. d) [Cs]/[Pb] atomic ratio as a function of position measured at the phase boundary. Reproduced with permission.[87] Copyright 2019, Wiley-VCH.
transportation.\textsuperscript{[38,89]} In addition, the functionalized graphene or cation doping of CsPbI\(_3\) NCs were also developed to improve the humidity stability of the solar cell device (Figure 7a–c).\textsuperscript{[90]}

In situ formation of quantum-sized CsPbI\(_3\) grains is another way to increase the surface energy and improve the phase stability of perovskite CsPbI\(_3\) at room temperature. During the formation of CsPbI\(_3\) grains from solution process, the colloidal in the precursor plays a key factor on the CsPbI\(_3\) grain size. Zhao et al.\textsuperscript{[65]} presumed that the introduction of high dielectric H\(_2\)O could change the ionization degree of the precursor solutions and increase in proton activity or I\(^{-}\) concentration, which contributes to reduction of the CsPbI\(_3\) grain size (Figure 7d). Zwitterion was also demonstrated to be an effective additive in tuning the PbI\(_2\)/dimethyl sulfoxide (DMSO) colloids (Figure 7e).\textsuperscript{[91]} The electrostatic interaction between zwitterion and PbI\(_2\)/DMSO colloids can break the layered structure of the colloids to decrease the colloid size. As a consequence, the zwitterions molecules maintain the grain size by impeding further grain growth.

### 3.2. Surface Engineering—Functionalization or Dimension

In addition to the size effect, surface ligand functionalization also plays a crucial role on the phase stability by tailoring the surface energy and forming nanoscale encapsulation layers of perovskite grains.

The phase transition from perovskite CsPbI\(_3\) to nonperovskite \(\delta\)-CsPbI\(_3\) could be greatly accelerated by moisture that causes distortion of the corner sharing octahedral framework ([PbI\(_6\)]\(^{4-}\)). It is demonstrated that the surface ligand functionalization could significantly improve the phase stability of CsPbI\(_3\) perovskite by suppressing the lattice distortion triggered by moisture or polar solvents and increasing the energy barriers of octahedral rotation (Figure 8a–c).\textsuperscript{[92–94]} Moreover, the surface ligand could interact with shallow- or deep-level defects in CsPbI\(_3\) to significantly reduce defect density.\textsuperscript{[92,95]} There are two categories to stabilize the CsPbI\(_3\) perovskite with surface functionalizing ligand.

The first method is to form a surface cation termination on the perovskite surface with long-chain ammonium cations. Similar
with the examples widely used in organic–inorganic PSCs, the
phenylethylamine (PEAI) cation was introduced to modify the sur-
face of CsPbI$_3$ perovskite. The PEAI cation forms a surface cation
termination on the top of CsPbI$_3$ instead of a 2D capping layer as
in the organic–inorganic counterpart. The cation exchange to form
the 2D perovskite seems hard to happen in CsPbI$_3$. The surface
cation termination not only improves the stability but also exhibits
passivation effects with improved $V_{OC}$ and fill factor (FF). Wheeler
et al. have shown that the incorporation of oleylammonium (OA$^+$)
processing stabilizes the CsPbI$_3$ perovskite in the cubic
$\alpha$-phase whereas the use of PEA$^+$ additives stabilizes the CsPbI$_3$
perovskite in the tetragonal $\beta$-phase where the octahedra are slightly tilted.$^{[96]}$
The transformation related to the [Pbl$_6$]$^{10-}$ rotation was also shown
in the study of Wang et al.$^{[92]}$ Through a surface capping
with 4-aminobenzoic acid, the designated angles between Pbl$_6$
octahedra are 111.20° and 73.93°, being closer to ideal 90° for
cubic phase, respectively. However, the corresponding angles
on Cs-terminated surface are 113.83° and 65.15°, respectively.$^{[92]}$
Polymers with amide groups have also been applied to stabilize the
CsPbI$_3$ perovskite. Li et al. have incorporated polyvinylpyrroldione
(PVP) into the solution processing of CsPbI$_3$ perovskites.$^{[97]}$ They
claimed that PVP could interact with CsPbI$_3$ via molecular bond-
ing. The CsPbI$_3$ perovskite thin films with PVP additive are highly
stabilized, 75% of the initial PCE is retained after the encapsulated
PSC is exposed to ambient air with 50% relative humidity (RH) for
500 h. Surface capping with the long-chain ammonium cations
shows a universal way to stabilize the CsPbI$_3$ as well as improve
the PCE through defect passivation.$^{[95,98]}$

Different from surface cation termination, CsPbI$_3$ crystal
structure could also be stabilized by incorporation of the large
ammonium cations into the precursor, forming layered 2D or
“quasi-2D” perovskites.$^{[99–101]}$ Liao et al. used a dimension engi-
neering method by introducing a bulky ammonium cation to
form stable 2D cesium lead iodide perovskite $\text{BA}_2\text{CsPbI}_4$ ($\text{BA} = \text{CH}_3(\text{CH}_2)_3\text{NH}_3$). The 2D $\text{BA}_2\text{CsPbI}_4$ shows excellent sta-

tility but PCE is below 5%.$^{[102]}$ In addition to the 2D perovskite,
the “quasi-2D” structures are supposed to be more preferred for
high-performance devices. The most widely used PEAI has also

Figure 8. a) The calculated total energies of Cs$^+$- and 4-aminobenzoic-terminated CsPbI$_3$ surface as a function of angle-change. Reproduced with permission.$^{[92]}$ Copyright 2020, Wiley-VCH. b) Mechanism of the OTG-induced phase stabilization of CsPbI$_3$ perovskite. Reproduced with permission.$^{[93]}$ Copyright 2020, Wiley-VCH. c) Schematic illustration of the PVP anchored on the surface of CsPbI$_3$ crystals. Reproduced under the terms of the CC-BY 4.0 license.$^{[97]}$ Copyright 2018, The Authors, published by Springer Nature. d) Structure of PEA$_n$Cs$_{n-1}$Pb$_n$X$_{3n-1}$ and decomposition energy through DFT calculation. e) Device performance evolution under ambient atmosphere without sealing. d,e) Reproduced with permission.$^{[99]}$ Copyright 2018, Elsevier.
been adopted here in the precursor solution to prepare the quasi-2D CsPbI₃ perovskite film. Jiang et al. reported a dimensionality modulation of quasi-2D perovskites by adjusting the ratio of PEA⁺ to Cs⁺, yielding \( \text{PEA}_x\text{Cs}_{1-x}\text{Pb}_x\text{I}_{3n-1} \) (Figure 8d). The decomposition energy increased with decreasing \( n \) values thus improves the stability while decreases the bandgap, a proper \( n \) value between 40 and 60 could reach the best balance between stability and PCE (Figure 8e). Zhang et al. developed a method of incorporation of divalent ethylenediamine (EDA) lead iodides in CsPbI₃ perovskite thin films to form a “quasi-2D” perovskites. The introduction of ethylenediamine (EDA) cation avoids the undesirable formation of the nonperovskite \( \delta \)-phase and leads to very promising film stability for more than 1 week at 100 °C in dry air condition. DFT calculation suggests the enhanced stability of the “quasi-2D” Ruddlesden–Popper perovskite (EDA) \( \text{Cs}_{1-x}\text{Pb}_x\text{I}_{3n-1} \) is due to the strong I–I interaction of diamine cations with shortened interlayer distance (≈3.5 Å).

Large polar organic molecule additives are also useful for making stable CsPbI₃ perovskite thin films. These molecules normally combine a polar group which could anchor with the Pb–I framework and a big-size alkyl or aromatic group which could improve the hydrophobicity. Wang et al. reported a bulky organic ligand serving as organic terminal groups in which cyanoacetic acid were adopted as an anchor for bonding with the Pb–I framework of perovskite lattice. It is claimed that the large 2,4-dibutoxy phenyl unit applied in the terminal groups could efficiently hinder the octahedral tilting of the corner-sharing \( [\text{PbI}_6]^{4-} \) through a strong sterichindrance effect. Such effect increases the formation energy of orthorhombic nonperovskite \( \delta\)-CsPbI₃ with an edge-sharing \( [\text{PbI}_6]^{4-} \). The terminal groups could also passivate the surface electronic trap states via efficient coordination between carboxylate moieties and undercoordinated Pb\(^{2+}\) defects. The strong molecular interaction of the additive phases with as-crystallized CsPbI₃ could tune the surface energy and stabilizes the CsPbI₃ perovskite phase kinetically.

### 3.3. Compositional Tuning—Improving the Tolerance Factor

Compositional engineering is the most extended strategy to overcome the unfavorable Goldsmidh tolerance factor. Two directions are applied to improve the tolerance factor, big size A site cation doping to compensate the Cs⁺ to or reduce the \([\text{PbI}_6]^{4-}\) skeleton through B and X site doping. Cs is the largest one among inorganic monovalence positive ions in the APbX₃ perovskite phase, so the A site doping is focused on organic cations, such as DMAI doping. In 2015, Erperon et al. reported a HI additive to prepare the CsPbI₃ PSCs. After that, the “HI-related method” becomes the most extended strategy for fabrication of CsPbI₃ PSCs, and the best-performance device reach a PCE of 19%. Here, we categorize the HI additive, DMAI additive, and HPbI₃ precursor into the “HI-related method” or the “DMAI-related method” because the addition of HI in the precursor solution will react with the \( N, N\)-dimethylformamide (DMF) solvent to form the byproduct DMAI.

\[
\text{HCON}(\text{CH}_3)2 + \text{HI} + \text{H}_2\text{O} \rightarrow (\text{CH}_3)2\text{NH}_2\text{I(DMAI)} + \text{HCOOH}
\]  

Ke et al. demonstrated this reaction and synthesized the DMAI from the reaction of DMF and HI directly (Figure 9a). They claimed that the so-called all-inorganic CsPbI₃ films processed with HI-related method were in fact CsₓDMAIₓ₋₃CsPbI₃ films and the “HPbI₃” was actually DMAPbI. The calculated tolerance factor of CsₓDMAIₓ₋₃PbI₃ is 0.9 (Figure 9b), and its bandgap is 1.7 eV (Figure 9c). Different from directly adding HI into the DMF solvent, the “HPbI₃” in the “HPbI₃” method was first prepared and then used as one precursor to fabricate the inorganic perovskite film. The annealing temperature from 180 to 210 °C was normally used, which is much higher than the sublimation temperature of DMAI (around 150 °C). Thus, how much DMAI remains in the final perovskite film is still not very clear.

Meng et al. carefully investigated the formation process of CsₓDMAIₓ₋₃PbI₃ with a DMAI additive at a temperature of 180 °C. It was found that a Csₓ₁ₓDMAIₓ₋₁PbI₃ perovskite formed first, and then the Csₓ₁ₓDMAIₓ₋₁PbI₃ continued to change into CsPbI₃ perovskite, and quickly transformed to \( \delta\)-CsPbI₃ (Figure 9d,e). The Csₓ₁ₓDMAIₓ₋₁PbI₃ perovskite expresses a narrow bandgap of 1.67 eV, which is consistent with samples prepared from the “HPbI₃”-related method, but much smaller than of the high temperature processed pure CsPbI₃ (1.73–1.75 eV) (Figure 9f).

On the contrary, Wang et al. claimed that a pure \( \beta \)-phase CsPbI₃ perovskite was formed instead of the DMAI containing inorganic perovskite phase. Therefore, the DMAI used here is an additive rather than dopant. Undoped \( \alpha \)- and \( \gamma \)- CsPbI₃ were also reported with the HI-related method. In addition to the DMAI, the FAI additive was also studied by Shao et al. It was found that 15% of the FA⁺ dopant could greatly improve the environment-phase stability and ultraviolet stability of the Cs-rich perovskite film.

\( B\)- and X-site doping could also optimize the tolerance factor through minimize the \([\text{PbI}_6]^{4-}\) skeleton. The formation energy of the B-site is large; therefore, B-site doping is more difficult compared with that of A-site and X-site cations. \( \text{Sn}^{2+}, \text{Ca}^{2+}, \text{Mn}^{2+}, \text{Sb}^{3+}, \text{Bi}^{3+}, \text{Eu}^{2+} \) were considered to be potential suitable candidates for B-site doping. The further study on their effect of B-site doping on the crystal structure, phase stability, and especially the electronic properties of CsPbX₃ is still necessary.

Another way to increase tolerance factor is X-site doping of I anion with the smaller-size Br, or Cl which will form CsPbX₃ alloy perovskites. \( \text{CsPbI}_3\text{–}_{1_x}\text{Br}_x\text{Br}_x \) exhibit much better phase stability compared with undoped CsPbI₃. However, the Br doping also faces the photoinduced phase separation problem in which the CsPbI₃–ₓBrₓ will separate into a Br-rich and a I-rich phase under continues irradiation. Moreover, the Br alloying induces an undesired blue shift of the absorption edge and an enlarged bandgap up to 1.9 eV.

### 4. CsPbI₃ Perovskite Solar Cells

Up to now, the PCE of the inorganic CsPbI₃ solar cells still lags behind the HOILP counterparts. This is not only because of the lower theoretical efficiencies limited by their wider bandgaps, but also due to the impeded carrier transport between the CTL and CsPbI₃ caused by mismatched energy levels and interfacial defects.
4.1. Charge Transfer Layer

Perovskite solar cells (PSCs) are usually composed of transparent conducting oxide (TCO), electron transport layer (ETL), light-absorbing perovskite layer, hole transport layer (HTL), and the metal electrode. Among them, the CTL not only reduces the potential barrier between perovskite and electrode, but also promotes the charge collection. The energy alignment can extend the depletion region for substantial suppressing of the charge recombination, which is extremely desirable for obtaining high open-circuit voltage ($V_{OC}$) and FF. Energy-level match is dependent on the conduction band offset (CBO) between the ETL/perovskite and the valence band offset (VBO) between the HTL/perovskite. Optimum position of the conduction band of the ETL is 0–0.3 eV higher than that of the perovskite (Figure 10b), whereas the optimum position of the valence band of the HTL is 0–0.2 eV lower than that of the perovskite layer (Figure 10c).[^125–127]

Bilayer structure and new materials are two common ways to improve the properties of CTL.[^128–130] Ethanol solution of thiourea was used to obtain the ZnO–ZnS ETL, the CsPbI$_3$ PSC with a PCE of 16.9%, and the large-area module (active area is 8 cm$^2$) with a PCE of 11.8% were prepared.[^131] Bai et al. introduced a SnO$_2$/ZnO bilayer ETL to CsPbI$_3$ PSCs. The optimized PSC shows an excellent PCE of 16.39%.[^86] Other bilayer ETL like ZnO/PCBM, ZnO/TiO$_2$, ZnO@C$_{60}$, and SnO$_2$@C$_{60}$ were also used for the inorganic PSCs.[^28,132–135]

The bilayer HTLs, such as Spiro-OMeTAD/ MoO$_3$, poly-3-hexylthiophene (P3HT)/MoO$_3$, or poly[bis(4-phenyl)(2,4,6trimethyl-phenyl)amine] (PTAA)/MoO$_3$ were also studied for the inorganic PSCs.[^90,86,128,136] Yuan et al. adopted an undoped conjugated polymer instead of Spiro-OMeTAD to fabricate the poly[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-alt-3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b][thiophene-4,6-diyl]] (PTB7)/MoO$_3$ bilayer hole transport material.
(HTM). The performance of CsPbI\(_3\) PSCs were highly improved because of the negligible band bending/barriers at the NCs/PTB7 interface and the photogenerated internal dipole effect in PTB7 by the interchain charge transfer from benzothiophene to thienothiophene moiety.\(^{[38]}\) Tian et al. combined a dopant-free polymer poly[5,5\(^{-}\)-bis(2-butyloctyl)(2,2\(^{\prime}\)-bithiophene)-4,4\(^{-}\)-dicarboxylate-alt-5,5\(^{-}\)-2,2\(^{\prime}\)-bithiophene] (PDCBT) (with deeper-lying highest occupied molecular orbital (HOMO), \(-5.3\) eV) and MoO\(_3\) as HTL to promote the energy-level matching with anode, reaching a significant \(V_{\text{OC}}\) of 1.30 V.\(^{[42,86]}\) Furthermore, inorganic materials like CuI, CuSCN, NiMgLiO, etc. were also very promising HTL candidates due to their excellent thermal stability, but their fabrication condition need be to be further optimized.\(^{[16,137–140]}\)

4.2. Interface Layer

Interface layer are interlayers inserted between perovskite and CTls passivate the interface defects and adjust the energy levels. Inorganic materials with excellent thermal and photostability, like NaOH, KOH, and Ba(OH)\(_2\), can reduce the density of surface defects effectively and promote the band energy alignment. Meng et al. introduced solution-processed Ba(OH)\(_2\) as a surface modifier at the SnO\(_2\)/CsPbI\(_3\) interface, remarkably enhanced \(V_{\text{OC}}\) from 0.87 to 1.07 V.\(^{[137]}\) Ye et al. developed an inorganic shunt-blocking layer lithium fluoride (LiF) between SnO\(_2\) and inorganic perovskites, which shifts the conduction band of SnO\(_2\) minimum from 4.3 to 4.01 eV and the corresponding CsPbI\(_3\)-Br\(_x\) PSC exhibits a PCE of 18.64% (Figure 11a,b).\(^{[141]}\) Li et al. incorporated layer-structure-tunable 2D black phosphorous (BP) to enhance the exciton dissociation efficiency in inorganic perovskites. The energy-level, work function, and relative permittivity can be tuned by adjusting the layers of BP, which promotes the carrier transfer and improves the PCE obviously (Figure 11d).\(^{[137]}\)

Moreover, organic materials are also commonly used as interface modification. A multifunctional molecule, 5-amino-2,4,6-triiodoisophthalic acid (ATPA), is fixed on TiO\(_2\) and CsPbI\(_3\) interface by reacting with dangling hydroxyl group on TiO\(_2\) surface which improves the electron extraction property. The optimized CsPbI\(_3\) PSC delivers a PCE of 18.12% with suppressed hysteresis.\(^{[141]}\) Wang et al. developed a crack-filling interface engineering method using choline iodine (CHI), which promotes the level alignment at interfaces between the β-CsPbI\(_3\)/ETL and β-CsPbI\(_3\)/HTL. The best PSC prepared by this method reaches a recording PCE of 18.4%.\(^{[17]}\)

When organic halides act as the interface layer, it also performs the following additional functions: 1) suppressing the spontaneous octahedral tilting of perovskite by the chemical bond between organic salt and perovskite; 2) introducing large organic groups to improve the hydrophobicity and enhancing the stability of PSCs. For example, P-phenylenediammonium iodide (PBDI) was used to post-treat CsPbI\(_3\) films and the suppress phase conversion (Figure 11c).\(^{[98]}\)

Figure 10. a) Parameters (different interface defect densities) of PSCs with different CBO values. \(J–V\) curves of PSCs with b) different CBO values of ETL/perovskite interface and c) different VBO values of absorber/HTM interface. a–c) Reproduced with permission.\(^{[125]}\) Copyright 2015, Elsevier.
5. Conclusion

Inorganic perovskite show superior photo- and thermostabilities, but suffer from phase transformation issues at room temperature and in the presence of water. In addition, deep-level defects in the bulk and surface, as well as the energy-level mismatch at interfaces are obstacles restricting the improvement of device performance. Additive engineering, compositional tuning, and interface engineering are reported to solve these problems. However, although tremendous efforts and progress have been made by researchers, further and deeper investigations are still needed to completely solve these issues. The following directions could be effective to help the further development of inorganic PSCs:

5.1. Advanced Characterization and Theoretical Research

In addition to the research on the performance of inorganic perovskite devices, photophysical characterization and theoretical calculation of inorganic perovskite materials also have great significance. The photophysical characterization is helpful to better understand the degradation process and mechanism of inorganic perovskite, and provide guidance on how to improve the stability. The theoretical calculation can not only study the interface properties, but also predict optimized device structure, material, and thickness of each structural layer.

5.2. New Transport Layer and Electrode Materials

Although inorganic perovskites have excellent thermal stability, HTL materials such as Spiro-OMeTAD and PTAA need to be doped by small molecules to improve their conductivity. Thus, the overall performance of the cells is limited by the volatile dopants. The design of undoped organic transport materials and develop of inorganic transport materials are necessary to further improve the device performance of inorganic PSCs. In addition, the commonly used electrodes like gold and silver are active metals, which can diffuse into perovskites and react with halides, resulting in perovskite decomposition. Carbon electrode has been used by researchers and showed better charge extraction. More importantly, carbon electrode is hydrophobic, and can act as a waterproof protective layer retarding undesirable phase transformation. Thus, technologies of using carbon electrode in inorganic PSCs are very important and need to be seriously developed to achieve real long-term stable inorganic PSCs for practical applications.

5.3. Large-Scale Application and Flexibility

The realization of large-scale preparation is the basis of industrial application, while the realization of flexible preparation determines the scope of its application. However, there are few reports on large-scale or flexible all-inorganic PSC, so this research field is expected to be explored in the near future.

5.4. Multijunction Tandem Solar Cells

Multijunction tandem devices are demonstrated to boost the efficiency and overcome the Shockley–Queisser limit for single-junction solar cells. Due to the proper bandgap and
superior thermostability, inorganic perovskites are competitive candidate for using as top cells in tandem solar cells, but they are rarely reported. One of the obstacles is the lack of a technique to make inverted inorganic PSCs. Although great progresses have been made in the study of inorganic PSCs, but most of them are based on n-i-p structures. However, most of the efficient tandem cells are based on p-i-n structures. So, it is urgent to develop technologies for efficient and stable inverted inorganic PSCs.

5.5. Water Splitting

The potential in photolysis of water requires more than 1.23 V. While the inorganic PSCs has large bandgap and large voltage, which are suitable for the photolysis of water. At present, some inorganic PSCs, such as CsPbBr3, have been used for water splitting, but the short survival time in water limits further development and application. In the future, water can be isolated by introducing a hydrophobic layer to improve the survival time of inorganic PSCs.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

energy levels, inorganic perovskites, solar cells, stabilities, structures

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