

Dimethylammonium cation stabilizes all-inorganic perovskite solar cells

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Facing the poor environmental stability of traditional methylammonium or formamidinium-based lead halide perovskites, scientists turn their attention to inorganic lead halide perovskites (ILHPs) with narrow bandgaps, excellent thermal stability and reduced ion migration compared to their organic/inorganic counterparts^[1–4]. Up to now, the PCEs for ILHP solar cells exceed 21%^[5]. Especially, the preferred black ILHP (e.g. CsPbI₃) with the smallest bandgap of ~1.7 eV and single-halide composition for avoiding phase separation is crucial for high-performance single-junction solar cells and can be applied in tandem devices as the top cells^[6, 7]. However, small Cs⁺ (167 pm) in CsPbI₃ with a tolerance factor close to 0.8 is unsuitable for the 3D PbI₃⁻ framework^[8]. The mismatched size of cations will induce lattice strain and the perovskite spontaneously transforms to undesired non-photoactive yellow phase (δ -phase, like NH₄CdCl₃) (Fig. 1(a))^[9, 10]. Therefore, improving lattice symmetry and reducing lattice strain are the strategies for inhibiting the phase transition of ILHPs. Reducing the lattice strain by increasing the specific surface area of all-inorganic perovskite crystals to make nanocrystals can improve the phase stability. This usually requires the introduction of long-chain alkyl amines (e.g. oleic ammonia) in the precursor solution, which is widely used in quantum-dot solar cells. Luther *et al.* demonstrated that phase-stable colloidal CsPbI₃ quantum dots gave a PCE of 13.43% due to large contribution of surface energy^[11, 12]. The disadvantage is the negative effect of many grain boundaries between nanocrystals and organic ligands to carrier transport, which seems to be more suitable for electroluminescent devices rather than solar cells. Therefore, much efforts have been devoted to improving the phase stability of black-phase ILHPs at room temperature to obtain high-performance PSCs^[13]. At present, the effective strategy is cation engineering, including the use of additives DMAI and hydriodic acid (HI).

Previously, adding HI to the precursor to produce HI-PbI₂ or the so-called hydrogen lead iodide (HPbI₃) precursor is a widely-used approach to stabilize black α -CsPbI₃^[14]. Snaith

et al.^[15] first added HI to CsPbI₃ precursor solution to reduce the annealing temperature from 310 to 100 °C and obtained uniform and stable black-phase ILHPs^[16]. Then, Zhao *et al.* reported stabilized black CsPbI₃ by a low-temperature deposition and by using pre-synthesized PbI₂·xHI, which was made from DMF, PbI₂, and HI. Combined with larger ethylenediammonium cation, α -CsPbI₃ solar cells gave a PCE of 11.8%^[17]. DMA⁺ byproducts (Fig. 1(b)) resulted from the chemical reaction of HI and DMF in the precursor solution. Almost all efficient and stable ILHP solar cells have incorporated HI, HPbI₃ or DMA⁺ in their precursor solutions^[18–21]. Later, Yuan *et al.* used HPbX₃ (X = I, Br) as the precursor combined with phenylethylammonium cation to make low-dimensional α -CsPbI₃, yielding a PCE of 12.4% with enhanced stability^[22]. HPbI₃ made by dissolving HI and PbI₂ in DMF could increase the PCE to 17%^[23, 24]. However, the mechanism for HI or HPbI₃ to improve the device performance has been unclear. It was argued that the A-site of the prepared ILHPs mixed with organic cation DMA⁺, thus yielding a stable black organic-inorganic perovskite phase. Whether DMA⁺ exists, the content of DMA⁺ in the lattice, the properties for DMA⁺/Cs⁺ mixed perovskite phase, and even the phase evolution process during thermal treatment still need deep investigation.

Kanatzidis *et al.*^[25] compared the films made with HI and DMAI additives by nuclear magnetic resonance (NMR) and found that both films exhibited the characteristic peaks of DMA⁺, so they thought that DMA⁺ entered the A-site of perovskite. Qi *et al.*^[26] used highly-sensitive time-of-flight secondary ion mass spectrometry to prove DMA⁺ existence in perovskite. Further studies indicated that DMA⁺ was generated by the hydrolysis of DMF accelerated by HI. Liu *et al.*^[27] analyzed the products of HI-accelerated DMF hydrolysis by using in-situ thermogravimetry Fourier transform infrared spectroscopy, and the spectra showed two peaks corresponding to DMA⁺ volatilization and PbI₂ decomposition. Both HI and HPbI₃ additives helped to produce DMA⁺ in perovskite, leading to high PCE and stability. Seok *et al.*^[18] also used DMAI additives and obtained PCE over 20% by continuous dripping of methylammonium chloride solution. Liu *et al.*^[28] used HPbI₃ additive combined with a surface treatment to increase PCE to 20.8%. Meng *et al.* directly introduced DMAPI₃ and achieved a PCE over 20%^[19]. By using DMAAc solvent, they developed

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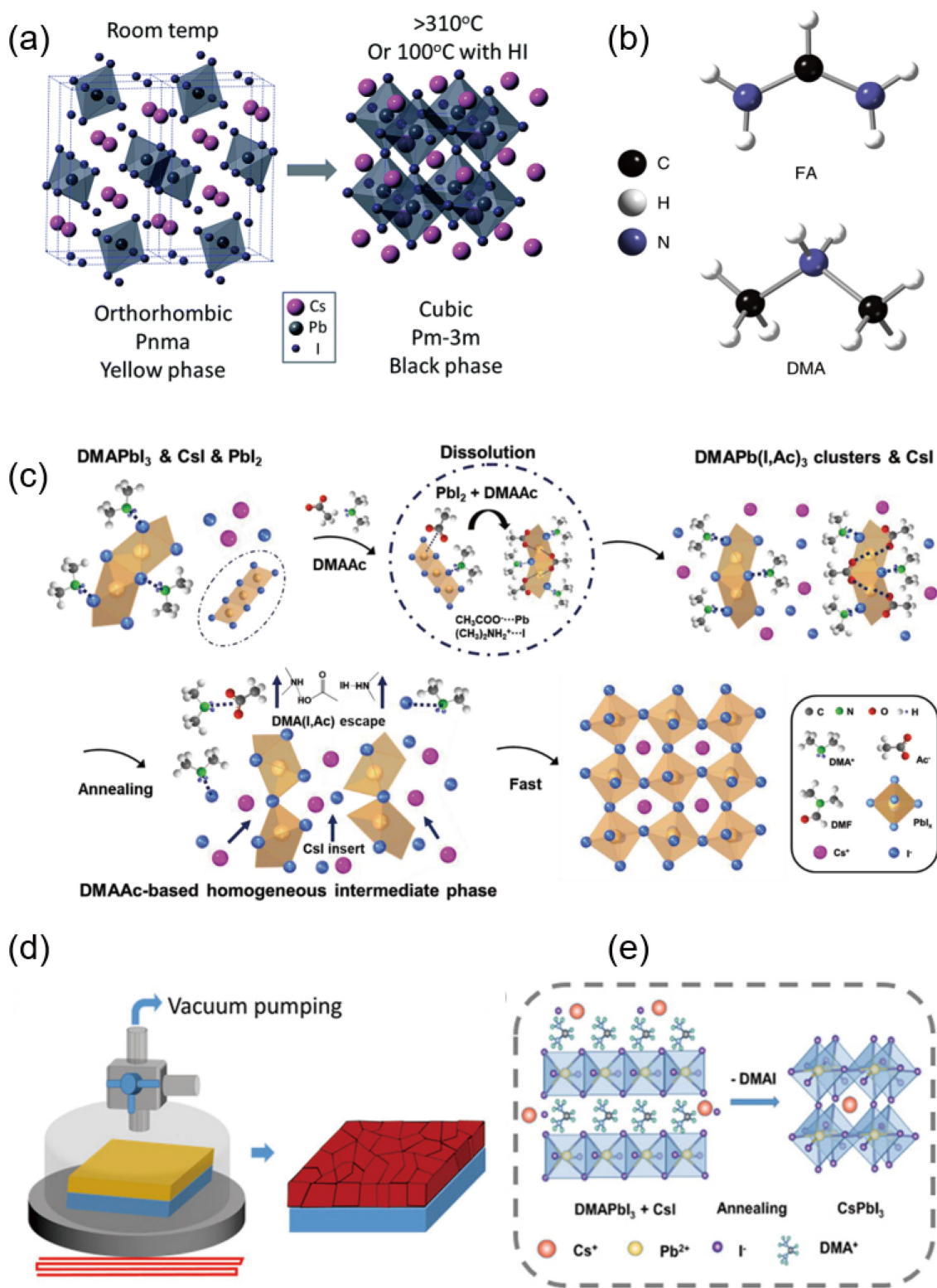


Fig. 1. (Color online) (a) Schematic structures for CsPbI₃ phases. Reproduced with permission^[15], Copyright 2015, Royal Society of Chemistry. (b) Structures for FA (top) and DMA (bottom) cations. Reproduced with permission^[25], Copyright 2018, Nature Publishing Group. (c) Schematic for crystal structure evolution from precursor solution to γ -CsPbI₃ and possible chemical interaction. Reproduced with permission^[21], Copyright 2022, Wiley. (d) Schematic for vacuum-assisted thermal annealing of CsPbI₃ film. (e) The conversion of 1D DMAPbI₃ film to 3D CsPbI₃ through cation exchange between Cs⁺ and DMA⁺. Reproduced with permission^[1], Copyright 2022, Wiley.

DMAPb(I, Ac)₃ intermediate to eliminate Cs₄PbI₆ intermediate phase, yielding a PCE over 21% (Fig. 1(c))^[21]. Pang *et al.*^[29] recently modified DMAI-additive fabrication route by using CsI in excess to obtain black phase γ -CsPbI₃ perovskite at ~100 °C. Subsequent dipping of the film into isopropanol solution realized the stoichiometric balance between DMAPbI₃

and Cs₄PbI₆ intermediates. Song *et al.* indicated that vacuum-assisted thermal annealing is effective for controlling the morphology and crystallinity of DMA⁺-based CsPbI₃ films to obtain PCE exceeding 20.06% along with enhanced stability (Figs. 1(d) and 1(e))^[1]. DMA⁺ assists low-temperature crystallization of black phase CsPbI₃ through forming intermediates.

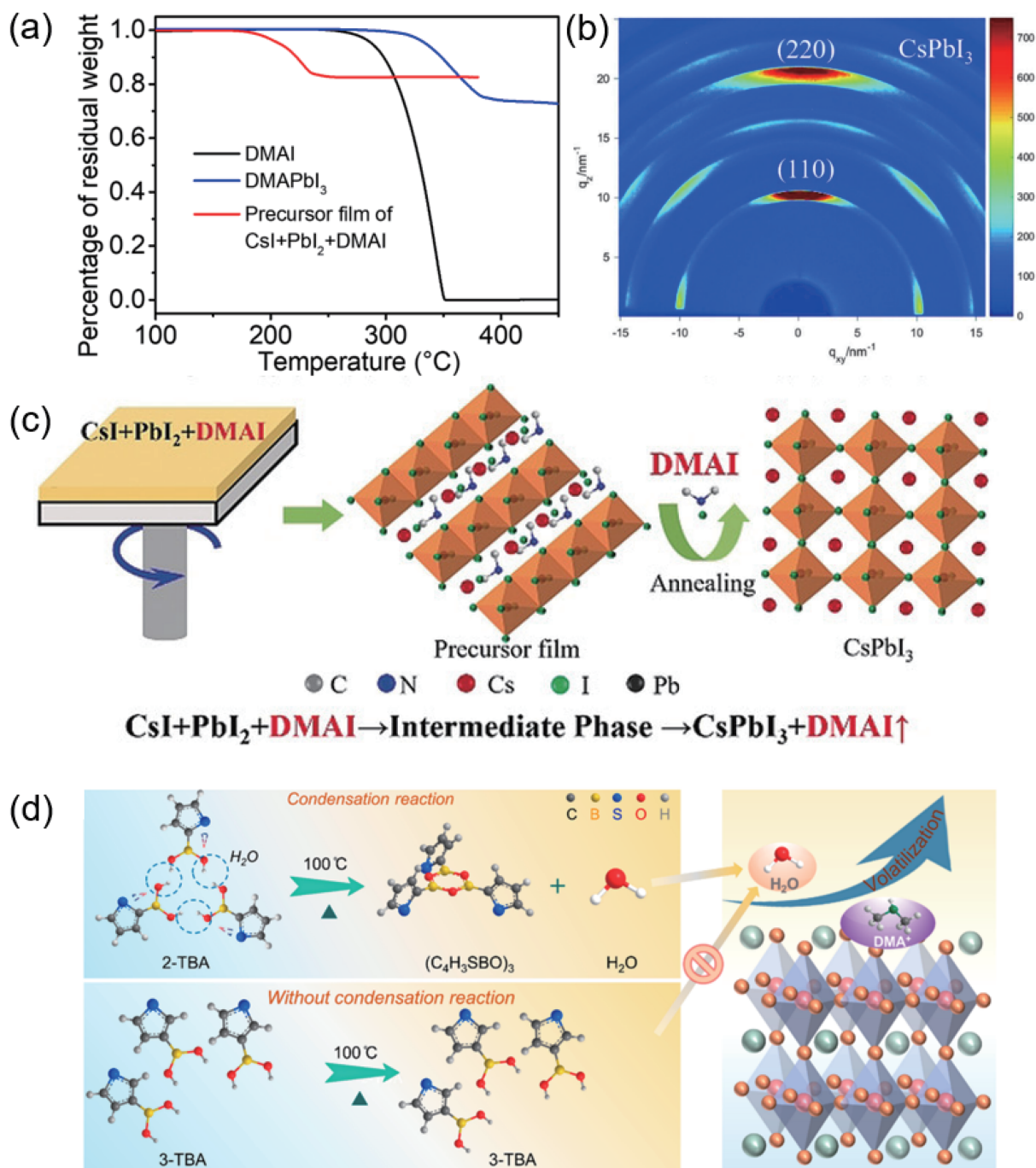


Fig. 2. (Color online) (a) TGA curves for DMAI, DMAPbI₃ powders and the powder scratched from the precursor film of CsI+PbI₂+DMAI. (b) GI-WAXS for β -CsPbI₃ films. Reproduced with permission^[32], Copyright 2019, AAAS. (c) Schematic for black-phase CsPbI₃ formation by using DMAI additive. Reproduced with permission^[33], Copyright 2019, Wiley. (d) Schematic for 2-TBA condensation reaction (top) and 3-TBA without condensation reaction (bottom); schematic for DMA⁺ removal by H₂O from the condensation reaction. Reproduced with permission^[36], Copyright 2022, American Chemical Society.

The enhanced phase stability and photovoltaic performance in HI or DMA⁺ modified ILHP solar cells is mainly attributed to lattice regulation, e.g., change of lattice parameters, relaxation of lattice strain, oscillatory variation of lattice structure, etc.

Introducing DMA⁺ into ILHPs contradicts the original intention of making all-inorganic PSCs. The excess DMA⁺ prefers to exist at the top surface of the final perovskite film in an inhomogeneous spatial distribution^[30]. The local heterogeneity in composition at the film surface can cause heterogeneous film morphology and increase structural defects

throughout the film^[31], thus deteriorating device performance. How to remove the organic component to obtain phase-pure all-inorganic perovskite is a challenge. Some researches showed that increasing annealing temperature and changing annealing environment could help to remove DMA⁺ components. Zhao *et al.*^[32] indicated that annealing at 210 °C for 5 min was enough to eliminate DMA⁺ component to obtain β -CsPbI₃ with good orientation (Fig. 2(a), Fig. 2(b)). They also found that DMAI residues in the films could deteriorate device performance. Combining DMAI with phenyltrimethylammonium chloride (PTACl), they achieved a PCE of

19.03% (Fig. 2(c))^[33]. Decreasing annealing temperature to 180 °C while simultaneously extending annealing time could also remove DMA⁺, but the device performance was damaged due to the created defects in films^[34, 35]. Recently, Liu *et al.*^[36] developed a low-temperature strategy to remove the residual DMA⁺ via 2-thiopheneboric acid oligomerization at the surface. 2-Thiopheneboric acid joins in the condensation reaction, releasing H₂O molecules, which purge DMA⁺ from CsPbI₃ film surface at ~100 °C (Fig. 2(d)). Meanwhile, the remaining boro-thiophene trimer moiety acts as a Lewis base anchoring group to passivate Pb⁰ defects.

In short, DMA⁺ additive helps ILHP solar cells to realize >21% PCEs^[20, 21, 37, 38]. Several groups also tried other additives (e.g., zwitterion, ionic liquids, and zinc-based Lewis acid) to interact with perovskite crystals to inhibit intrinsic phase transition. We should try different approaches to develop phase-stable all-inorganic perovskites.

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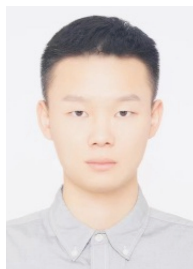
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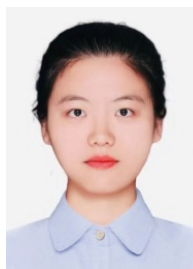
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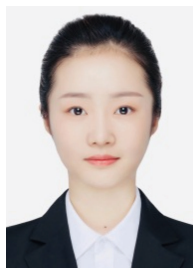
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