

Review

Recent Advances on the Strategies to Stabilize the α -Phase of Formamidinium Based Perovskite Materials

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Abstract: Perovskite solar cells (PSC) are considered promising next generation photovoltaic devices due to their low cost and high-power conversion efficiency (PCE). The perovskite material in the photovoltaic devices plays the fundamental role for the unique performances of PSC. Formamidinium based perovskite materials have become a hot-topic for research due to their excellent characteristics, such as a lower band gap (1.48 V), broader light absorption, and better thermal stability compared to methylammonium based perovskite materials. There are four phases of perovskite materials, named the cubic α -phase, tetragonal β -phase, orthorhombic γ -phase, and δ -phase (yellow). Many research focus on the transition of α -phase and δ -phase. α -Phase FA-based perovskite is very useful for photovoltaic application. However, the phase stability of α -phase FA-based perovskite materials is quite poor. It transforms into its useless δ -phase at room temperature. This instability will lead the degradation of PCE and the other optoelectronic properties. For the practical application of PSC, it is urgent to understand more about the mechanism of this transformation and boost the stability of α -Phase FA-based perovskite materials. This review describes the strategies developed in the past several years, such as mixed cations, anion exchange, dimensions controlling, and surface engineering. These discussions present a perspective on the stability of α -phase of FA-based perovskite materials and the coming challenges in this field.

Keywords: α -Phase FA-based perovskite; stability; mixed cations; anion exchange; dimensions controlling; surface engineering



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1. Introduction

Nowadays, due to the shortage of the non-renewable energy sources and many environmental issues from the consumption of fossil fuel, renewable energy sources will play a more and more important role in society. As one important renewable and clean energy source, solar energy has been a hot spot for research concerning various new energy sources [1]. Especially, the solar cells based on halide perovskite materials have attracted much attention due to their unique characteristics such as their proper bandgap (E_g), low cost, long carrier diffusion length, and high power conversion efficiency (PCE) [2,3]. They are considered as the promising candidate materials for the next generation photovoltaic devices. It was first reported by Miyasaka and coworkers and 3.8% PCE was achieved [4]. Up to date, PCE of photovoltaic devices based on halide perovskite have been reached a best efficiency of 25.8% in 2021 [5,6]. However, the poor stability of the halide perovskite is still a bottleneck for application in solar cells. In fact, the stability of the perovskite materials mainly depends upon the structures and compositions of perovskite

materials. For example, MAPbX₃ (X = I, Cl, Br) are typical hybrid perovskite materials and have been thoroughly studied in solar cells. However, its E_g is 1.55 eV, beyond the range of the optimal bandgap for solar cell (1.1–1.4 eV) and formamidinium based perovskite materials (FAPVs), which have a smaller bandgap, were reported by Eperon and coworkers [7]. FAPVs have more advantages and fascinating properties over methylammonium based perovskite materials (MAPVs), such as broader adsorption range, smaller bandgap (1.48 eV), higher efficiency, longer hole-diffusion length (~813 nm), better thermal, and light stability [8–15]. FAPVs have a typical perovskite chemical formula ABX₃ (A = organic cation, B = metal cation, X = halide anion). The Goldschmidt tolerance factor (t) was defined to predict the phase stability of perovskite materials. The Goldschmidt tolerance factor is calculated by the following equation:

$$t = (R_A + R_X) / \sqrt{2}(R_B + R_X) \quad (1)$$

In this equation, R_A , R_B , R_X are the ionic radii of A, B, and X, respectively [16]. When t ranged between 0.8 and 1.0, the stable cubic structure of perovskite materials can be obtained. When only FA⁺ is used as the cation, it suffers from a thermal instability that its trigonal structures (α -phase, black color) transform into unwanted hexagonal structure (δ -phase, yellow color) gradually at room temperature since it is bigger than 1 [16,17]. Hence, improving the stability of α -phase FAPVs is very important to boost the commercialization of FAPVs.

Many methods, such as mixed cations (anions) [18], additive engineering [19], surface engineering [20,21], and epitaxial growth [22,23] have been used to improve the stability of FAPVs. The stability of α -phase FAPVs is affected by environment (temperature, humidity) or its intrinsic structures. Environmental stability is an open challenge. Lee et al. reported the stability of FA_{0.9}Cs_{0.1}PbI₃ perovskite against the light and humidity was improved due to partial substitution of Cs⁺ for FA⁺. PCE was improved from 14.9% to 16.5% due to the suppressed charge recombination [24]. In addition, many researchers reported α -phase FAPVs was stable at room temperature in humid or desiccated air ranges from a few hours to a few days [25–31]. Moreover, the stability over months also has been reported by using surface engineering [32]. But a thorough understanding of the phase transition of FAPVs is also lack and the stabilization mechanism is not clear.

Herein, we review different strategies, such as mixed cations or anions, dimensional controlling, surface engineering and additives to improve the stability of FAPVs. Meanwhile, the structures and properties are also reviewed. We discuss crystal structures with respect to investigate the phase transition mechanism and stabilization mechanism in a molecular-level structure. Particularly, we reviewed the hydrogen bonding for stabilizing the α -phase. Finally, we will discuss the challenges and future outlook for the stability of α -FAPVs.

2. The Strategies Applied to Stabilize the α -FAPVs

2.1. Mixed Cations Hybrid Perovskites

As mentioned, mixed cations are used to improve the stability of α FAPVs. Since the large size of FA⁺, partially replacement of FA⁺ with organic (such as MA⁺) or inorganic cations (Cs⁺, Rb⁺) can adjust the value of t , and occupy the A-site in APbI₃ devices for enhancing the stability of α -phase FAPVs [33].

We mainly discuss APbX₃ perovskites materials. A is mixed cations (Cs⁺, Rb⁺, MA⁺ or FA⁺). Pb is lead. X is iodine, bromine or mixed anions. The ratio of mixed cations can affect the phase stability of perovskites materials. For example, FA_xMA_{1-x}PbI₃ film was synthesized at room temperature. In FA_xMA_{1-x}PbI₃ materials, the stable α -phase can be formed with the ratio $x \geq 0.2$ and FA⁺ was partially replaced by MA⁺. The lattice parameters and optical bandgap of FA_xMA_{1-x}PbI₃ ($1 \geq x \geq 0.2$) at 298 K varied in accordance with Vegard's law [34]. Kim et al. studied the effect of Cs/FA ratio in Cs_xFA_{1-x}Pb (I_{0.94}Br_{0.06})₃ perovskites. When the molar ratio of Cs/FA was 17:83, the stability is excellent and PCE can be achieved to 16.5% [35]. Li et al. reported FA_{1-x}Cs_xPbI₃ alloy has lower δ -to- α -phase tran-

sition temperature than pure FAPbI₃ and CsPbI₃ [36]. FA_{1-x}Cs_xPbI₃ showed the stability phase under high humidity conditions. FA_{1-x}Cs_xPbI₃ solar cells have the best PCE of 16.1%. Kawachi et al. reported that α -phase and heat capacity of high-quality single crystals of Cs_xFA_(1-x)PbI₃ [37]. The multiple first-order transitions disappeared and phase transitions emerged at 300 and 149 K after doping with 10% Cs⁺ [37]. In addition, Rb⁺ have the similar properties with Cs⁺. Rb⁺ is hard to form a stable RbPbI₃ perovskite due to too small of a size, but it can stabilize phase of FAPbI₃ by reducing enthalpy [38]. Rb_{0.05}FA_{0.95}PbI₃ own superior stability under high humidity condition (85%) and the complete phase conversion of α FAPbI₃ by incorporating 5% Rb to FAPbI₃. The PCE of Rb_{0.05}FA_{0.95}PbI₃ based solar cell was 17.16% [39].

In addition to the above single ion substitution, double mixed-cations incorporated into FAPbI₃ is also an effective method to improve the phase stability. In 2016, the PCE and outputs of Cs_x(MA_{0.17}FA_{0.83})_(100-x)Pb(I_{0.83}Br_{0.17})₃ were first investigated by Saliba and coworkers [40]. The PCE of high efficiency perovskite solar cells reached 21.1% and the output could be achieved at 18% under operational conditions after 250 h when different ratios of Cs/MA/FA cation were used. The XRD spectra illustrated that the yellow δ phase and PbI₂ peak would disappear completely with different amounts of Cs⁺ (5, 10, 15%) (Figure 1a,b). The absorption and photoluminescence spectra proved that blue-shift occurred with the substitution of Cs⁺ from 0 to 15%. The processing conditions of thermal stability and film formation have been investigated (Figure 1c,f). The tolerance factor was tuned to a cubic lattice structure which matches the α -phase [40]. Gallardo et al. reported that two and three cation-doped hybrid perovskite nanopowders have different characterization [41]. The optical E_g values of the MAPbI₃ and FAPbI₃ were 1.53 eV and 1.45 eV, respectively. The E_g values would decrease when MA⁺ was introduced into FAPVs. In FA_xCs_yMA_(1-x-y)PbI₃-type perovskites, the perovskite structure would be more stable with addition 10% Cs⁺ to substitute the FA⁺ and E_g was 1.47 eV. X-ray diffraction showed that the phases of MAPbI₃ or FAPbI₃ changed after 4.5 months, the phases of FA_xMA_(1-x)PbI₃-type perovskites were stable over time, cubic phases of FA_xCs_yMA_(1-x-y)PbI₃-type perovskites were also stable over time with 10% Cs⁺ [41]. Derbali et al. studied the structure, morphological and properties of K⁺ based mixed-halide perovskite materials [42]. The ionic radius of K⁺ is 133 pm. K_xFA_{0.80-x}MA_{0.20}PbI_{2.8}Cl_{0.2} (FAMA-K10%) perovskite films was fabricated by incorporation K⁺ into FAMA. The tolerance factor of FAMA and FAMA-K10% were 1.02 and 0.99, respectively. XRD indicated K⁺ can enhance the intensities of the photoactive α -phase and suppress the δ -phase. K⁺-doped demonstrated better crystallinity and reduced the bandgap [42]. Zhang's group studied the effect of cation substitution with MA⁺, Cs⁺, Rb⁺ by First-principles calculations [43]. The basic building unit of α -phase and δ -phase of FAPbI₃ was the PbI₆ octahedrons. The cubic α -phase has been formed when PbI₆ connected to each other in the form of a corner to corner. When three cations were doped, the transition temperature of FAPbI₃ was affected. This effect can be studied by an approximate relation (see the formula 2). This indicated that α -phase was stabilized at low temperature and three cations doped have the lowest transition temperatures at the high concentration of 25%. In addition, the band structure was also studied (Figure 2a,g). The E_g were 1.57 eV, 1.61 eV and 1.69 eV in Cs⁺, Rb⁺ and MA⁺ doped system. These cations can stabilize the black phase of FAPbI₃, but this was only short-term stability. So the mixing energies of these multication systems were also calculated (see Equation (3)). Moreover, Park et al. also investigated the effect of the A-site cation on the phase stability of the perovskite structure by using machine-learning models. They proposed triple cation phase diagrams can emphasize the concept of effective cation radius based on the mixture of cations [44].

$$T_C = T_{C,0} \frac{\Delta H}{\Delta H_0} \quad (2)$$

$$E_{\text{mix}} = E(\text{M}_x\text{FA}_{1-x}\text{PbI}_3 - xE(\text{MPbI}_3) - (1-x)E(\text{FAPbI}_3)) \quad (3)$$

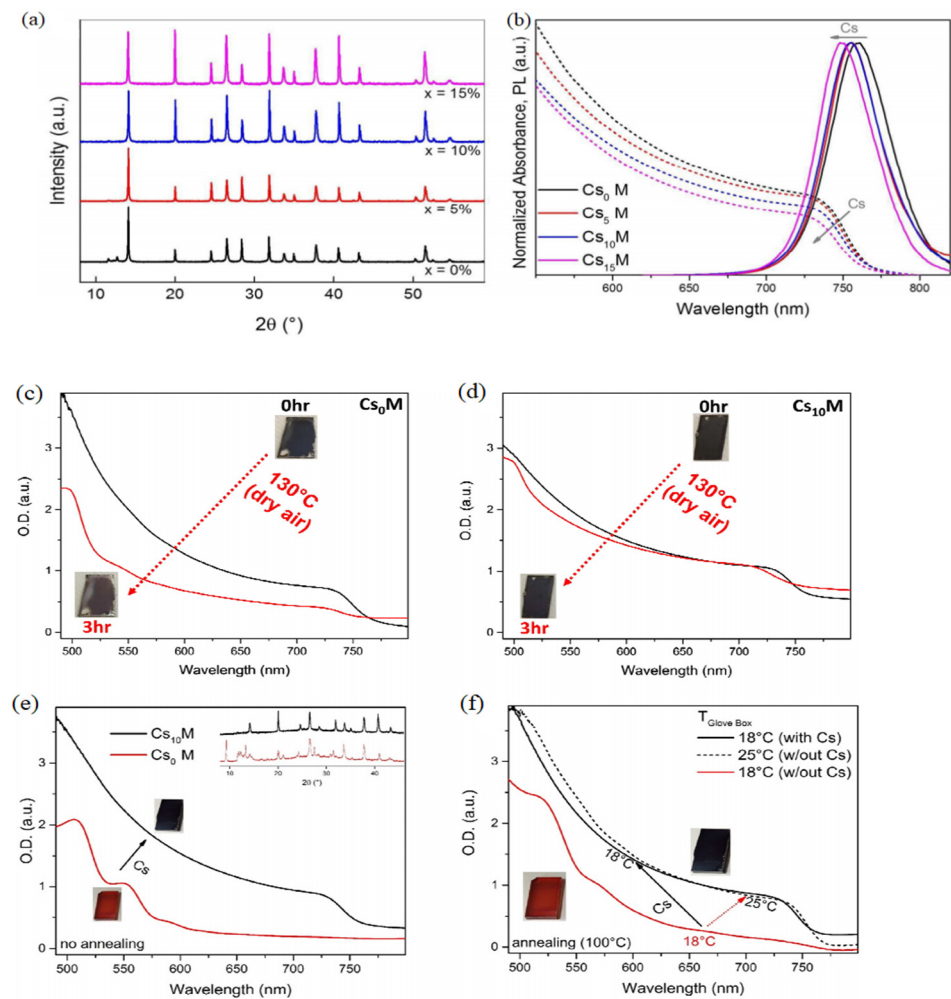


Figure 1. Different spectrum of perovskite with different amounts of Cs (a) XRD, (b) Absorbance and PL spectra; UV-vis absorption of (c) Cs_0M and (d) Cs_{10}M films which were annealed at 130 °C for 3 h in dry air; (e) absorption spectra of as-fabricated materials which were not annealed at room temperature. The perovskite characters of Cs_{10}M can be shown in the inset XRD data; (f) absorption spectra showed perovskite phase of Cs_0M formed at 25 °C (dashed black line) and perovskite phase of Cs_{10}M formed at 18 °C (solid black line) by using the spin coating. Reprinted with permission from Ref. [40]. Copyright 2016 Royal Society of Chemistry.

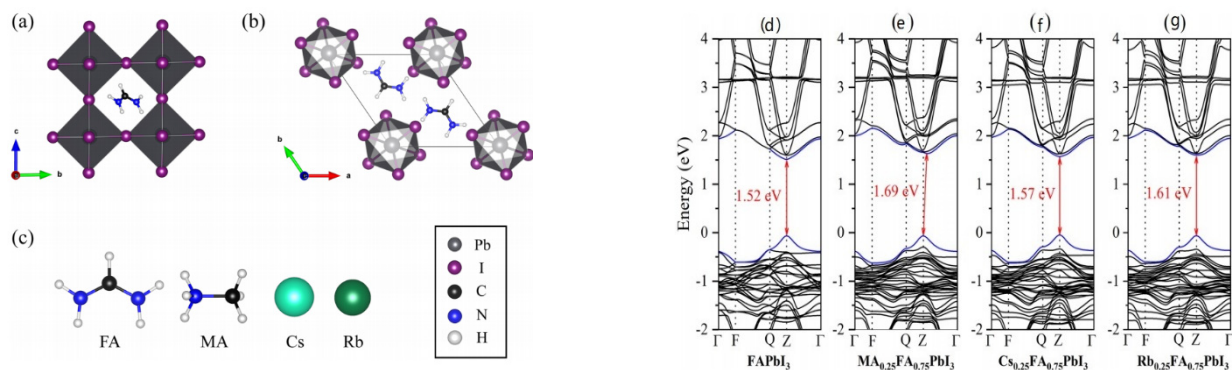
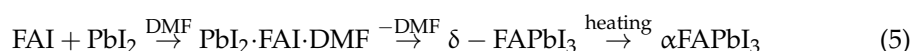
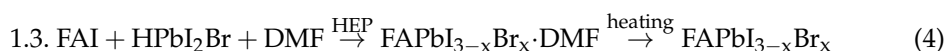


Figure 2. Structures of α -phase (a,b) δ -phase of pure FAPbI_3 ; (c) The structures of four cations (FA^+ , MA^+ , Cs^+ , and Rb^+); Band structure of α - FAPbI_3 (d), α - $\text{MA}_{0.25}\text{FA}_{0.75}\text{PbI}_3$ (e), α - $\text{Cs}_{0.25}\text{FA}_{0.75}\text{PbI}_3$ (f) and α - $\text{Rb}_{0.25}\text{FA}_{0.75}\text{PbI}_3$ (g). Reprinted with permission from Ref. [43]. Copyright 2019 AIP Publishing.

2.2. Anion-Exchanged

Anion exchange, such as substitution I^- with Br^- , is another positive method on tuning the bandgap and improving the stability of FAPVs. The interaction between Br^- and surrounding ions is stronger than that of I^- [45].

In 2018, Li et al. used Cs^+ and Br^- to improve stability of α -FAPbI₃ [46]. Deep research found that Cs^+ doping was not enough to stabilize black-phase and Br^- anion can stabilize the α -phase of FAPbI₃. Finally, Cs^+ and Br^- co-doped FAPbI₃ have some advantages, such as higher performance optoelectronics, good stability and a long carrier lifetime of 1.23 μ s (Figure 3a,c) [46]. Jeon et al. researched the stability of $(FAPbI_3)_{1-x}(MAPbBr_3)_x$ when the value of x ranged between 0 and 0.3 [47]. MAPbBr₃ can stabilize the α -FAPbI₃ and improve PCE. According to XRD spectra, the pure FAPbI₃ has a hexagonal non-perovskite ($P6_3mc$) after annealing at 100 °C. And then a strong (111) diffraction peak at 13.9° 2 θ of the trigonal perovskite phase ($P3m1$) appeared when MA⁺ cation and Br^- ions (15 mol%) were added to FAPbI₃ (Figure 3d). A complete bilayer on a mesoporous TiO₂ was successfully fabricated by using solvent-engineering technology. $(FAPbI_3)_{1-x}(MAPbBr_3)_x$ has many advantages compared to the pure FAPbI₃ (Figure 3e). The PCE of $(FAPbI_3)_{1-x}(MAPbBr_3)_x$ can be achieved to 18.4% (Figure 3f) [47]. Long and co-workers developed a halide-exchange process (HEP) reaction (Figure 3g,h) [48]. XRD exhibited the structure stability of HPbI₂ (Figure 3i). The large-grained and compact FAPbI_{3-x}Br_x thin films can be deposition without using antisolvent. The stability of FAPbI_{3-x}Br_x can be enhanced by reduced bromide. Br-doping can inhibit the α -phase conversion into δ -phase and stabilize the final α -phase. The reaction was described as:



Finally, the efficiency of PSC device was 19.0% without appreciable hysteresis. Rehman et al. analyzed the charge-carrier dynamics and mobilities across the range of compositions of FAPb(Br_yI_{1-y})₃. The valence band varied from 4p to 5p and the bandgap energy decreased by exchanging I^- with Br^- . The PL emission of FAPb(Br_{0.67}I_{0.33})₃ can record the laser excitation with an intensity of 7.2 W cm⁻² following 5 min [49]. The PL have shift to a new low-energy PL feature at around 785 nm (1.58 eV). XRD spectra showed the crystalline phases were formed with different contents of y . It was found that the bandgap can be tunable between 1.48 and 2.23 eV [50]. MA_{1-x}FA_xPbI_{3-y}Cl_y was firstly prepared through annealing at temperature of 80–110 °C. When Cl was doped, the average J_{sc} and V_{oc} have increased to 19.04 mA/cm² and 1.120 V, respectively. And then the PCE achieved to 15.95% [51].

In addition, the stabilization mechanism of FAPVs was also studied by Nan and co-workers [52]. The deep research found that 8H-FAPbX₃ intermediate phase. Its structure and phase transition are shown in Figure 4. The locations and effects on phase stability of cations and anions were investigated. Smaller halides increased the thermodynamic stability due to their being located at the corner-sharing sites. The smaller cations stabilized the 3C phase due to occupying cubic cages (especially smaller Cs⁺). We can understand the intrinsic stabilization mechanism of FAPVs at molecular-level [52].

In a word, anion-exchange is an essential method to stabilize α -FAPbI₃, and it can further improve phase stability since X sites and A/B-sites have strong interaction [16].

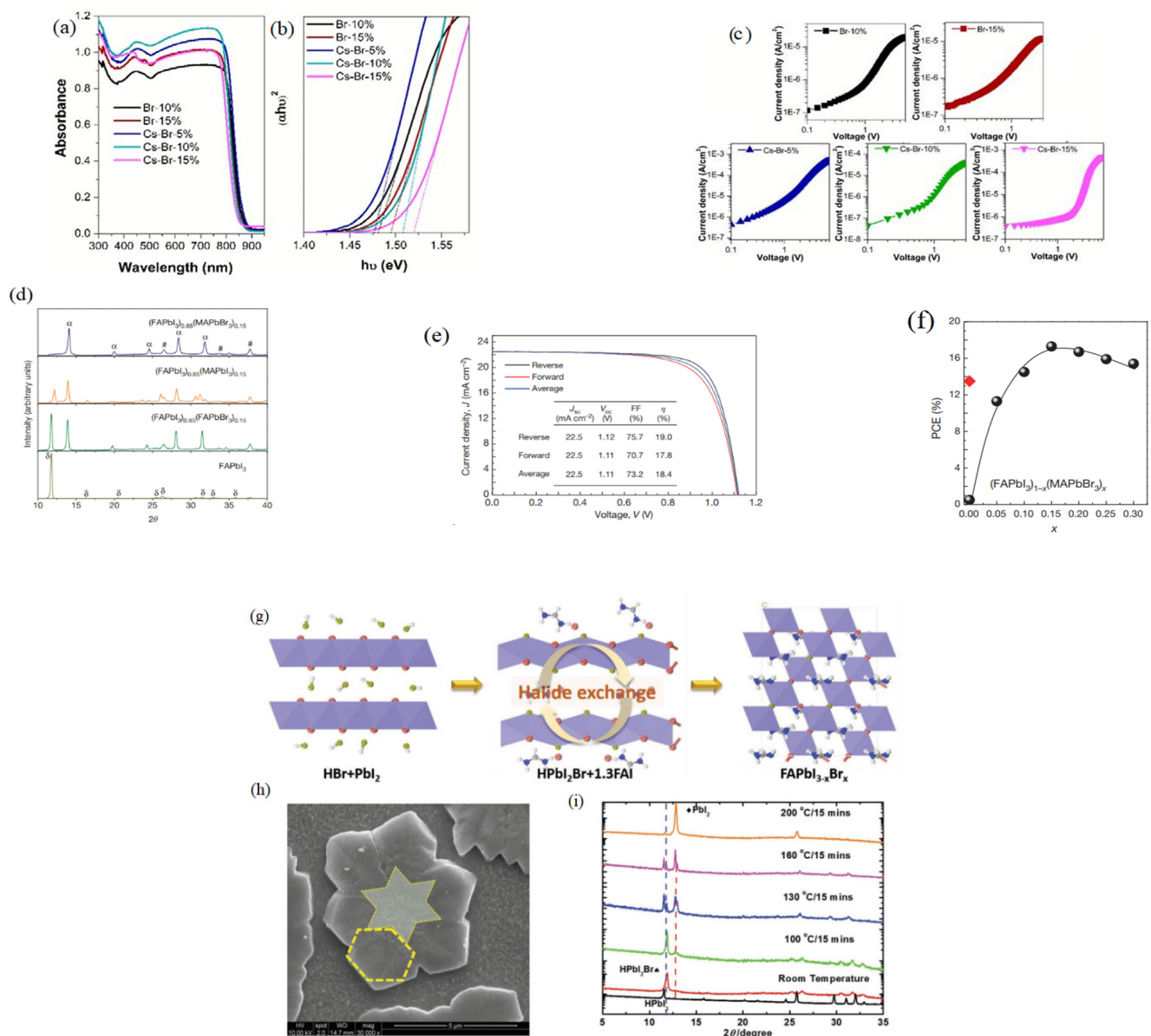


Figure 3. (a) Absorbance spectra of stable FA-based halide perovskite and Tauc plot (b); (c) The I-V curves of doped formamidinium-lead-halide-based hole-only devices with the different structures (Reprinted with permission from Ref. [46]. Copyright 2018 Royal Society of Chemistry). (d) XRD spectra of four FA-based perovskites annealed at 100 °C for 10 min; (e) The red line and the black line indicated PCE values of pure FAPbI_3 and $(\text{FAPbI}_3)_{1-x}(\text{MAPbBr}_3)_x$ annealed at different temperature (100 °C, 150 °C), respectively. And then the α -phase was formed; (f) J-V curves of $(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$ perovskite material. (Reprinted with permission from Ref. [47]. Copyright 2015 Nature). (g) Schematic diagram of intermediate synthesis of HPbI_2Br and its halide exchange processing; (h) SEM of HPbI_2Br ; (i) XRD spectra of HPbI_2Br material at different temperature. Reprinted with permission from Ref. [48]. Copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

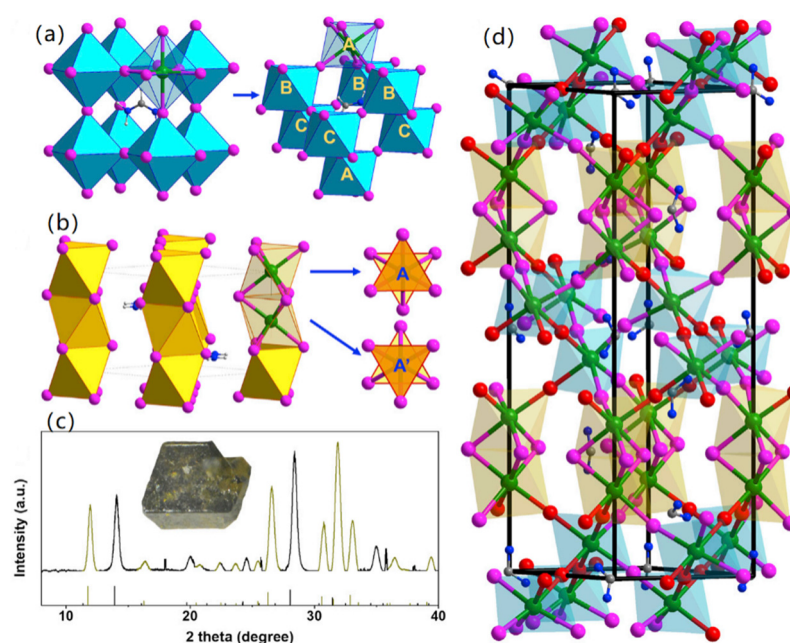


Figure 4. (a) Structures of α -phase FAPbI₃ along different axis ([100] and [111]); (b) Structures of δ -phase of FAPbI₃ along the [0001] axis and A and A' were the two types of [PbI₆] octahedrons. (c) XRD of a 3C-FAPbI₃ single crystal with a phase transition; (d) Structure of 8H-FAPbX₃. Br (Red); I (purple); Pb (green); N (blue); C (gray); H (white). Reprinted with permission from Ref. [52]. Copyright 2021 Elsevier.

2.3. Control the Dimensions of Perovskites

3D perovskite materials have intrinsic instability. In order to improve the stability of FAPVs, some strategies, such as reducing dimension, forming multidimensions (mixing 3D perovskites with low-dimensional or formation of Ruddlesden-Popper type perovskite), can be used [53]. A systematic evolution of the dimensionality of the perovskite structure can be formed. The bandgap and binding energy were increasing when the dimensionality was decreasing. In other words, the dimensionality can affect the E_g of the perovskite materials. For example, the E_g values of multidimensions were affected by the 2D confinement effect [53].

Low-dimensional perovskites have higher stability, excellent optoelectronic properties and better moisture resistance than three-dimensional perovskites [54,55]. Reducing the dimensionality can tune the optoelectronic properties at morphological and molecular levels [56,57]. Meanwhile, lowering the dimensions also have some disadvantages. Since low-dimensional perovskites have some drawbacks, such as strong exciton-phonon interaction, intrinsic quantum-confinement, lower device performance [58]. The crystal structural dimensionalities of 2D, 1D and 0D are shown in Figure 5a,b [59]. Zero-dimensional perovskites are usually composed of isolated inorganic octahedral clusters and small cations and they are connected by H bonding. Photovoltaic performance of zero-dimensional perovskites always were limited due to their strong intrinsic quantum-confinement. 1D perovskites can be called perovskite nanowires and are $\langle 110 \rangle$ oriented perovskites. 1D perovskite ($A'_2A_mB_mX_{3m+2}$) can be formed when the value of m is 1. And it has BX_6 octahedral unites which can interconnected with strong interaction by corner-sharing to form the 3D framework [59]. Huang et al. reported a new 1D inorganic-organic hybrid perovskite has high stability and humidity response [60]. The structure was composed of 1D inorganic perovskite-like chain, $[(Me_3)DAB(Me_3)]^{2+}$ dications and water molecules. In compared to 3D perovskite materials, 2D halide perovskite materials are environmentally stable. The 2D perovskites include $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ orientated families. For example, the formula of $(RNH_3)_2BX_4$ or $(NH_3RNH_3)BX_4$ is typical $\langle 100 \rangle$ orientate 2D perovskites. $(C_{16}H_{13}N_3)PbBr_4$ is a typical $\langle 110 \rangle$ orientated 2D perovskites. This perovskite has layered structure due to the functional

cation [59–61]. There are many synthesis methods, such as solution-phase growth, chemical vapor deposition. Lee et al. synthesized the phase-pure FAPbI_3 films. 2D phenylethylammonium lead iodide was added to the precursor solution and then FAPbI_3 was fabricated. The PCE was achieved to 20.64% [62]. 2D perovskite materials have good optical and electronic properties due to direct band-gaps. This also affect device performances and stability [63]. The stable 2D- $\text{IBA}_2\text{FAPb}_2\text{I}_7$ has been formed [64]. The further research exhibited that the level of PbI_2 and $\delta\text{-FAPbI}_3$ near the surface have been reduced due to IBAI treatment and electronic trap states caused by impurities at or near the surface of the perovskite can be passivated [64]. In addition, there are quasi 2D perovskites which is a hybrid dimensionality between 3D and 2D. This family have the Ruddlesden-Ropper crystal structure [65]. Perumallapelli et al. investigated the morphology, structure, optical properties of OA-based 2D and quasi-2D perovskites. Compared to the 3D counterpart, the low binding energy of Pb indicated the more electron-rich environment around the Pb centers [66]. In 2016, the reduce-dimensionality (quasi-2D) has been reported [67]. These materials have good stability. The origins of instability of RABX were explained by computational methods and the stability of dimensionally-tuned perovskites were investigated by DFT [67]. The DFT simulation of energetics was shown in Figure 5c. Dimensionality of perovskite have been tuned by changing the value of n in the series $\text{PEA}_2(\text{CH}_3\text{NH}_3)_{n-1}\text{Pb}_n\text{I}_{3n+1}$. The structure is 2D ($n = 1$), quasi-2D ($n > 1$) and 3D ($n = \infty$).

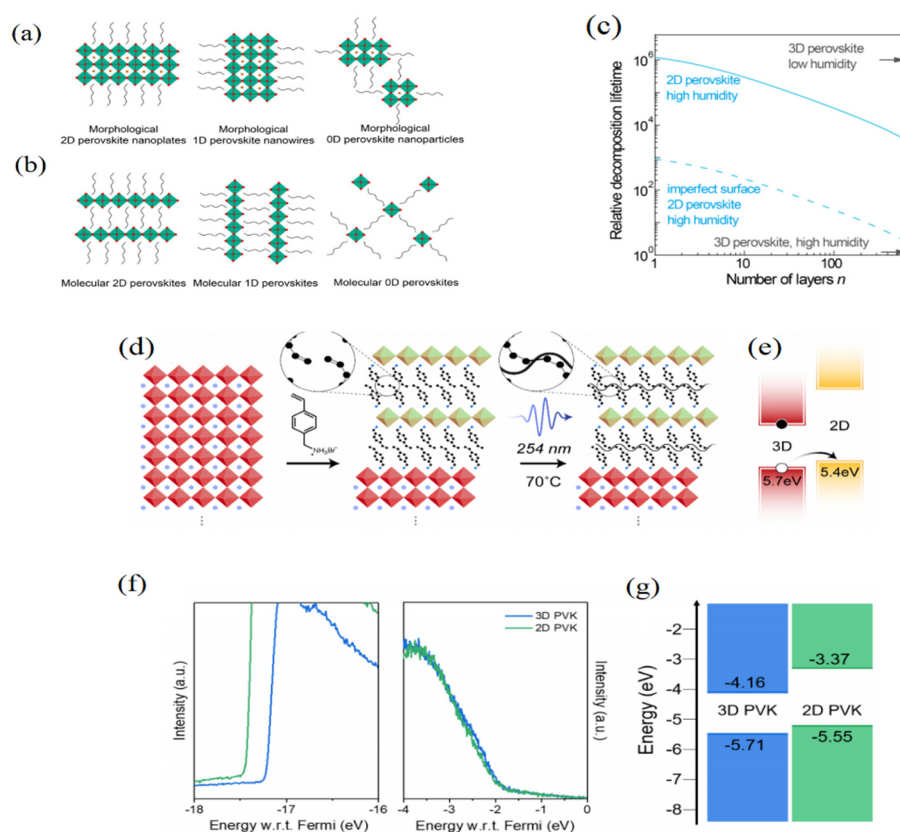


Figure 5. (a) The different morphological perovskites, and (b) different molecular perovskites. (Reprinted with permission from Ref. [59]. Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim). (c) DFT simulation of the formation energy of 3D and 2D perovskite with different n values. (Reprinted with permission from Ref. [67]. Copyright 2016 Royal Society of Chemistry). 2D/3D heterostructures have formation and optical properties by using the ligand VBABr. (d) Schematic diagram of processing which cross-linked 2D perovskites were formed by using the VBABr; (e) Energy level of the 2D/3D interface. (Reprinted with permission from Ref. [68]. Copyright 2019 ACS Publication). (f) UP spectra of the 3D perovskite and the 2D perovskite. (g) Energy levels of the 3D and 2D perovskites. Reprinted with permission from Ref. [69]. Copyright 2021 Science.

Multi-dimensional have been developed since it has outstanding photophysical properties, such as higher PCE [70,71], longer diffusion lengths [71,72], low exciton binding energies [73,74], low-temperature solution processability [75]. 2D perovskites sometimes do not have the ideal photovoltaic performances due to their larger bandgap, weaker carrier transport [76,77]. 2D/3D perovskites have attracted much attention due to their long-term stability and high photo conversion efficiency. The 2D/3D multidimensional perovskite can be defined as $M_2A_{n-1}B_nX_{3n+1}$, where M is a large cation; A is FA, MA or Cs; B is Pb or Sn; X is I, Br, Cl; and n is the number of metal halide sheets. The structures of 2D or 3D are determined by the value of n. The 3D perovskite have been formed when n is ∞ ; the 2D perovskite can be occurred when n is 1. However, it is different to obtain phase-pure crystals of higher n-value perovskites. Quasi-2D (i.e., $n = 30, 40, 50, 60$) and quasi-3D ($n \leq 3$) are usually represented as 3D/2D perovskites [77,78]. Meanwhile, the optical E_g of $M_2A_{n-1}B_nX_{3n+1}$ increased when the value of n decreased. In 2014, Smith et al. reported the Mesoscopic PSCs with a PCE of 4.73% using quasi-2D perovskites ($PEA_2MA_2Pb_3I_{10}$; $n = 3$). It has large open-circuit voltage (V_{OC}) of 1.18V due to the increased bandgap of 2.06 eV [79]. Grancini et al., in 2017, showed one-year stable perovskite devices were formed by using an ultra-stable 2D/3D perovskite junction [80].

In addition to mixture 2D/3D perovskites, the other 2D/3D perovskite type has the bilayer structure. The bilayer structure of 2D/3D perovskite was first formed in 3D MAPbI₃. Proppe's group selected the ligand 4-vinylbenzylammonium (VBA), which has similar structure to phenethylammonium, to build the 2D/3D bilayer structure of $(VBA)_2PbI_4/(MAPbBr_3)_{0.15}(FAPbI_3)_{0.85}$ (Figure 5d,e) [68]. The 2D perovskites were formed only at the top surface of the 3D layer. 2D/3D film exhibited faster decay and lower trap state densities. PCE was 20.4% and its initial efficiency (90%) was also retained after 2300 h. Recently, Cai et al. reported that the 2D/3D structure of $(CF_3-PEA)_2FA_{0.85}MA_{0.15}Pb_{2I7}/FA_{0.85}MA_{0.15}PbI_3$ have better chemical and thermal stability. PCE achieved 23.1% [81]. The structure, optoelectronic properties, and stability of 3D perovskite can be affected by 2D perovskite. The surface of the 3D perovskite can be passivated and the grain size can be increased by adding 2D perovskite. Besides, it also provided a hydrophobic umbrella to reduce the water-induced degradation, which result the stability of 3D perovskite was enhanced and did not compromise the optoelectronic properties [81]. In 2021, improving the stability of 3D perovskite materials were reported by Zhang and co-workers. Its surface was treated by using 2D layered perovskites [69]. The energetics for hole transport can be changed due to surface treatment (shown in Figure 5f,g). This energetics can increase out-of-plane transport rates and improve stability of PSCs. The PCE achieved 24.7% and 90% of PCE was still retained after 1000 h under 1-sun operation conditions [69].

Many methods have been used to prepare mixture 2D/3D perovskites. The $CsPbI_3 \cdot xEDAPbI_4$ was synthesized by a one-step method [82]. A- $CsPbI_3$ perovskite films were stabilized by introducing the 2D perovskite of $EDAPbI_4$. According to UV-vis and PL spectra, the 2D/3D perovskite of $CsPbI_3 \cdot 0.05EDAPbI_4$ were formed. Ke et al. reported the stability of single-junction solar cells could be improved by using mixed 2D/3D perovskite composite absorbers deliver and PCE was 20.09% [83]. The mixture 2D/3D perovskites were prepared by another process, the two-step method. Stable 2D/3D hydrid perovskite solar cells were demonstrated by Zhou and coworkers [84]. A 2D/3D hydrid structure was formed due to the incorporation of 2-thiophenemethylammonium (ThMA). XRD spectra showed the orientation and crystalline growth of 2D/3D perovskite have been induced by ThMA spacer cations. The PCE can be achieved to 21.49% and a stabilized PCE was 21.1% since a high open circuit voltage (V_{OC}) was 1.16V and a very notable fill factor (FF) could reach to 81% [84]. These processes mentioned above are called solution process. Of course, there are the other strategies to synthesize 2D/3D perovskite. For instance, the vapor process was been used. This process has some advantages, such as large scale and well-controlled reaction rates. In 2019, 2D/3D perovskite materials were prepared with a solid-vapor reaction method [85,86]. Similar to 2D/3D perovskites, 1D/3D multidimensional perovskites have been studied. Yu and co-workers reported that HA^+ was added to $FAPbI_3$ -based

perovskite and 1D/3D structure of FAPbI₃ were formed [87]. HA⁺ has strong hydrogen bond, which can increase the grain size and crystallinity of perovskite materials. HA⁺ has abundant H bond donor and acceptor sites. Thus, reactions between HA⁺ and [PbX₆]^{4−} occurred and 1D-HA-phase formed. Moreover, H bond interaction formed between 1D-HA-crystal and FAPbI₃ due to N-H and I-H [87]. FTIR spectra made clearly that the stretching vibration of N-H in FAHA (~3397 cm^{−1}) was red-shifted. The deeper research revealed that the HA based 1D-phase has the “rivet”-like structure which passivated the grain boundary of 3D perovskite and can improve the stability of FAPbI₃-based perovskites [87]. The PCE can be achieved to 21.20% when HA⁺ was added.

2.4. Surface Engineering and Growth Control

Surface Engineering has been playing an important role in improving the efficient and stable FAPVs. The situation of the materials surfaces influences the surface defect density, the charge transport and injection between the functional layers. Surface confinement is one of surface engineering. It includes two aspects: controlling the growth of the perovskite crystal, confining the charge carriers [88,89]. The pure cubic-FAPbI₃ was synthesized at room temperature by using surface functionalization [90]. Long-chain alkyl (LA) or aromatic ammonium cations can be used to stabilize the phase since it was important in the surface functionalization. The surface functionalization can decrease the surface energy of the α-phase. The origin of the surface LA-induced phase stabilization can be understood by DFT and the formation energy was calculated by Equation 6 [89,90].

$$E = \frac{E_{(PEA \text{ or } EA)_2(FA)_{n-1}Pb_nI_{3n+1}} - nE_{PbI_2} - (n-1)E_{FAI} - 2E_{PEAI \text{ or } FAI}}{n} \quad (6)$$

where $E_{(PEA \text{ or } EA)_2(FA)_{n-1}Pb_nI_{3n+1}}$ is the total energy, E_{PbI_2} is the energy of PbI₂, $E_{PEA \text{ or } FAI}$ is the energy calculated from gas phase PFAI or FAI, respectively. $E_{(PEA \text{ or } EA)_2(FA)_{n-1}Pb_nI_{3n+1}}$, E_{PbI_2} , E_{PEAI} , E_{FAI} are the calculated energy of (PEA or EA)₂(FA)₂Pb_nI_{3n+1}, PbI₂, FAI, PEAI and EAI, respectively. The calculated formation energy (E) of δ-FAPbI₃ and α-FAPbI₃ were −4.93 eV and −4.48 eV, respectively. The δ-phase was more stable than α-phase at room temperature (RT).

However, the surface energy can be reduced by the surface PEA termination. This confirmed that replacement of surface FA with PEA cation was thermodynamically favorable regardless of the n value (shown in Figure 6a,c). The schematic of the proposed growth processes under various LA/FA ratios (α) is shown in Figure 6d,f. Under low α values, the amount of LA cations was not enough to stabilize the perovskite lattice. When α value was higher, LA cations were sufficient and occupied all surface sites. Under proper α values, the surface ligand cations were equilibrium with the free cations in the solution and LA cations were used to modify the perovskite surface in order to stabilize it. Moreover, this FAPbI₃ perovskite stabilized at RT over several months has excellent photophysical properties. So the surface chemistry on the thermodynamical of perovskite materials is very important. Recently, Lu et al. investigated the conversion from δ- to α-FAPbI₃ at 100 °C by the MASN vapor treatment method [91]. SCN[−] ions can absorb on the surface of δ-FAPbI₃ and replace iodide ions. Then the top layer of face-sharing octahedra was disintegrated and the corner-sharing architecture of α-FAPbI₃ has been changed (shown in Figure 6g,h). The PCE of this perovskite solar cell was more than 23% and this perovskite was thermally stable. PSCs remained at ~90% of initial value after 500 h.

Zhang et al. firstly reported the surface layer of 3D perovskitoid (Me-PDA) Pb₂I₆ was modified by using simple surface treatment with MePDAI₂. This resulted that surface texture was smooth, charge-carrier mobility was higher and surface-defect density was reduced [92]. (Me-PDA)Pb₂I₆ and MAPbI₃ have different crystal structures (Figure 7a). 3D corner-sharing octahedra dimers ($Pb_2I_6^{2-}$) of (Me-PDA) Pb₂I₆ can replace every octahedron with an edge-sharing octahedra dimer as the basic motif. Figure 7b,c revealed that the octahedra dimers formed along the b direction and 3D framework formed by corner-sharing along a, b, and c directions. Moreover Me-PDA²⁺ occupied the rectan-

gular A-site cavities [92]. Deng et al. used anti-solvent free spin-coating method to fabricate the higher performance FAPVs at low temperature. In that method, a small amount of MABr was dropped after spinning the perovskite precursor without using the anti-solvents [93]. The δ to α -phase transformation energy was significantly reduced due to MABr application. PCE could be up to 18.5% [94]. Majeed's group reported that $\text{Cs}_{0.05}(\text{FA}_{0.95}\text{MA}_{0.05})_{0.95}\text{Pb}(\text{I}_{0.95}\text{Br}_{0.05})_3$ perovskite was synthesized by using anti-solvent method [95]. KBr in the CB anti-solvent, which was added to this perovskite, inhibited nonradiative recombination and was beneficial to charge extraction at interfaces. As a result, the PCE was significant boosted from 15.36% to 18.29% and a long-term stability of 1080 h under 30–50% was obtained. Moreover, anti-solvents are crucial impact on the perovskite crystal growth kinetics and formation of α -FAPbI₃ phase [95]. Our group used carboxylates to stabilize the α -phase of FAPbI₃ by surface engineering method. The effect of different amount of Ac^- was studied. When Ac^- was introduced into the system, the preference of crystal growth orientation (012) and the barrier energy of two phase (α -phase and δ -phase) have been changed. The mechanism of Ac^- on stabilizing the α -phase is shown in Figure 7d,g [96].

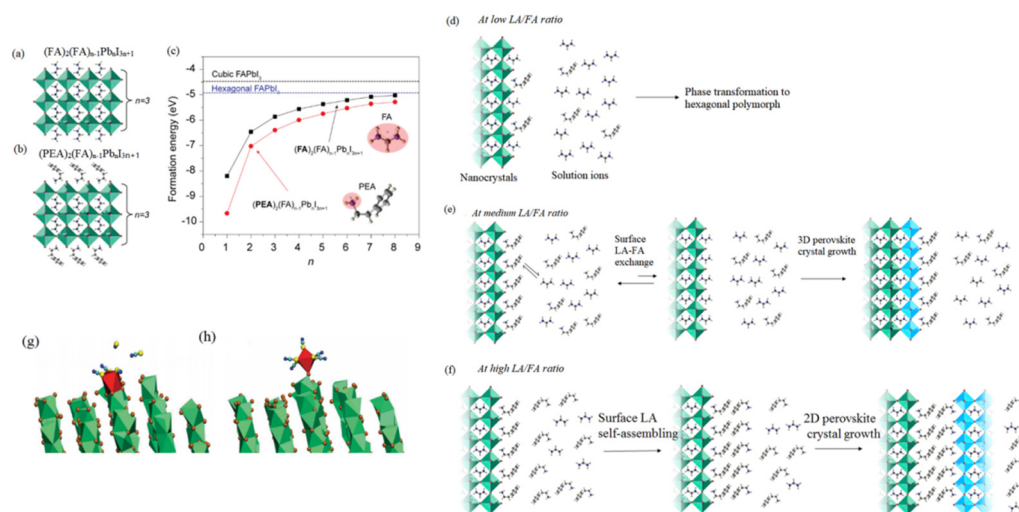


Figure 6. Structures of the (a) $(\text{FA})_2(\text{FA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ and (b) $(\text{PEA})_2(\text{FA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$; and (c) Corresponding the calculated formation energies. The growth processes with different α ratios. (d) the hexagonal phase perovskite was formed at a low α value; (e) A new 3D cubic perovskite was formed at a proper α value; (f) layered perovskites were formed by self-assembly at a high α value. (Reprinted with permission from Ref. [90]. Copyright 2017 ACS Publications). MD simulations displayed the initial face-sharing octahedra (g) conversion into the corner-sharing octahedra (h). Pb-I (green); iodideis (orange balls); octahedra (red); S (yellow); C (light blue); N (dark blue). Reprinted with permission from Ref. [91]. Copyright 2020 Science.

Another method of surface engineering is surface passivation. Surface passivation can reduce the density of surface traps and enhance the device's luminescence efficiency. Current surface passivation methods include forming a 2D perovskite layer by the reaction of ammonium halides and introducing a monolayer of small molecules without forming the 2D perovskites on the surface of 3D perovskite. In 2019, atomic-level passivation mechanism of ammonium salts was reported. Different ammonium salt, such as ethylammonium iodide, imidazolium iodide and guanidinium iodide were used to modify the surface of $\text{FA}_{0.9}\text{Cs}_{0.07}\text{MA}_{0.03}\text{Pb}(\text{I}_{0.92}\text{Br}_{0.08})_3$ perovskite. α -FAPbI₃ was formed when 10 mol% $[(\text{C}_2\text{H}_5)\text{NH}_3]\text{I}$ was doped. In this process, the formation of the mixed FA/MA structure was the main factor and this structure was similar to 1D/2D or 2D/3D perovskite materials. Meanwhile, Cs/EA, Cs/EA/FA were also formed. Finally, PCE could be controlled from 20.5% to 22.3%, 22.1%, and 21.0%, respectively [97]. Wang et al. demonstrated a nanocrystal-pinning method for defects passivation [98]. 2-bromoethyltrimethylammonium bromide

(BETAB) was used to modify $\text{FA}_{1-x}\text{MA}_x\text{PbI}_3$ films. Nanocrystal was correlation with the charge sites on perovskite surface [97,98]. The generation of metallic Pb (0) was retarded and multiple types of trap density were decreased due to the introduction of BETAB. Another ammonium salt benzyltriethylammonium chloride ([BATAm]Cl) was used as modifier and can make the surface passivation. The PCE was 20.45% and retained 84% after 30 days. The stability of the device was good [99].

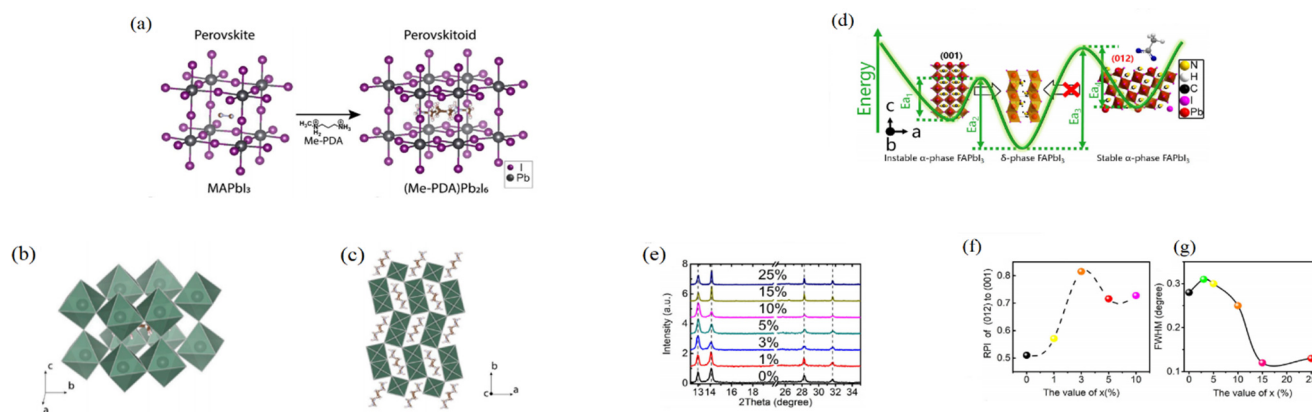
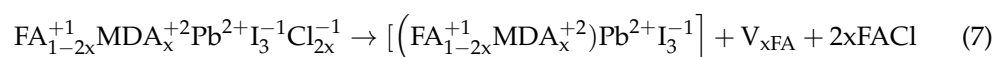


Figure 7. (a) The structures of $(\text{Me-PDA})\text{Pb}_2\text{I}_6$ and MAPbI_3 ; Side view (b) and top view (c) of crystal structure of $(\text{Me-PDA})\text{Pb}_2\text{I}_6$. (Reprinted with permission from Ref. [92]. Copyright 2021 Elsevier Inc.). The stability of the $\alpha\text{-FAPbI}_3$ was affected by adding Ac^- . (d) Schematic illustration; (e) The calibrated XRD spectra of the perovskite materials with different amount of AC^- ; (f) The evolution of RPI of XRD diffraction peak (102) to peak (001); (g) FWHM of (001) with different amount of AC^- . Reprinted with permission from Ref. [96]. Copyright 2021 Wiley-VCH GmbH.

In addition, using additive is another important way to stabilize α -phase of FA based perovskite materials. Some additives will affect the hydrogen bonding. In 2016, Lee et al. reported that H bonding was important in stabilizing octahedral tilts in hybrid perovskites [100]. Direction of the H bonding between the organic molecule and the anion framework was also important in optimizing solar cell efficiency. The Figure 8a,b show the Octahedral tilting (Ground-state, GS) and no Octahedral tilting (High-symmetry, HS), respectively. The lattice parameters, the effective ionic radii and the tolerance factors (shown in Figure 8c) were calculated by first-principles calculations. The rotation of the staggered MA cation around the C-N bond was hindered due to the strong hydrogen bonding [100,101]. The ground-state structure has the three strong hydrogen bonding interactions, $\text{H}_\text{N}(1)\text{-I}_\text{A}(1)$, $\text{H}_\text{N}(2)\text{-I}_\text{E}(2)$, $\text{H}_\text{N}(2')\text{-I}_\text{E}(2')$. The high-symmetry structure has only one weaken hydrogen bonding, $\text{H}_\text{N}(1)\text{-I}_\text{A}(1)$. Aleksandra et al. investigated the chemical bonding of FAPbX_3 . Its chemical bonding was different from MA. FAPbX_3 has stronger hydrogen bonding, the π -anion bonding and more hindered motion inside the perovskite inorganic cage [102]. Hong et al. reported that a new additive (guaninium, G) can stabilize the FAPVs [103]. They used it to tune the properties of $\alpha\text{-FAPbI}_3$ due to its special functional units. The novel perovskite structure can be formed, which has low dimensional G_2PbI_4 . It has been established by solid-state NMR that G interacted with the perovskite lattice at the atomic level. The NMR displayed that the microstructure of bulk mechanochemical FAPbI_3 was formed when 10 mol% GI doped. NMR spectrum contained four G peaks and these were different from the peaks of neat GI or G_2PbI_4 , which illustrated the new G/FA-based iodoplumbate phase formed. The structural changes of FAPbI_3 were investigated by a sensitive diagnostic tool (^{14}N NMR). The narrower ^{14}N SSB manifolds manifested that GI affected the crystallographic symmetry of the 3D perovskite due to the narrower ^{14}N SSB manifolds (See Figure 8f). TEM images also illustrated that new G environments modified by the proximity of the α -phase of 3D perovskite was formed (shown in Figure 8g,h). According to Figure 8i, the mixed hybrid perovskite structures were formed due to a number of different tautomeric forms and their propensity to dimerization

by H bonding [103]. Methylenediammonium dichloride (MDACL_2) was used as additive to stabilize the α -phase FAPbI_3 since MDA has more H groups [104]. Larger number of H bonds were formed between MDA and I^- . So smaller amount of MDA can structurally stabilize the α - FAPbI_3 . The XRD illustrated that there was no any impurity peak originating from FACl or MDACL_2 , when MDACL_2 was added to the FAPbI_3 (shown in Figure 8d). This result implied that the FAPbI_3 perovskite lattices included MDACL_2 , and the number of H bonds between PbI_2 and MDA increased (shown in Figure 8e). The band gap has been changed due to introduction of the MDACL_2 . It was confirmed by DFT and compared for two cases as Equations (7) and (8).

FA vacancy:



Cl insertion:

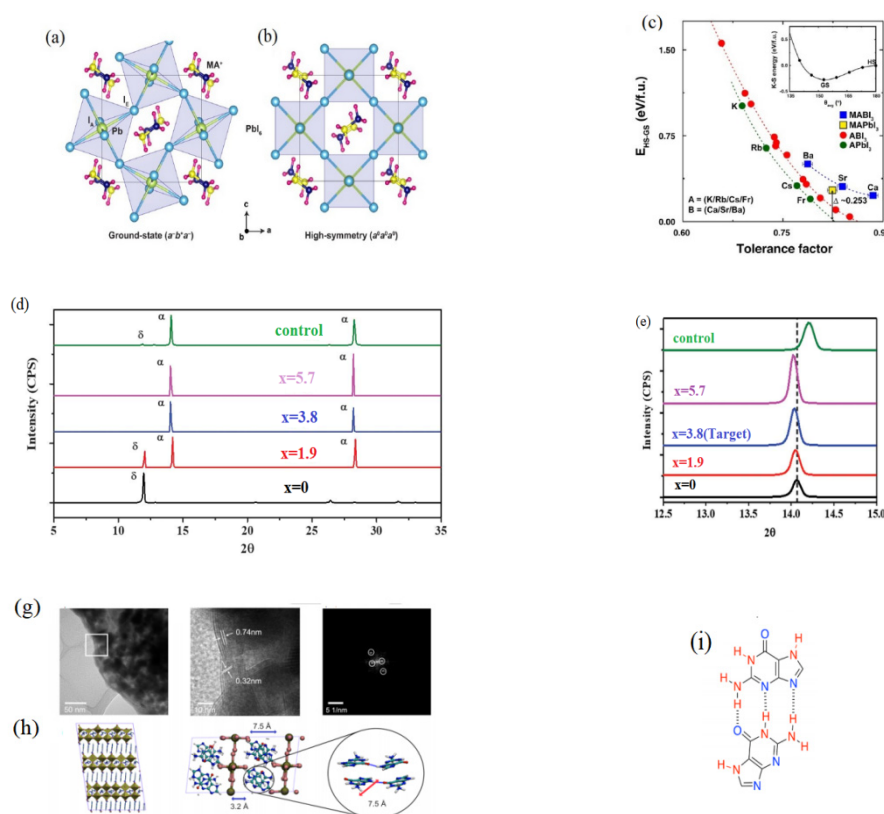


Figure 8. (a) The ground state of α - MAPbI_3 ; (b) High symmetry structures of α - MAPbI_3 ; (c) Corresponding the energy of α - ABiI_3 (red), α - APbI_3 (green), α - MABiI_3 (blue), and α - MAPbI_3 (yellow). The difference of t can be seen according to the horizontal error bars of the α - MABiI_3 hybrid structures. (Reprinted with permission from Ref. [100]. Copyright 2016 ACS Publications). XRD patterns of FAPbI_3 : $x\text{MDACL}_2$ perovskite. (d) The perovskite was exposed to 80% humidity for 24 h and annealed at 150°C for 10 min. (e) The perovskite synthesized with different x values ($x = 0, 1.9, 3.8$, and 5.7 mol%) and (001) orientation peaks was magnified. Reprinted with permission from Ref. [102]. Copyright 2019 Science. (f) ^{14}N NMR spectra of α - FAPbI_3 (top) and G-containing α - FAPbI_3 (bottom). (g) A lower magnification TEM image and high-resolution TEM image of $\text{G}_2\text{FAn}_{n-1}\text{Pb}_n\text{PbI}_{3n+1}$ ($n = 20$) perovskite; (h) The structure of $\text{G}_2\text{FAPb}_2\text{I}_7$ optimized by DFT. (i) The structure of H bond (HB) dimer, including H bond donating (red) and accepting sites (blue). Reprinted with permission from Ref. [103]. Copyright by 2019 Angewandte Chemie International Edition.

According to Equations (7) and (8), the FA cation vacancies and the insertion of Cl^- with a small ionic radius can be assumed. The band gap (1.47 eV) with FA vacancy was bigger than that of origin FAPbI_3 (1.45 eV). That of the Cl insertion has been increased to 1.69 eV. PCE of the related device could reach to 23%. In 2020, the impact of strain relaxation on performance of α - FAPbI_3 was studied by Kim and coworkers [105]. They found that 0.03 mol fraction of both MDA and Cs cations could decrease lattice strain, increase carrier lifetime, reduced Urbach energy and defect concentration. PCE could achieve to 24.4%. The dual replacement of FA^+ sites with MDA^{2+} and Cs^+ can relax the lattice strain of MDA-stabilized α - FAPbI_3 .

In this paper, we mainly introduce Pb-based perovskite. However, the toxicity of lead is high and this can affect their practical application. Some Pb free perovskite solar cells based on FA have also been investigated [106,107]. For example, Li et al. used MA/FA exchange to form $\text{MA}_x\text{FA}_{1-x}\text{SnI}_3$ perovskites materials with 9.11% PCE. The devices of these materials demonstrated good stability [107]. If the stability of Sn-base FA perovskites materials can be improved in the future, these materials will be widely applied.

3. Summary and Future Outlook

FAPVs materials have been studied in the last few years. FAPVs materials have two phases, α -phase (black) and δ -phase (yellow). α -phase FAPVs tend to transform into δ -phase at room temperature. Inherent intrinsic instability of α -phase FAPVs is a very bothering problem. Improving the stability of α -phase perovskite is a key point. In this article, we have reviewed recent strategies to stabilize the α -phase of FAPVs materials including cation-doped (alkali metal cations, MA^+), anion-exchanged, multi-dimensional perovskites (2D perovskites, 2D/3D perovskites) and surface-engineering. At first, cation-doped and anion-exchanged are very useful methods to stabilize FAPVs. For example, alkali metal cation-doped perovskite, especially Cs^+ cation, have been used to improve the stability and PCE of perovskite materials. Furthermore, controlling the dimensions of perovskites is another strategy to stabilize the phase. 2D/3D bilayer structure has higher PCE and trap state densities. The 2D perovskites were formed only at the top surface of the 3D layer, it is effectively stabilized the α -phase beneath though. Controlling the surface composition is an important strategy to form bilayer structure. Surface engineering including surface confinement and surface passivation, has become an emerging effective technology to stabilize α -phase FAPVs. Finally, we discussed the influence of some additives. These additives mainly influence the H bonds in the materials. Direction of the H bonding between the anion framework and the organic molecule was also important to boosting the solar cell efficiency.

Although many research have been reported to improve the stability of FAPVs, a deep understanding of the mechanisms of surface engineering and additives are still not clear. We accentuate the importance to improve the stability of α -phase FAPVs and the key effect of hydrogen bonding in the FAPVs. For the practical application of FAPVs in solar cells, there are still a lot of works related to phase stability to carry out. We hope that more stable α -FAPVs and deeper understanding of the related stabilizing mechanisms will be revealed in the coming future.

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