

# Research Progress in the Stability of Organic-Inorganic Hybrid Perovskite Solar Cells

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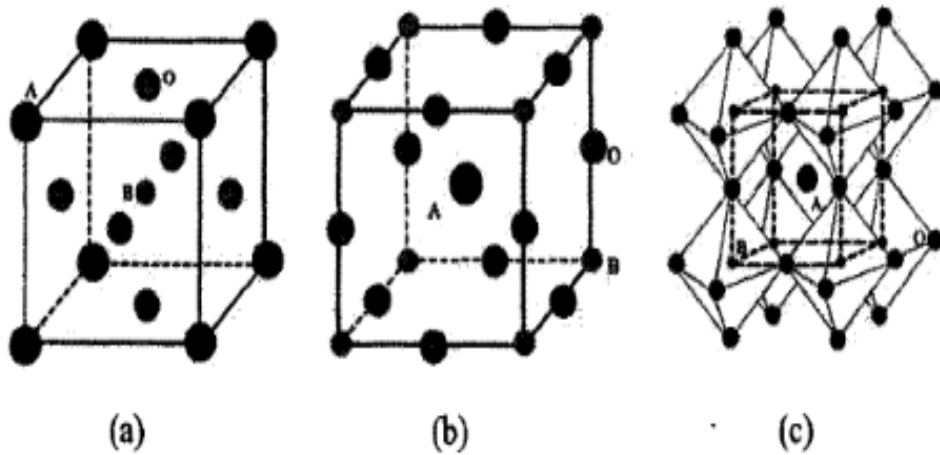
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**Abstract.** Organic-inorganic hybrid perovskite solar cells (PSCs) has attracted growing attention in recent years due to its outstanding photovoltaic performance. After extensive studies in material designs and device engineering, the efficiencies of PSCs have been improved to 24.2%. On the other hand, the inadequate stability of PSCs is hindering the application to real life. Starting with the stability of organic-inorganic PSCs, this article analyzed and concluded the impact of doping A-site and X-site ions on the stability of perovskite respectively. Next, it put forward the prospects for possible development directions of this field in the future.

## Introduction

With the liberation of productivity, humans have increasingly high demands for energy. However, traditional fossil fuel fails to keep up with the development of the times due to a significant shortage. According to BP's latest statistics of the world's energy, the total amount of coal, petroleum and natural gases will be used up in about 150 years [1]. Meanwhile, the burning of traditional non-renewable energy inevitably gives off CO<sub>2</sub>, SO<sub>2</sub>, nitric oxides and particulate matters. It results in environmental problems such as greenhouse gases and acid rain, which threaten the survival and development of human society. Now humans have a stronger sense of crisis due to the depletion of energy in the future and are thus more desperate to find a path of energy consistent with the concept of sustainable development. Among all energy, solar power is most favored by all countries. It is because solar power is not only the source of energy on the earth but also characterized by free pollution to the environment and constant energy output. Humans have carried out extensive explorations of solar cells. Now the power conversion efficiencies (PCEs) of silicon solar cells has exceeded 40%.

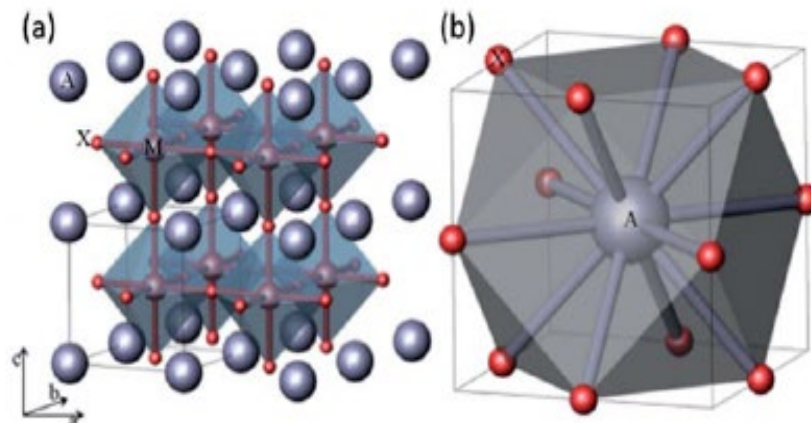
Due to its low costs and adjustable natures, PSC is one of the fundamental research focuses. PSC has enjoyed rapid development and become a popular research topic since 2009 due to its low costs and research thresholds [2]. As its PCE grew from 3.8% to today's 24.2% [3], PSC's great potential was revealed. The compound with the lattice structure similar to CaTiO<sub>3</sub> is known as perovskite material. Perovskite is a mineral called perovski, which was first discovered by Gustav Rose in the Ural Mountains of Russia in 1839 and named after the Russian Mineralogist Lev Perovski. Later, perovskite was used to describe any compound material with the same crystal structure as perovskite. Its chemical formula is AMX<sub>3</sub>. A is either a sizeable inorganic cation or a small organo-functional group, such as cesium (Cs<sup>+</sup>) and methylammonium (MA); B is commonly a divalent metal cation (Pb<sup>2+</sup> or Sn<sup>2+</sup>); C is a halide, such as Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>. Changing the species and sizes of A, B and X can adjust the optical and electronic properties of the perovskite material and achieve expectant cell performances.



**Figure 1.** Crystal structure of perovskite-type composite oxides

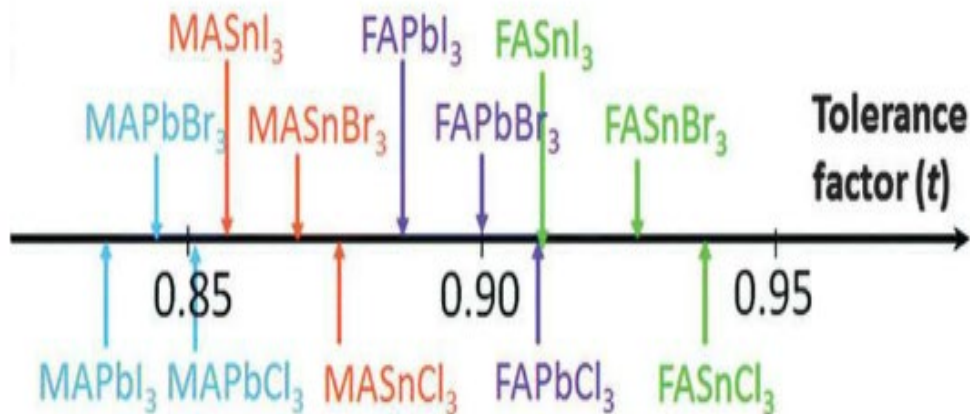
In figure 1 (a), eight vertices of the cube are occupied by element A. The center of the cube, that is, the center of the cell, is occupied by element M. Element X is located at six centers, and the ratio of A, M and X is 1:1:3, which constitutes the chemical composition of  $AMX_3$ . Figure 1b is another conversion form of figure 1a. The eight vertices of the cube are occupied by M element, while the center of the cell is occupied by element A, and element X is located at the midpoint of 12 edges of the cube. It can be seen that the basic structure of Perovskite-type materials can be seen as an infinite extension of 8  $MX_6$  octahedral joints around A ion [4].

In fact, perovskite family materials can be divided into inorganic oxide perovskite ( $AMO_3$ ) and halide perovskite ( $AMX_3$ , X = Cl, Br, I). Among them, inorganic oxide perovskite includes intrinsic type and doping type. Halide perovskite can be divided into alkali metal halide perovskite and organic metal halide perovskite. The absorber material used in perovskite solar cells is perovskite, a three-dimensional organic metal halide [5].



**Figure 2.** Structure of perovskites

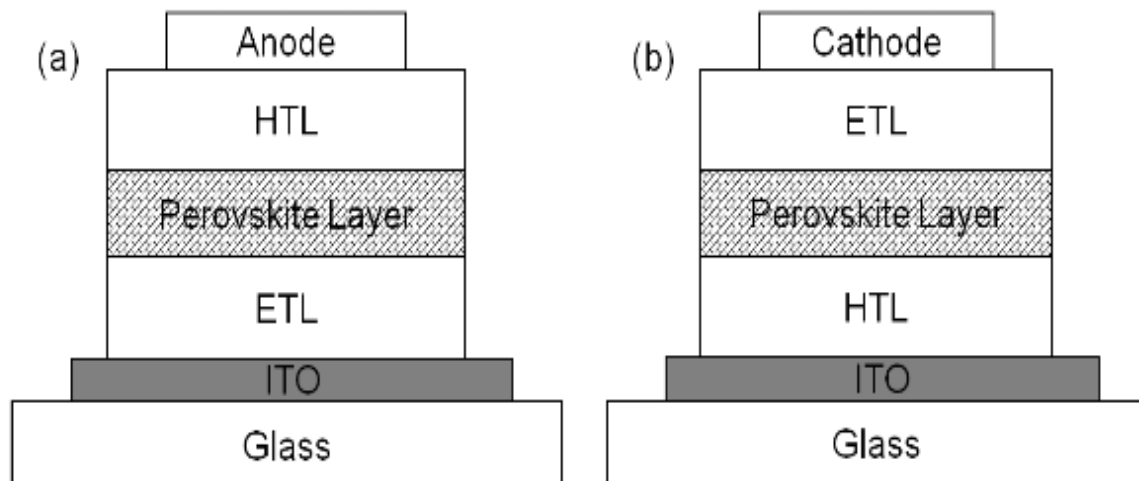
In this kind of perovskite halide crystal material with  $AMX_3$  structure, there is a very important parameter to measure its crystal structure, called tolerance factor  $t$ . Among them,  $R_A$ ,  $R_M$  and  $R_X$  are the radii of the corresponding ions. In order to ensure the cubic structure and high symmetry of the crystal, the size of  $t$  should be between 0.813 and 1.107. In organic-inorganic perovskite, the B position is usually occupied by larger Pb or Sn atoms. Therefore, position A must be large enough to meet the requirement of tolerance factor. However, if the group is too large, it will not work. Otherwise, the cubic structure will be broken and the symmetry of the crystal will be weakened [6]. Therefore, it is necessary to carefully evaluate the radius of group A in place of position A. Figure 3 is the distribution range of tolerance factors of some perovskite materials reported at present.



**Figure 3.** Distribution range of tolerance factors of some perovskite materials reported at present

### Device structure and working mechanism of perovskite solar cells

Perovskite solar cells have a variety of devices, but they can be divided into two types, positive and inverted, as shown in figure 4. Because perovskite solar cells are originally derived from fuel-sensitized solar cells, the definition of positive structure is fuel-sensitized solar cells, which is a little different from organic solar cells [7]. The positive structure of organic solar cells is just similar to that of perovskite solar cells. The two structures of perovskite solar cells will be introduced separately.

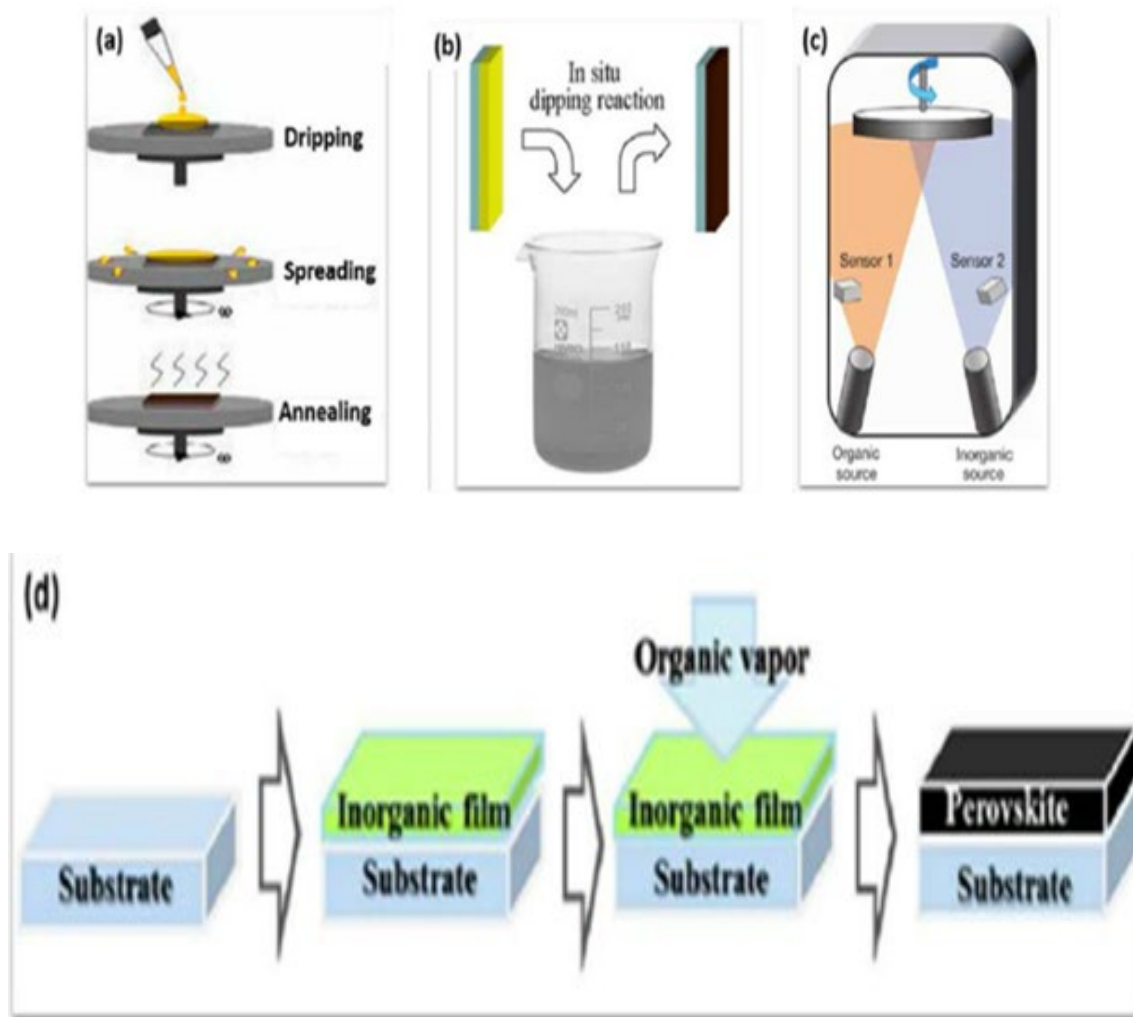


**Figure 4.** Positive structure a and inverted structure b of perovskite solar cells

Figure 4a is the positive device structure of perovskite solar cells. From bottom to top, it is ITO conductive glass, electron transport layer, perovskite optical absorption layer, hole transport layer and anode. Among them, the electron transport layer can be a porous structure or a planar structure.

### Preparation technology of perovskite layer

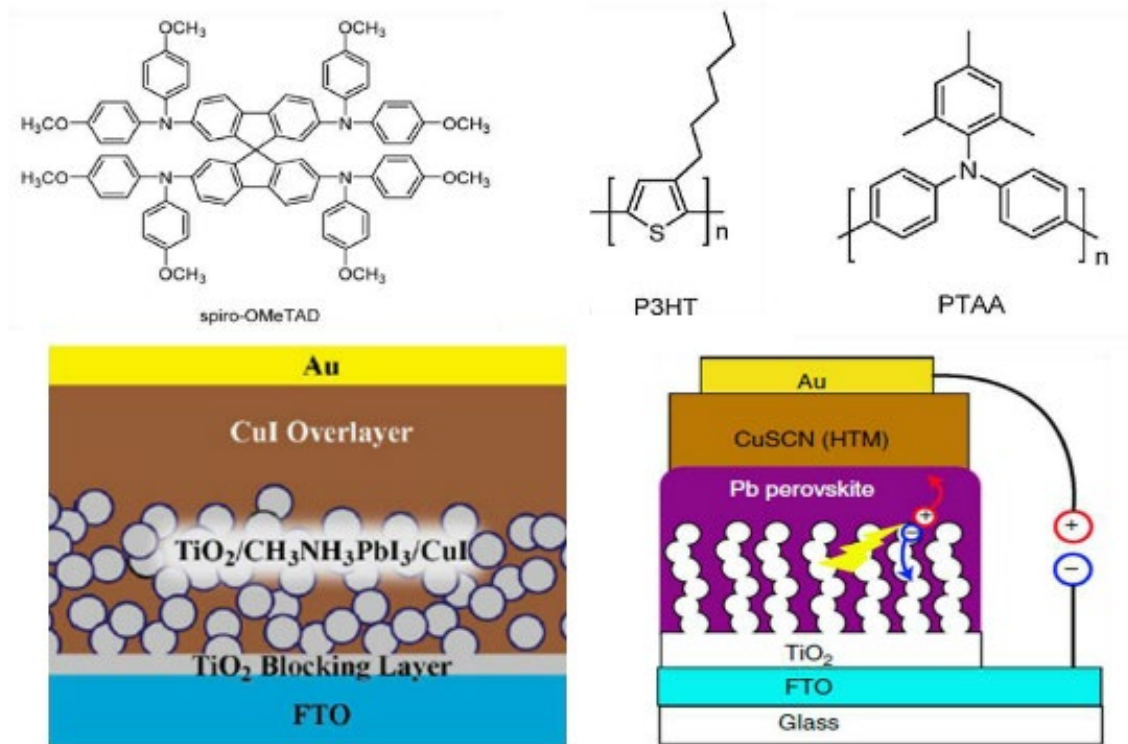
In perovskite solar cells, it is very important to control the preparation process of perovskite layer, because the surface coverage of perovskite layer, the size of crystal particles and the quality of crystallization directly determine the performance of the cell [8]. The preparation process of perovskite mainly includes several methods, one-step spin coating, two-step infiltration, two-source co-evaporation, organic vapor deposition, etc. as shown in figure 5.



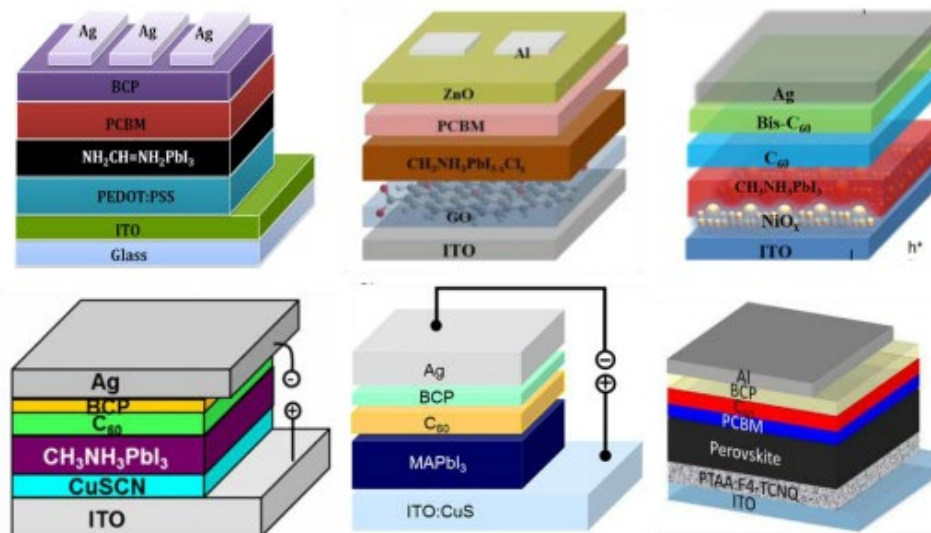
**Figure 5.** Several common preparation processes of perovskite layer ((a). One-step spin coating (b). Two-step infiltration method (c). Dual-source co-evaporation method (d). Organic vapor deposition method)

### Hole transport layer

Hole Transport Layer Material (HTM) consists of organic and inorganic materials. Most HTM reported in the literature mainly includes Spiro-OMeTAD, PTAA and P3HT. Among them, Spiro-OMeTAD and its derivatives are the most. The main inorganic hole transport materials are CuI and CuSCN [9]. At present, the highest photoelectric conversion efficiency of organic HTM battery has reached 20.1%, while that of inorganic HTM perovskite battery has reached more than 12%. Because the photoelectric conversion efficiency based on organic HTM cells is relatively high, the mainstream of current research is focused on organic HTM. However, due to the high cost of organic HTM, it will inevitably restrict the process of its industrialization, and high efficiency and low cost organic HTM needs further development. Although the battery technology based on inorganic HTM is relatively low, compared with organic HTM, inorganic HTM is relatively cheap, its hole mobility is relatively high, and its photothermal stability is relatively good, so it has great prospects in the future industrialization process. Figure 6 and figure 7 are several common hole transport layer materials in positive and inverted structures, respectively.



**Figure 6.** Several kinds of hole transport materials used in the forward structure



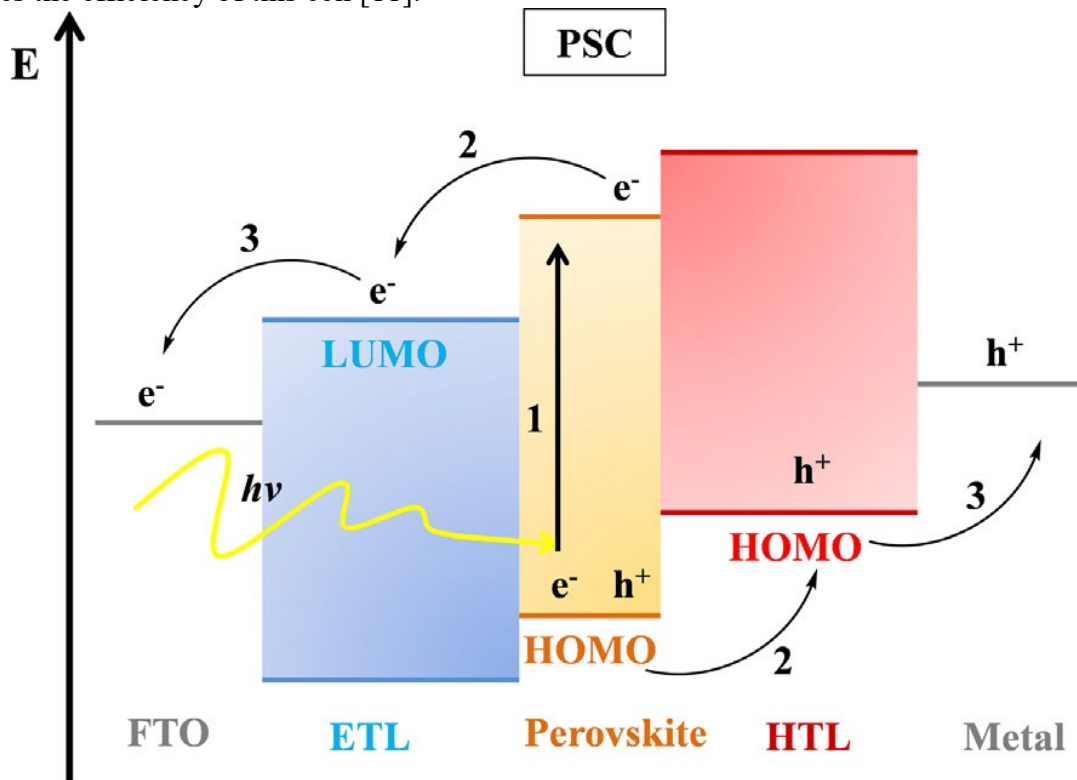
**Figure 7.** Several kinds of void transport materials used in inverted structures

The structure of traditional PSCs is divided into the perovskite layer, the transporting layer, and the electrode. As shown in the figure below, it consists of the glass electrode, the electron transporting layer, the perovskite layer, the hole transporting layer, and the metal electrode. The perovskite layer produces excitons after absorbing solar power. Then the negative and positive charges form an electron-hole pair under the action of the built-in electric field. Next, produced electrons and holes are transported at the electron transporting layer and the hole transporting layer respectively to form currents. When the battery is connected with the load and exposed to sunshine, it does external power and outputs energy [10].

Generally, the LUMO energy level at the electron transporting layer is slightly lower than the CBM (Conduction Band Minimum) at the perovskite layer. The HOMO energy level at the hole transporting layer is slightly higher than the VBM (Valence Band Maximum) at the perovskite layer. This structure ensures a minimum energy loss. Also, the electron/hole barrier layer is added between



the perovskite layer and the transporting layer. Due to potential barriers, the transporting layer only transports holes/electrons, which lowers the recombination probability of holes and electrons and improves the efficiency of this cell [11].



**Figure 8.** Schematic diagram of PSCs

The PSC has several advantages over other types of solar cells. Firstly, perovskite has a widely-adjustable direct bandgap. Taking  $\text{MAPbI}_3$  for instance, the VBM energy level consists of the 6s~I 5p hybrid anti-bond orbit of Pb. The CBM energy level mainly consists of 6p unoccupied molecular orbital of Pb.  $\text{MA}^+$  is in charge of balancing the charge and supporting the structure. Thus, it has a limited impact on the bandgap. Replacing  $\text{I}^-$  with  $\text{Cl}^-$  and  $\text{Br}^-$  in the perovskite can adjust the bandgap and thus meets real demands. Secondly, perovskite has a low level of exciton binding energy, namely 37~57 meV. It can divide electrons and holes under dim light at room temperature, which is favorable for extensively applying PSCs. Thirdly, perovskite has the function of bipolar transmission. When the perovskite contacts n-type semiconductors, it displays the natures of p-type semiconductor. Conversely, it displays the natures of n-type semiconductor when contacting p-type semiconductors. This bipolar transmission function substantially improves the cell's conversion efficiency [12]. Fourthly, the defects of perovskite materials (low formation energy such as  $\text{MA}_i$  and  $\text{V}_{\text{Pb}}$ ) are shallow. In other words, there are few deep defects that lead to severe recombination, which increases the distance for carrier diffusion and substantially lowers the compounding probability of electrons and holes.

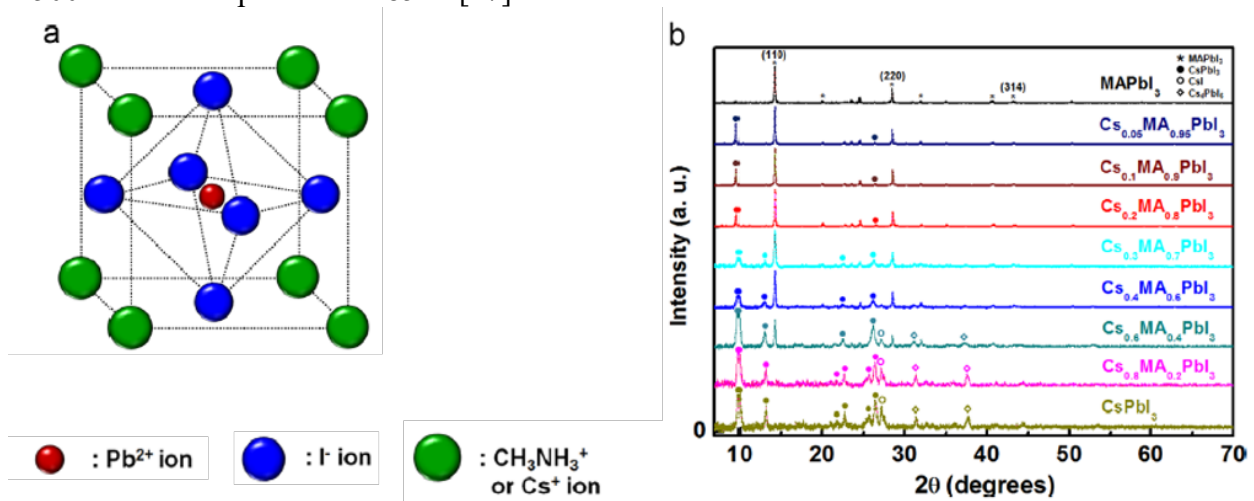
### Regulation and Control of PSCs

Thanks to the huge efforts in material designs and device engineering, the PCE of organic-inorganic PSCs has reached 24.2%. Despite all this, the instability of PSCs hinders its application in real life. The ammonium in organic-inorganic PSCs easily interacts with the water and  $\text{O}_2$  in the air. Therefore, the perovskite can degrade easily, which substantially lowers its PCE. Hence contemporary PSCs are mostly used in sealed conditions and can only be used repeatedly for one year. Conversely, silicon solar cells can be used repeatedly for 20 years [13]. Therefore, a majority of studies concerning PSCs focus on improving stability performance. The stability of PSCs mainly relies on the perovskite light absorption layer, the electron, and hole transporting layer and the stability between each interface. For example, there are many surface defects at the commonly used

TiO<sub>2</sub> electron transporting layer (ETL), which speeds up the decomposition of perovskite under ultraviolet ray. To solve this problem, scientific researchers specially tried improving TiO<sub>2</sub>, replacing TiO<sub>2</sub> or converted the UV ray into visible light. There are various directions for adjusting the stability of cells. The following part focuses on discussing the stability of the light absorption layer [14].

### Regulation and Control of A-Site Ions

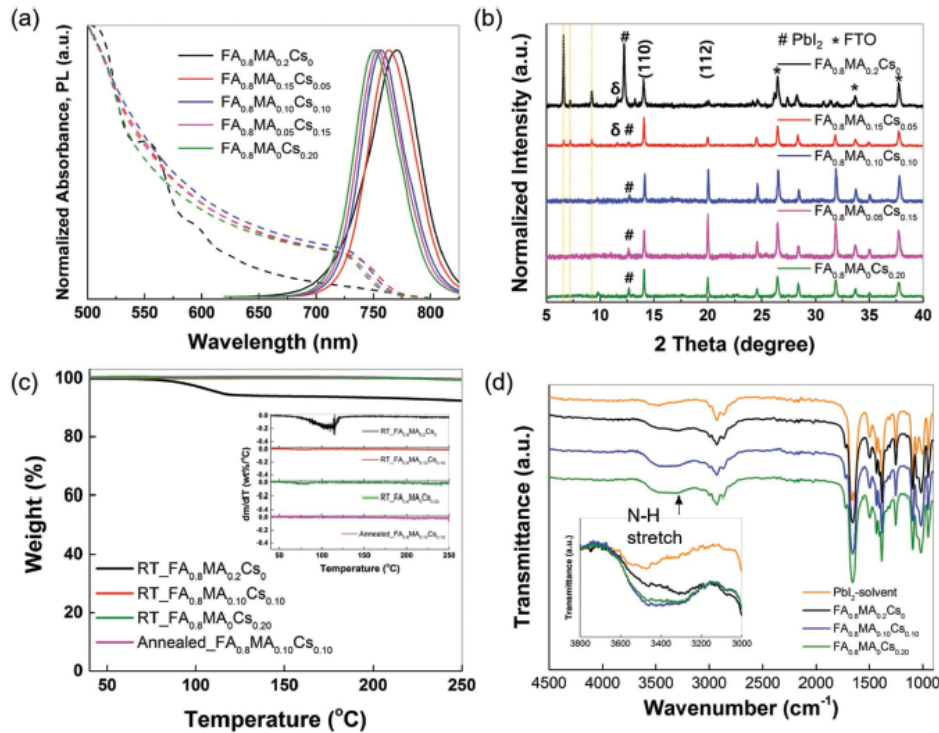
Doping A-site ions into perovskite changes the lattice parameter and thus affects the bandgap of PSCs. Meanwhile, replacing partial or all organic A-site ions with inorganic ions helps to improve the stability between water and O<sub>2</sub> with perovskite [15]. Also, regulating and controlling A-site ions adjust the PCE and stability of PSCs. The Cs ion and MA ion are similar in size. Therefore, replacing Cs ion with MA ion does not affect the lattice structure. Kim et al. doped Cs ions into traditional organic perovskite lattice MAPbI<sub>3</sub> to form Cs<sub>x</sub>MA<sub>1-x</sub>PbI<sub>3</sub> [16]. And the proportion of Cs ions can be adjusted to control the bandgap between 1.52~2.05 eV. When the doping concentration of Cs ions is 10%, Cs<sub>0.1</sub>MA<sub>0.9</sub>PbI<sub>3</sub> displays the best cell performances ( $J_{SC}=10.10\text{mA}\cdot\text{cm}^{-2}$ ,  $V_{OC}=1.05\text{V}$ ,  $FF=0.73$  and  $PCE=7.68\%$ ). It has better performances than MAPbI<sub>3</sub> and CsPbI<sub>3</sub>. However, the stability of the cell sees no significant improvement, because the HTL (PEDOT: PSS) easily oxidizes the Al electrode. Hence the inorganic hole transporting material can be used to replace traditional PEDOT: PSS hole transporting layer to improve the overall stability of the cell. It improves the optimal efficiency to 18.45%. Meanwhile, the device can maintain 86.7% of efficiency after being used in air for 500 h at the temperature of 85°C [17].



**Figure 9.** (a) Crystal structure and (b) XRD patterns of Cs<sub>x</sub>MA<sub>1-x</sub>PbI<sub>3</sub> perovskites

The technology of multi-component ion doping at A-site refers to doping one or several types of new ions at A-site based on the regulation of binary-component ion doping at A site to improve the stability and re-productivity of perovskite cells. Saliba et al. achieved the tertiary-component doping of Cs, FA and MA for the first time into Cs<sub>x</sub>(MA<sub>0.17</sub>FA<sub>0.83</sub>)<sub>1-x</sub>Pb(I<sub>0.83</sub>Br<sub>0.17</sub>)<sub>3</sub> perovskite material. It was found that a small amount of Cs improved the thermal resistance of the thin film and restricted the formation of yellow phases in the thin film without changing the bandgap [18]. Grätzel et al. found that doping A-site ions facilitated the room-temperature crystallization of the perovskite phase. It avoids the high-temperature annealing processing in the traditional method and can improve the production and application of PSCs [19]. Grätzel fixed the concentration of FA ions at 80% to change the proportion of Cs to MA (FA<sub>0.8</sub>Cs<sub>x</sub>MA<sub>1-x</sub>) and change the band gap correspondingly (Figure 4.a). Without the doping of Cs ions, the lattice could not fully convert into the perovskite phase at room temperature. If the doping of Cs reached 10%, unstable yellow phases disappeared, and the lattice entirely converted into the photoactive black phase (Figure 4.b). According to the TGA, the lattice's weight significantly lowered at the temperature of 70°C without the doping of Cs; conversely, there was no significant change in weight when Cs ions were doped at 70°C, meaning the lattice contained no residual solvent from preparation. The FTIR further found the N-H bond had stronger vibration

after Cs was doped into the lattice, meaning the interactions of  $\text{MA}^+$  and  $[\text{PbI}_6]^{4-}$  grew stronger. It was because Cs can replace the solvent molecule and cooperate with  $[\text{PbI}_6]^{4-}$  octahedron, facilitating the room-temperature crystallization of the perovskite phase (Figure 4.c and Figure 4.d). According to the studies of the cell efficiency, the battery reached 17.7% of PCE when  $x=0.1$ . The battery's efficiency did not decline but increased slightly after repeatedly working for 300 h in darkness and dry conditions.

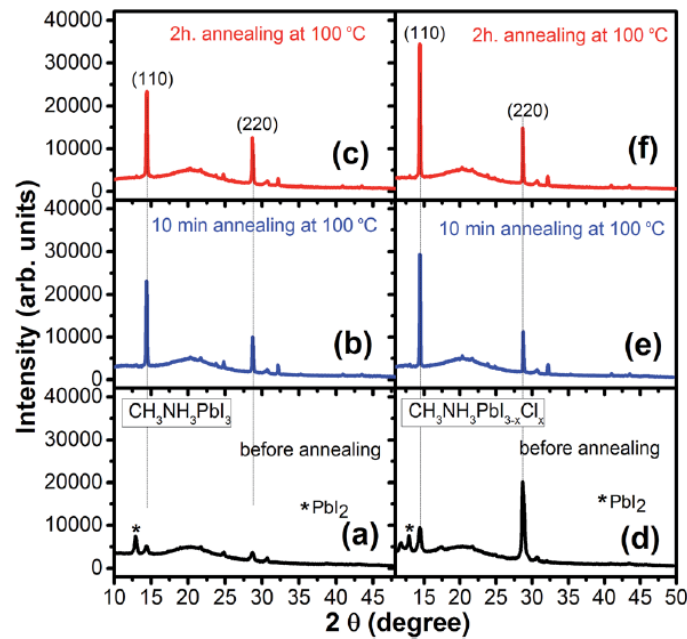


**Figure 10.** (a) PL spectra and UV-vis absorption spectra  $\text{FA}_{0.8}\text{Cs}_x\text{MA}_{1-x}$  perovskite thin film, (b) XRD data, (c) TGA curves, (d) and Fourier transform infrared spectrometer spectra [19]

### Regulation and Control at X-Site Ions

The PSCs based on traditional solution processing has high sensitivity and low reproductivity. The same lattice structure and cell efficiency can hardly be made even at the same parameter conditions. Substituting I ions with other hexogen ions (such as Br and Cl) is another feasible path for improving the stability and reproductivity of PSCs. There are wide differences between  $\text{Cl}^-$  and  $\text{I}^-$  in radius. Therefore, Cl can only be doped into the perovskite lattice at a low doping concentration. After the doping of Cl, the perovskite thin film has a higher crystallization degree, better coverage and a more stable structure [20]. Shirai et al. doped  $\text{Cl}^-$  into the precursor solutions through the interdiffusion method and obtained  $\text{MAPb}_{3-x}\text{Cl}_x$ . By comparing the XRD pattern of both  $\text{MAPbI}_3$  and  $\text{MAPb}_{3-x}\text{Cl}_x$ , the peak intensity of the (110) and (220) planes increases as the time of annealing lengthens after the doping  $\text{Cl}^-$ , while the  $\text{MAPbI}_3$  sees no significant change in the peak intensity at 10 minutes after the annealing. Thus, it can be seen the perovskite lattice has slower growth, a higher crystallization rate and fewer defects in the lattice after being doped with  $\text{Cl}^-$ . Therefore, doping  $\text{Cl}^-$  into perovskite produces perovskite cells with better photostability. It can work for two months continuously in sealed conditions and work for 2 h alternately between short and open circuit conditions under continuous illumination.





**Figure 11.** The XRD patterns of perovskite films before annealing and after annealing for different periods of time: (a) to (c), MAPbCl<sub>3</sub>; (d) to (f), MAPbI<sub>3-x</sub>Cl<sub>x</sub>

### Co-Regulation and Control of A-Site and X-Site Ions

Furthermore, the A-site ions and X-site ions can be doped at the same time. Regulating the X-site ions helps to change the bandgap of perovskite materials, while regulating A-site ions improves the crystallization and coverage of thin films. The doping of both A-site ions and X-site ions makes it easier to get the PSCs with a higher PCE and stability. Bolink et al. carried out triple-cation co-doping on the A site and Br doping on X site of the perovskite material, which obtained the perovskite material whose molecular formula is Cs<sub>0.5</sub>FA<sub>0.4</sub>MA<sub>0.1</sub>Pb(I<sub>0.83</sub>Br<sub>0.17</sub>)<sub>3</sub>. The PCE of this device is 15.6% (JSC=16.9mA·cm<sup>-2</sup>, VOC=1.14V, FF=0.81), with a small hysteresis and relatively high stability. It can work for five days normally under continuous illumination without leaving behind significant degradation.

### Conclusion

In conclusion, appropriate doping of A-site and X-site ions into the organic-inorganic hybrid perovskite effectively improves the efficiency and stability in PSCs. The reason is that different levels of doping restricts the transformations of the perovskite phase at room temperatures and improves the film-forming properties of perovskite. Apart from stability, the development of PSCs is hindered by other factors, including complicated and expensive preparation techniques, the toxicity of Pb and the difficulty of large-scale preparation. Therefore, future directions of developing PSVs include spinning coating and non-vapor deposition, searching for substitute elements for Pb and carrying out large-scale preparation to lower costs. It is also necessary for scientific scholars to keep exploring the relationship between the structure of perovskite and its optical and electronic properties, ionic mobility and recombination mechanism to guide experiments better with theories.

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