Transactions on Computer Science and Intelligent Systems Research
ISSN: 2960-1800, eISSN: 2960-2238 | Volume 10
ISET 2025

Doping Strategies for Promising Matel Halide Perovskite Based Solar Cells

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Abstract. The metal halide perovskites have been broadly utilized as key materials in the development of solar cells due to their outstanding optoelectronic advantages. However, several challenges remain, including poor stability under high temperatures and humid conditions, the toxicity associated with lead at the B-site, and initial efficiency losses caused by ion migration. To address these issues, researchers have explored ion doping at various lattice sites. This paper first introduces the crystal structure of metal halide perovskites and highlights the advantages of perovskite-based solar cells. It then summarizes recent progress in ion doping at the A- and B-site, focusing on its impact on optoelectronic performance and the stability of perovskite solar cells. In the future, targeted doping at the A-site and B-site is expected to remain a crucial strategy for enhancing the performance and reliability of metal halide perovskite-based solar cells.

Keywords: Metal halide perovskites; doping; solar cells.

1. Introduction

Metal halide perovskites (ABX_3) have attracted widespread attention as a consequence of their outstanding photoelectric properties. As a new type of semiconductor materials, the metal halide perovskites ABX_3 have advantages such as long carrier diffusion length, large absorption cross-section, high color purity, high photoluminescence quantum efficiency and tunable emission wavelengths. These properties make them highly promising for applications in solar energy conversion. Among third-generation photovoltaic technologies, metal halide perovskites based solar cells have emerged as leading candidates due to their high efficiency values, simple fabrication processes, minimal infrastructure requirements, and rapid manufacturing times [1]. However, several challenges still hinder their practical applications. The metal halide perovskites typically exhibit poor stability when exposed to light, heat and electron beams. Moreover, the lead (Pb) in the B-site of most perovskite compositions poses significant environmental and health risks due to its toxicity. To address these limitations, doping strategies have been broadly employed to enhance the performance of metal halide perovskites. Such doping involves substituting ions at the A-, B-, or X-sites of the ABX_3 structure. The A-site doping can enhance the stability of the metal halide perovskites, while B-site doping can reduce Pb^{2+} toxicity and simultaneously enhance long-term device stability. Through doping, it is possible to improve the optoelectronic properties, broaden the emission range, promote better film crystallization, enhance charge transport, and mitigate lead-related toxicity [2].

This paper will first introduce the structure characteristics of the metal halide perovskites, followed by a discussion of their advantages as photovoltaic materials. Finally, it will list several examples illustrating the enhancement of solar cell performance through A-site and B-site doping strategies.

2. Theoretical basis analysis

2.1. Structure of metal halide perovskites

The general chemical formula of metal halide perovskite materials is ABX_3, where A typically represents monovalent cations such as MA^+, FA^+, Ag^+, Li^+, Na^+, K^+, Rb^+, and Cs^+. B is commonly a divalent or multivalent metal cation, including Pb^{2+}, Sn^{2+}, Sn^{4+}, Cd^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Sb^{3+}, RE^{3+},

Al^{3+}, Bi^{3+} and others. X represents Cl^-, Br^- and I^- or other halide anions. Metal halide perovskite generally crystallizes in a cubic structure. In this structure, a regular octahedral symmetry structure is created by the B-site and X-site ions. The A-site cation occupies the voids created at the center of the octahedron structure while the center of the octahedron holds B-site cation to form a cubic symmetry structure of BX_3, thereby forming a three-dimensional periodic structure. Figure 1 illustrates the unit cell structure of the metal halide perovskite material.

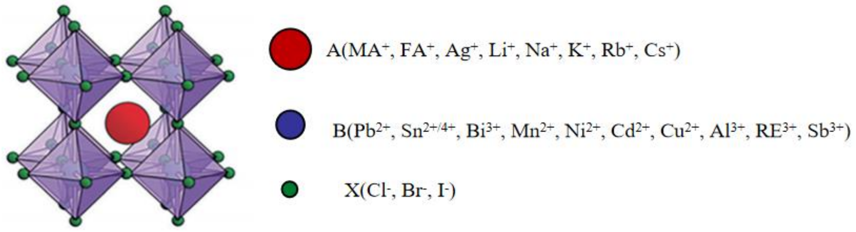

Fig. 1 Schematic of the structure of metal halide perovskite ABX_3 [1].

2.2. Advantages of the metal halide perovskites based solar cells

The metal halide perovskites are a type of light-absorbing material which have potential applications for solar cells due to their excellent optoelectronic properties [3]. These include high extinction coefficient, broad-spectrum light absorption covering the visible and near-infrared regions, excellent charge carrier mobilities and low exciton binding energy, which enable long diffusion length exceeding 1 μm [4]. Metal halide perovskites can be broadly classified into organic-inorganic metal halide-based perovskites (OIMHP) and inorganic metal halide-based perovskite. OIMHP are highly regarded for the electrical and optoelectrical performance and are broadly applied in photovoltaic solar cells owing to their suitable bandgap energies, typically around 1.5 eV. The most well-known OIMHP is the lead-based $MAPbX_3$ ($MA = CH_3NH_3$; X can be halogens like Cl, Br or I), which have demonstrated excellent photon conversion efficiency. Inorganic metal halide perovskites, which feature inorganic cations at the A-site, are also regarded as an important component in the development of solar cells due to their excellent thermal and chemical stabilities and promising photovoltaic performance. Compared with quantum dots (QDs) of organic-inorganic metal halide-based perovskites, those of inorganic metal halide perovskites exhibit better luminescence stability, higher photoluminescence quantum efficiency (with $CsPbBr_3$ QDs reaching efficiencies above 95%), and improved color purity [2].

3. Enhancing the performance of matel halide perovskites based solar cells

The performance of solar cells can be significantly enhanced by first improving the intrinsic properties of perovskite materials. The performances of the metal halide perovskites can be effectively enhanced through doping at different lattice sites. The A-site doping contributes to an increase in the tolerance factor, thereby improving the structural stability of the perovskite material. B-site doping reduces the toxicity associated with Pb^{2+} ions and modifies the B–X bond length, which in turn enhances phase stability. X-site doping allows for band gap modulation and enables precise control over the emission wavelength.

3.1. Doping at the A-site

For organic-inorganic hybrid metal halide perovskite materials such as general formula APbX3, where A represents MA, FA, or Cs and X corresponds to Br, Cl, or I, the presence of organic cations at the A-site results in susceptibility to thermal stress and moisture. This intrinsic instability compromises the overall photovoltaic performance of the material. To address this issue, A-site doping has emerged as an effective method to enhance the optoelectronic properties of perovskite-based solar cells. Doumbia et al. [4] investigated the effects of FA doping at the A-site of methylammonium lead bromide ($MAPbBr_3$) by varying the FA content (0%, 2%, 4%, 6%, 8%, and 10%). Based on a comprehensive analysis using various characterization techniques, FA incorporation can improve the films' optical absorption, structural integrity, and morphological uniformity. Among those $MA_{1-x}FA_xPbBr_3$ thin films, the sample with 6% FA doping exhibited the most favorable properties, including the smallest band gap of 1.92 eV. These findings demonstrate that FA doping can effectively reduce the band gap of perovskite materials, thereby enhancing the stability and performance of the corresponding solar cells.

In addition to doping organic cations at the A-site of the organic-inorganic hybrid metal halide perovskite, inorganic metal cations can also be the dopants. Duan et al. [5] doped Cs into $MAPbI_3$ to synthesize $Cs_xMA_{1-x}PbI_3$ perovskite materials with varying Cs contents (0%, 5%, 10%, 30%, and 50%). This study revealed that the crystal structure of the perovskite was significantly influenced by the Cs doping concentration. Notably, the sample with 10% Cs doping exhibited a prolonged carrier lifetime due to suppressed electron–hole and Auger recombination, suggesting improved charge transport properties. Consequently, $Cs_{0.1}MA_{0.9}PbI_3$ shows strong potential for enhancing the photovoltaic conversion efficiency of perovskite solar cells.

3.2. Doping at the B-site

B-site doping can effectively suppress migration of the ions and enhance the long-term stability of perovskites devices. This is attributed to the wide variety of potential dopants available for the B-site, especially the transition metal ions. Recent studies have shown that doping in the B-site of the metal halide perovskites can improve both optical properties and operational stability. These improvements result from enhanced Pb-X bonding strength and a reduction in defective densities. In the case of $CsPbI_3$, maintaining the integrity of the PbI_6 octahedral framework in the cubic phase is challenging, as the A-site Cs^+ ion is relatively small and tends to displace from the lattice center, resulting in structural distortion [6-9]. Huang et al. [10] explored the use of transition metal ions with smaller ionic radii than Pb^{2+} as B-site dopants. Metal cations Mn^{2+}（$r = 97$ pm) and Zn^{2+}（$r = 74$ pm) have been doped in the quantum dot (QD) of the colloidal perovskite $CsPbI_3$ to explore if the cubic structure of $CsPbI_3$ could be stabilized by B-site doping during purification process. The result shown that doping with Mn^{2+} and Zn^{2+} reduced the lattice constant and shrank the volume of the PbI_6 octahedra, thereby enhancing the structural stability and increasing the effective Goldschmidt tolerance factor of $CsPbI_3$. These results confirmed that introducing smaller metal ions at the B-site improves the internal structural stability and tolerance to phase transitions caused by grain growth during purification. This paper offers promising implications for the fabrication of stable and efficient perovskite solar cells. Huang and his team fabricated doped QD solar cells with a configuration of FTO/c-TiO2/QDs/Spiro-OMeTAD/Ag and the performance of QD solar cells are shown in fig.2. According to the fig.2, the doped QD solar cells can display the highest power conversion efficiency of 13.5% and it is much higher than that of the pure QD solar cells.

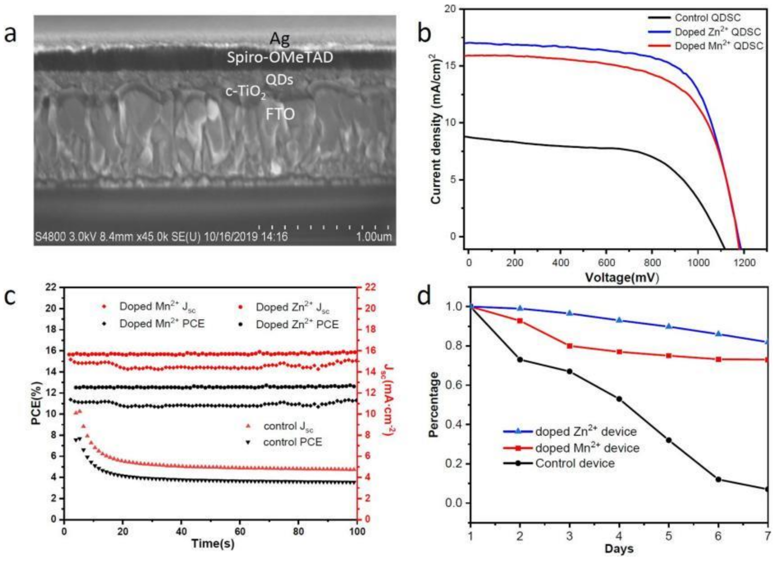

Fig.2 Performance of QD solar cells [10].

Since the lead-based halide perovskites based solar cells have toxicity with the presence of lead and can be unfriendly to the environment, lead-free photovoltaic devices have been developed by substituting lead with less toxic and environmentally friendly metals such as cadmium, copper, and zinc. Transition metals are highly regared to be the light absorbers in photovoltaic solar cells due to their ability to enhance visible light absorption through *d-d* electronic transitions. Jellali et al. [11] synthesized a novel Cd-based perovskite $DMACDdCl_3$ (DMA= $CH_3(NH_2)CH_3$) and chose Zn^{2+} and Cu^{2+} ions to partially substitute the Cd^{2+} ions in the B site. This research successfully fabricated Cu^{2+} doped $DMACd_{0.97}Cu_{0.03}Cl_3$ hybrid perovskite and the Zn^{2+} doped $DMACd_{0.98}Zn_{0.02}Cl_3$ hybrid perovskite and analyzed the effects of different metal dopants on the electronic and optical properties of the Cd-based perovskite $DMACDdCl_3$. According to the UV-Vis-NIR absorption analysis, the gap energy of pure $DMACdCl_3$ hybrid perovskite is 5.36eV; while the gap energy of the Cu^{2+} ions doped $DMACd_{0.97}Cu_{0.03}Cl_3$ hybrid perovskite can be decreased toward 2.51eV, therefore the semiconductor properties of the Cu^{2+} doped $DMACd_{0.97}Cu_{0.03}Cl_3$ hybrid perovskite can be improved. Besides, the Zn^{2+} doped $DMACd_{0.98}Zn_{0.02}Cl_3$ hybrid perovskite remains the same gap energy. This analysis revealed that partly doping Cu^{2+} ions in the Cd^{2+} ions could result in “cold” white emission which has a CCT of 7117K and a CRI of about 71. And when the Cd atoms are partially substituted with Zn atoms, the emitted light exhibited a CCT about 11,028K and a CRI of 84 and a blue shift appeared. Based on this research, the Cu doped hybrid perovskite could be favourable materials for solar cells.

4. Conclusion

Metal halide perovskite based solar cells have attracted widespread attention as a consequance of their advantages advantageous properties, including color purity, a large absorption cross-section, high photoluminescence quantum yield, long carrier diffusion length and tunable emission wavelength. Despite these merits, their commercial application has been hindered by poor long-term stability and the toxicity associated with lead components. Current research highlight that the stability of the perovskite materials, mainly including thermal stability and humidity stability, is a critical factor influencing the overall durability of perovskite solar cells. To address this issue, doping at various lattice sites has been widely investigated. For example, A-site doping has been explored to decrease the band gap and improve structural and operational stability of the solar cells, while B-site doping is effective in suppressing ion migration and enhancing long-term device stability. Additionally, to mitigate the environmental concerns associated with lead, researchers have investigated substituting Pb^{2+} with less toxic or environmentally benign metal ions such as Cd^{2+}, Cu^{2+}, and Zn^{2+} to develop lead-free photovoltaic devices. Although doping can improve the stability of the perovskite material, metal halide perovskites still face considerable challenges in terms of UV resistance, thermal endurance, moisture tolerance, and photostability due to their intrinsic structural characteristics. Beyond site-specific doping, composing perovskite materials with stable matrices such as glass-based materials, polymer materials, and metal framework materials has emerged as a promising approach to enhance environmental resilience without significantly compromising their intrinsic optoelectronic properties. This strategy is expected to attract increasing research attention in the future as a viable pathway toward the practical deployment of perovskite-based solar technologies.

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