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The Evolution of Tin-Based Perovskites Solar Cells

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The development of efficient and stable lead-free perovskite solar cells (PSCs) is the key to solving the problem of environmental pollution caused by the toxic element lead. In recent years, tin-based PSCs have become popular candidates for high-performance, environmentally friendly photovoltaic technology with certified power conversion efficiency (PCE) of over 14%, which shows great potential application. Herein, we briefly summarize the efficiency progress of tin-based PSCs and analyze some methods for improving their performance. We expect that these views will help accelerate the development of tin PSCs.

Perovskite solar cells (PSCs) have attracted worldwide attention due to their adjustable bandgap, long carrier diffusion length, high optical absorption coefficient, and the easy solution processing property of organic metal halide PSCs absorbents.[1-6] For the plumbum (Pb)-based PSCs, the highest PCE of lead-based PSCs has reached 25.7%,[7] which is equivalent to that of silicon-based solar cells. However, the toxicity of Pb to humans and the environment cannot be ignored, which greatly hinders the future commercialization of Pb-based PSCs. Therefore, it is necessary to develop non-lead perovskite materials to fabricate the next-generation PSCs.

People have been exploring environmentally friendly, less-toxic or nontoxic perovskite materials to replace Pb, such as Stannum (Sn), Germanium (Ge), Bismuth (Bi), Cuprum (Cu), and Stibium (Sb). Among these Pb-free candidate materials, Sn-based perovskite is considered to be the most promising candidate. Both Sn and Pb belong to the element of the carbon group (IVA), and they have similar external electron configuration (ns^2np^2) and ionic radius (149 pm for Pb^{2+} and 135 pm for Sn^{2+}), making Pb completely substituted in perovskite lattice without causing obvious phase segregation.[8] Moreover, Sn-based PSCs have some additional advantages: suitable optical band gap of 1.2−1.4 eV (closer to the optimal Schockley−Quiser limit of 1.34 eV) and small exciton binding energy (2−50 meV), high absorption coefficient (10^4−10^5 cm^{-1}), and high carrier mobility (μ_e (electron mobility) = 2000 cm^2V^{-1} s^{-1} for $MASnI_3$ and 60 cm^2V^{-1} s^{-1} for $MAPbI_3$).[9-11] Therefore, green and environmentally friendly Sn-based PSCS are expected to find promising applications in photovoltaic and other optoelectronic devices.

In the past few years, Sn-based PSCs have emerged as promising candidates for green photovoltaic technology, along with their efficiency rapidly increasing from about 2% to 14.81% by inhibiting the oxidation of Sn^{2+} to Sn^{4+}.[12] Encouragingly, Sn-based PSCs not only have PCE over 14 % but also have excellent stability. It is an attractive photovoltaic technology and will be further developed shortly. The amazing progress shows that it is a better candidate for the next generation of solar cells. Fig. 1 presents the efficiency evolution of Sn-based perovskites within just 6 years.

In general, the similar structure of Sn and Pb-based perovskite can be expressed by the formula ABX_3. The basic unit of cubic perovskite is a small octahedral unit cell (BX_6) in which the B cations are surrounded by halide anions. A is an organic cation, such as $CH_3NH_3^+$ (MA^+), $CH(NH_2)_2^+$ (FA^+), Cs^+, or some large cations (PEA^+). A cation is located in the cavity of the octahedron. X is halogen, such as I^-, Br^-, Cl^-, *etc*. The structural stability of the perovskite material ABX_3 depends on the tolerance factor t and μ, where r_A, r_B, and r_X are the radii of A, B, and X respectively. Usually, t is located between 0.9 and 1.0 to form cubic perovskite.[13] The investigation of this tolerance factor helps to understand the structural

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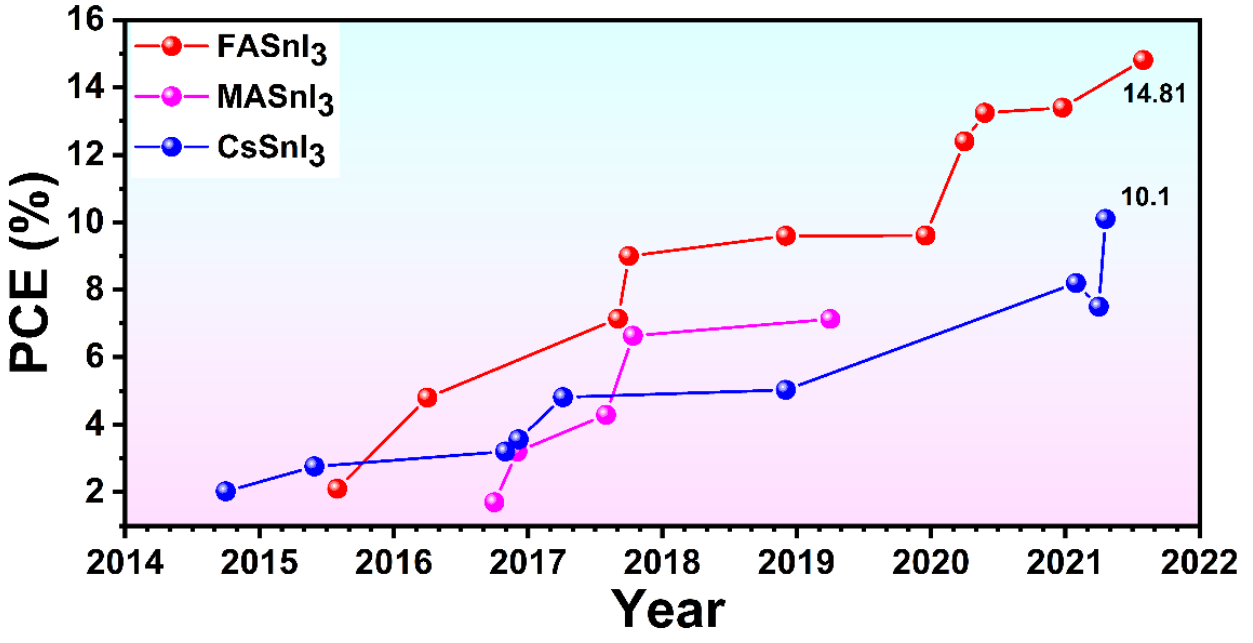

Fig. 1 Efficiency development of Sn-based Perovskite Solar Cells.

transformation of perovskite materials.

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$$

The octahedral factor μ is another important parameter, and μ is defined as

$$\mu = \frac{r_B}{r_X}$$

A stable BX_6 octahedral structure can be formed when μ ranges from 0.4 to 0.9.[14]

The research upsurge of Sn-based perovskites has not subsided, and other areas of research have attracted attention. such as, light-emitting,[15] photodetectors,[16,17] field-effect transistors, and others. Therefore, the development of environmentally friendly lead-free perovskite materials is an urgent need for the production of next-generation PSCs. Environmentally friendly lead-free perovskite materials should have a huge upside in photovoltaic research.

Although the PCE of Sn-based PSCs has achieved up to 14.81%, which still lags behind Pb-based devices. So far, short-circuit current density (J_{SC}) of Sn-based PSCs has almost reached its theoretical maximum. The main obstacle to keeping the PCE of Sn-based PSCs above 15% is its low open-circuit voltage (V_{OC}), which is the result of serious loss caused by carrier non-radiation recombination.[18,19] At present, the maximum V_{OC} of Sn-based perovskite has reached 0.94 V, which undoubtedly makes researchers see the dawn.[20] Therefore, for Sn-based PSCs, more basic research is needed to understand the root causes of its low V_{OC} and explore new solutions. Additionally, the fill factor (FF) of Sn-based PSCs is not high enough. In general, V_{OC} and FF can be improved simultaneously. If V_{OC} and FF reach above 1.0 and 0.80, respectively, PCE of Sn-based PSCs can also be expected to be comparable to Pb-based devices.[21] Another challenge is how to inhibit the oxidation of Sn^{2+} to improve the air stability of Sn-based PSCS. The stability of Sn-based PSCs has not yet met the requirements of commercialization. To improve the device performance, researchers have explored effective strategies including low-dimensional structure, reducing agents, device structure engineering, and crystal growth regulation. We boldly assume solutions for improving stability should be one of the focuses of future research.

Finally, the initial PCE of lead-based PSCS increased from 3.8% to 25.7%, which is hard to imagine the rapid rise of PSCs at that time. Therefore, with the progress of Sn-based PSCs in recent years, we should be optimistic to see more breakthroughs in this field in the future. We expect that Sn-based perovskites solar cells will bring us other unexpected miracles in the near future.

Conflict of interest

There are no conflicts to declare.

Supporting information

Not applicable.

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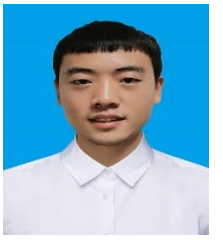

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