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Review

A brief review on the lead element substitution in perovskite solar cells

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ABSTRACT

Organic-inorganic halide perovskites have attracted huge attentions as the novel photoelectric function materials. So far, perovskite solar cells (PSCs) with prominent performance are still based on the lead halide perovskites, although they are potentially highly toxic. The issue of toxicity has become one of most crucial problems before its commercialization. Therefore, an increasing number of studies have focused on the lead element substitution in PSCs, and many excellent achievements have been reported. Alternative elements, e.g., Sn, Ge, Bi and Sb were successively used to fabricate lead-free perovskites, which provided potential possibility to tackle the toxicity issue. Recently, Sn–Pb hybrid perovskites were demonstrated to realize lead reduction without sacrificing the PCE. In addition, a new family of halide double-perovskites was explored and given high expectations. Here, we give a brief review on the lead substitution in PSCs, including theoretical explorations and experimental achievements, and finally we propose some perspectives.

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1. Introduction

Organic-inorganic lead (Pb) halides have been considered to be one of the most promising materials for high performance PSCs as the rapid development of power conversion efficiency (PCE) from 3.8% to 22.1% was witnessed in the past seven years [1–10].

The Pb-based perovskites were demonstrated to offer several appealing advantages such as intensive broad-band absorption, high charge carrier mobility and long charge diffusion length [11–13]. However, the commercialization of PSCs is still facing serious challenges, for instance, stability in ambient environment, intrinsic toxicity and anomalous hysteresis [14–20]. Apparently, the utilizing of lead halides could create seriously toxicological issues, which would inflict damage upon both human and environment [21–23]. Therefore, developing lead element substitution technology in PSCs without sacrificing the performance should be paid more attention.

Generally, the formula for widely-used perovskites is ABX_3 (A: $CH_3NH_3^+$ (MA^+), $CH(NH_2)_2^+$ (FA^+), Cs^+ , B: Pb^{2+} , Sn^{2+} ; X: Cl^- , Br^- or I^-). The basic unit for a cubic structure perovskite is an octahedron (BX_6), in which the B cation is surrounded by halide anions. The relative ion sizes determine the crystal structures and their electrical physical properties due to the structure distortions [24]. There has an empirically predicted Goldschmidt's tolerance rule to estimate the dimensions for perovskites: $t = (R_A + R_X) / \sqrt{2} (R_B + R_X)$ (where R_A , R_B and R_X are the ionic radii of A, B and X, respectively). For a high-symmetry cubic 3D perovskite, the ideal t should be in the range between 0.813 and 1.107, while low-dimensional derivatives (2D: layered, 1D: chain-like, 0D: isolated) would be generated when the t beyond this range [25–27]. The structural dimensionality has been used as one essential factor to evaluate the performance of photovoltaic materials, as it critically affects to the transport of carriers.

However, evaluation by only the structural dimensions is not adequately applicable to all photovoltaic materials. Xiao et al. introduced electronic dimensionality, which helps to understand the photovoltaic properties by describing the connectivity for the lower conduction band (LCB) and upper valence band (UVB) atomic orbitals [28]. They assumed that the electronic dimensionality, together with the structural dimensionality of the absorber materials, determined the performance of the solar cells. For instance, some materials, which exhibit structurally 3D but are electronically low-dimensional, would struggle to achieve excellent photoelectric performance. Thus, in this review, the structural dimensionality and electronic dimensionality are synthetically considered to comment on the new lead-substituted perovskites.

It has been demonstrated that the outstanding photovoltaic properties of lead-based perovskites were not only attributed to the high symmetry of structure, but also to the strong Pb 6s-I 5p anti-bonding coupling [29]. Therefore, the metal cations of Sn^{2+} , Ge^{2+} , Bi^{3+} , and Sb^{3+} , which have ns^2 lone pairs and can form octahedral structure with halogen anions, are assumed to be the candidates as lead substitution. So far, a large number of lead-substituted perovskites have been reported, and great progresses have been made in both theoretical calculations and experimental studies [30–36]. In this review, we primarily summarized recent advances of the lead element substitution in PSCs. The review can be divided into two major parts, (i) fully lead-substituted perovskites, (ii) partially lead-substituted perovskites. Concretely, theoretical calculations and experimental studies are involved to analyze the current situation and look forward to the future.

2. Fully lead-substituted perovskites

2.1. Pure-tin-halide perovskites ($MASnX_3$, $FASnX_3$, and $CsSnX_3$)

Tin (Sn) has been considered as the most promising alternative to lead, since both of them belong to the group IVA in the periodic table. Sn^{2+} has a similar radius as Pb^{2+} (Pb 1.49 Å and Sn 1.35 Å), and would cause no obvious lattice distortion after replacing/partially substituting for lead in perovskites [37]. Note that the Sn-containing perovskites were demonstrated not completely non-toxic due to the intrinsic instability, which may result in decom-

position into unstable products SnI_2 , and further immediate decomposition into HI (the acidifier), along with toxicologically inactive oxygenated Sn precipitates [22]. This problem can be mitigated by enhancing the stability of Sn-based perovskite solar cells. Besides, Sn is much easier cleared away from human body than Pb, with the data that tin is less than 400 days in contrast to that the lead is more than 20 years [38]. Taken together, Sn-based perovskites have the certain competitiveness than lead-based perovskites in the environmental aspects. Therefore, the pure-tin-halide perovskites have been widely researched as lead-free perovskites for a long time. The structural and electrical properties for the pure-tin-halide perovskites have been extensively studied by first-principles electronic structure calculations with density functional theory (DFT) and GW methods [39–54]. For the $MASnI_3$, a direct band gap of 1 eV–1.3 eV at the Γ point is in good agreement with the experimental values [39,40,55]. Compared to $MASnI_3$, the $FASnI_3$ has a more suitable band gap of 1.41 eV and a single stable phase over a broad temperature ranging up to 200°C [56]. Furthermore, it is found that the oxidation of Sn^{2+} to Sn^{4+} can be slowed down when the MA^+ organic cation was replaced by FA^+ [46]. Cs^+ is another frequently-used inorganic A cation. It was demonstrated that $CsSnX_3$ possesses higher hole mobility, and lower exciton binding energy (0.1 or 18 meV) than the conventional $MAPbI_3$ (30 meV) [50,51]. In addition, the 3D-orthorhombic $CsSnI_3$ perovskite is a p-type semiconductor with favorable bandgap of 1.3 eV and high optical absorption coefficient (10^4 cm^{-1} comparable to $CH_3NH_3PbI_3$) [52]. However, the $CsSnX_3$ was demonstrated to be a unique temperature-dependent phase-transition material that exhibited four polymorphs [53,57,58]. The transitions were caused by Cs^+ cation migration and the plasticity of the Sn–X–Sn angle [54].

The charge transport and recombination, doping densities, carrier lifetimes, mobilities and diffusion length of $MASnI_3$ were comprehensively studied. Noel et al. investigated the transient photo-induced THz response and determined that the mobility is $1.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and the diffusion length is 30 nm (Fig. 1a) [59]. Ma et al. obtained the long carrier diffusion lengths for electrons ($279 \pm 88 \text{ nm}$) and holes ($193 \pm 46 \text{ nm}$) by broadband transient absorption and time-resolved fluorescence spectroscopy (Fig. 1b). In addition, SnF_2 doping increased the life time by a factor of 10 and the diffusion length exceeded 500 nm [60]. Parrott et al. found that the carrier lifetime was significantly improved and the PL line width was drastically reduced at the temperature below $\sim 110 \text{ K}$, which implied that the phase transition from orthorhombic to tetragonal resulted in hindered solar cell performance (Fig. 1c) [61].

The power conversion efficiency (PCE) of pure-tin-halide PSCs is still much lower than that of pure-lead-halide PSCs [59,62–82]. Compared with Pb-based perovskites, the Sn-based perovskites have a lower crystallization barrier and solubility which enable that they can even be crystallized at room temperature [83]. In order to slow down the rapid crystallization rate, Kanatzidis and co-authors proposed a transitional $SnI_2 \cdot 3DMSO$ intermediate complex [63]. The crystal structure of intermediate compound $SnI_2 \cdot 3DMSO$ and the schematic of crystallization dynamic process of $MASnI_3$ perovskite thin film are shown in Fig. 2(a). The $SnI(DMSO)_3^+$ ions was linked by the lone I^- ions, and fractured by the MAI introduction. Additionally, they employed a low-temperature vapor-assisted solution process (LT-VASP) to prepare $MASnI_3$ thin films (Fig. 2b). The as-prepared thin film was proved to have lower doping level than that of films prepared by the conventional one-step method. Afterward, they reported that the low hole-doping level in the LT-VASP $MASnX_3$ films may be attributed to the excess Sn^{2+} compounds introduced by outgrowth of SnO and $Sn(OH)_2$ [64,65]. They also used a multi-channel inter diffusion deposition process to prepare the $FASnI_3$ thin film, as the schematic shown in Fig. 2(c) [66]. FAI was dissolved in PEDOT:PSS aqueous solution and

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