



Overview of Tin-Based Perovskite Solar Cells Stoichiometry and Energy Band Gap

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Abstract. Lead-free perovskites, especially Tin (Sn) based, have gained significant attention as promising candidates for solar cell applications due to their lower toxicity and potential for eco-friendly energy solutions. However, challenges such as precursor toxicity, complex film deposition methods, and instability in ambient conditions remain key obstacles to their broader adoption. This review provides an overview of the working principles of perovskite solar cells, emphasizing how stoichiometry affects the band gap in Sn-based perovskites. We aim to guide researchers in selecting optimal stoichiometric compositions for developing efficient and stable solar cells.

Keywords: photovoltaics, perovskite, stoichiometry, tin solar cell, energy band gap

1. Introduction

Achieving net-zero carbon emissions is a global priority, with clean energy sources like solar power playing a crucial role in reducing reliance on fossil fuels[1]. Perovskite solar cells (PSCs), where the perovskite material consist of ABX_3 stoichiometry (A is a large cation such as methylammonium (MA) formamidinium (FA) and Cesium (Cs); B is a smaller cation such as tin (Sn) and lead (Pb); and X is an anion such as halide (X)), have shown significant promise in this context (Fig. 1a) [2]. Lead (Pb)-based PSCs have demonstrated remarkable performance, with a certified maximum power conversion efficiency (PCE) of 26.1%[3-5]. However, Pb toxicity poses serious health risks, as reported by the Joint Food and Agriculture Organization of the United Nations (FAO)/WHO Expert Committee on Food Additives (JECFA) and the Institute for Health Metrics and Evaluation (IHME)[6, 7]. In 2017 alone, Pb exposure contributed to over one million deaths and 20 million disability-adjusted life years (DALYs)[8, 9]. Consequently, global regulatory bodies, including the European Union, have advocated for the reduction or complete elimination of Pb in electronic products[10].

To address these concerns, researchers have found tin (Sn) is the most promising candidate due to its electronic configuration ($[\text{Kr}] 4d^{10}, 5s^2, 5p^2$), ionic radius (Sn^{2+} : 118

pm), and coordination geometry (trigonal pyramid), which closely resemble those of lead [11]. Additionally, Sn-based perovskites offer several advantages, including low exciton binding energy, high absorption coefficients, long carrier diffusion lengths, high carrier mobility, and robust defect tolerance, making them strong candidates for solar cell applications [11]. However, despite a theoretical PCE of 33%, Sn-based PSCs (Sn-PSCs) have so far achieved only around 15% in practice [12, 13]. The main limitation arises from challenges like rapid oxidation and fast crystallization of Sn, leading to defects, uncontrollable film morphology, and instability in air or moisture. With Sn existing in two oxidation states (Sn^{2+} and Sn^{4+}), the slightly unstable Sn^{2+} easily oxidizes to Sn^{4+} [3, 4]. This oxidation enhances conductivity and mobility due to self-doping but also accelerates the degradation of perovskite crystals into tin halide [3, 4]. Proposed solutions involve optimizing the chemical composition of the perovskite layer, finding new interlayer materials, and advancing deposition techniques.

The development of the first Sn-based perovskite material by Fisher et al. in 1974 marked a significant milestone, followed by a comprehensive investigation led by Donaldson's research group [14]. Subsequently, Yamada et al. introduced the first hybrid Sn-based perovskite, which was further explored by Mitzi and colleagues through studies on dimensional reduction and the structural properties of these materials under pressure [15, 16]. These foundational discoveries have driven substantial research interest in Sn-PSCs. In 2014, Kanatzidis et al. reported the first Sn-PSCs with an efficiency of 6.4% in 2014, sparking a surge in studies exploring Sn for PSC applications [17].

This review offers a foundational overview of the working principles of PSCs, the impact of stoichiometry on the energy band gap and stability in Sn-PSCs. We also review the mixed cationic Sn-PSC including three-dimensional (3D), two-dimensional (2D), and quasi-2D–3D structures. This review article aims to guide readers in selecting the appropriate stoichiometry while developing solar cells.

2. Working principle of the perovskite solar cell

The operation of PSC begins with the absorption of photons (light) by the perovskite layer, which is sandwiched between charge transport layers and electrodes. When photons are absorbed, excitons (electron (e^-) — hole (h^+) pairs) are generated. Due to the low exciton binding energy in perovskite materials, these excitons quickly dissociate into e^- and h^+ . The electrons move to the conduction band (CB), while the holes remain in the valence band (VB) of the perovskite layer. These separated charges are then collected through the anode and cathode, with electrons transported via the electron transport layer (ETL, n-type material) and holes via the hole transport layer (HTL, p-type material), resulting in the flow of current, as illustrated in Fig. 1b. Eventually, PSCs architecture can broadly be divided into two categories: regular (conventional) and inverted architectures. When the perovskite active layer is deposited on an n-type material, it is called a conventional architecture. However, when it is deposited on a p-type material, it is known as an inverted PSC architecture.

3. Stoichiometry and band gap of Sn-based perovskite

Tin perovskites with a single organic cation, such as MA (methylammonium, CH_3NH_3), FA (formamidinium, $\text{CH}_3(\text{NH}_2)_2$), and Cs (cesium), are often used in both regular and inverted Sn-PSCs (Figure 1c). Methylammonium (MA) and formamidinium (FA) are

called A site cations. According to the literature, these perovskite structures can be further stabilized by using a mixed cation approach, which combines the advantages of various cations while minimizing their disadvantages[18].

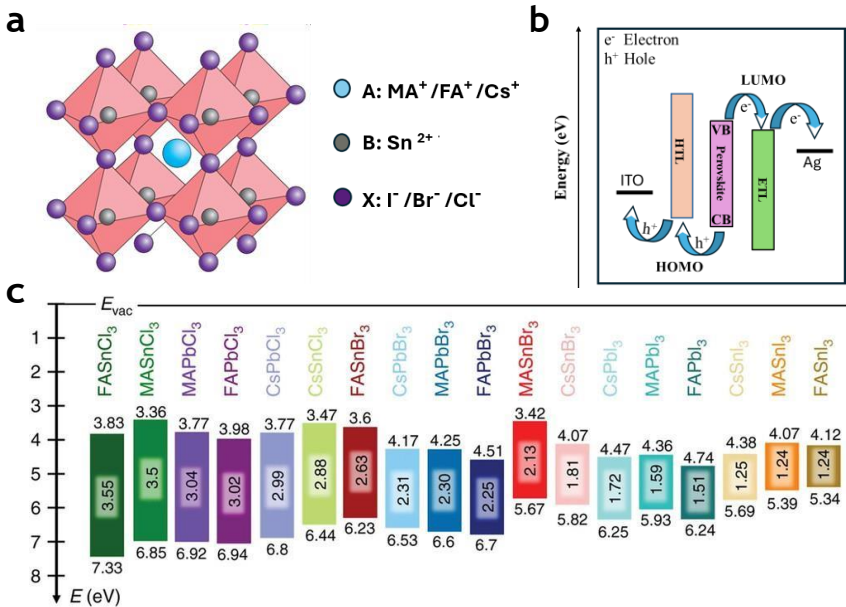


Fig. 1. (a) General structure of tin (Sn)-perovskite in a cubic (α) crystal arrangement (Adapted with permission of reference [2b]), (b) Energy diagram for an inverted perovskite solar cell (PSC), and (c) Energy levels for different Sn-based perovskite stoichiometric combinations (Adapted with permission [25]).

Various crystalline phases commonly observed in perovskite materials are cubic (α , where lattice parameters, $a = b = c$, and the angles between the lattice parameters (θ) are 90°), tetragonal (β , where $a = b \neq c$, and $\theta = 90^\circ$), and orthorhombic (γ , where $a \neq b \neq c$ and $\theta = 90^\circ$). The structural arrangements of these phases of perovskites vary with temperature and each exhibits unique properties affecting the material's overall properties in various applications. To optimize device performance, it is crucial to understand and control these phase transitions in perovskites, since phase stability affects the durability and efficiency of materials especially in solar cells, where phase transitions lead to changes in energy band gaps and thereby light absorption properties.

3.1 Single Cation

In single-cation perovskites, methylammonium tin iodide (MASnI_3) was the first to be used for Sn-PSCs, as reported by Snaith et al. in 2014[17]. The structure of this compound is similar to that of widely studied methylammonium lead iodide (MAPbI_3). The α -phase of MASnI_3 is produced using a hydroiodic solution approach. This phase has a low charge concentration of $1 \times 10^{14} \text{ cm}^{-3}$ and a conductivity of about $5 \times 10^{-2} \text{ S cm}^{-1}$, resulting in high electron mobility of up to $2000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Its bandgap of approximately 1.3 eV is narrower than that of MAPbI_3 (around 1.5 eV), which is beneficial for single-junction solar cells[19]. The bandgap of MASnI_3 can be adjusted by incorporating different halides, ranging from 1.30 to 2.15 eV, as seen in methylammonium tin bromide (MASnBr_3). However, β and γ phases of MASnI_3 , which appear at low temperatures, can lead to self-doping (increased conductivity).

These phases are also sensitive and susceptible to environmental factors, making MASnI_3 thermodynamically unstable[17].

The FA cation is often used to replace MA to enhance the performance of Sn-based PSCs. FASnI_3 , which is stable at room temperature, can adopt two main crystal structures: orthorhombic and cubic. With a bandgap of about 1.4 eV, FASnI_3 is narrower than Pb perovskites but wider than MASnI_3 [17]. Its bandgap can be fine-tuned with different halides, such as formamidinium tin iodide bromide (FASnI_2Br) (1.68 eV) and FASnBr_3 (2.40 eV). This FASnI_2Br is a mixed-halide perovskite where the 'A' site is occupied by FA^+ cation, the 'B' site is by Sn^{2+} , and the 'X' sites are by a mixture of I^- and Br^- anions. By adjusting the ratio of I to Br, the material's properties can be tuned. In this mixed halide approach, lattice parameters, band gaps, and other material properties can vary. The introduction of Br reduces carrier density by decreasing Sn vacancies, which leads to fewer defects, longer charge lifetimes, and improved performance in Sn-based PSCs. While FASnI_3 has similar thermal stability to MASnI_3 , its conductivity is lower. Finally, cesium tin iodide (CsSnI_3) is notable for its excellent air and thermal stability. Its stable lattice phases: cubic, tetragonal, and orthorhombic; contribute to its robust performance. The material CsSnI_3 exhibits similar optical and electrical properties to MASnI_3 , and its bandgap can be tuned from 1.3 to 1.7 eV with the addition of Br and chlorine (Cl)[20].

3.2 Mixed cations

A mixed-cation perovskite is one in which the 'A' site in the general formula ABX_3 is occupied by more than one cation. This approach aims to improve the material's stability, tunability and performance, which are crucial for applications such as solar cells. In 2016, Liu et al. introduced a mixed-cation Sn perovskite ($\text{MA}_{0.9}\text{Cs}_{0.1}\text{SnI}_3$). Their unoptimized inverted Sn-PSCs achieved a PCE of 0.33%, with a short-circuit current density (J_{sc}) of 4.53 mA cm^{-2} and a voltage (V_{oc}) of 0.22 V[21]. Similarly, Bian et al. used a mixed-organic-cation perovskite $(\text{FA})_x(\text{MA})_{1-x}\text{SnI}_3$ in inverted Sn-based PSCs[22]. They found that varying the ratios of MA and FA affected the perovskite film's crystallization and absorption, with band gaps tunable from approximately 1.26 to 1.36 eV. This adjustment improved film morphology and reduced charge recombination, leading to a PCE of 8.12% and a V_{oc} of 0.61 V for the $(\text{FA})_{0.75}(\text{MA})_{0.25}\text{SnI}_3$ PSCs. Han et al. developed $\text{Cs}_{0.2}\text{FA}_{0.8}\text{SnI}_3$ with an amorphous-polycrystalline structure, enhancing charge extraction and transport, and achieved a certified PCE exceeding 10%[23]. Subsequently, Loi et al. created a 2D-quasi-2D-3D Sn perovskite film by mixing 2D Sn perovskite with 0.92 M of 3D FASnI_3 for inverted p-i-n Sn-based PSCs, resulting in a PCE of 9.0%[24]. Tuning the A cations and X-anions in perovskite stoichiometry affects the crystal structure, bandgap, optical absorption, electrochemical properties, and stability of PSCs. Understanding this stoichiometry is crucial for advancing perovskite photovoltaics.

4. Future prospect and summary

In this review, we summarize the properties of Sn perovskites across three main aspects: different A-site cations, mixed cations, and various X-site halide ions. This article also discusses their crystal structures, energy levels, and impact on performance of Sn-PSCs. Currently, Pb-free perovskites (e.g., Sn based) are emerging as promising candidates for solar cell applications. Sn-based perovskites, in particular, are being extensively researched due to their lower toxicity and similar properties to Pb

perovskites. However, challenges related to oxidation (Sn^{+2} to Sn^{+4}), scalability and stability have limited their efficiency to below 15% so far. To improve these materials, researchers should focus on discovering new monovalent cations that can enhance crystal phase stability, provide thermodynamic stability, and offer self-defect passivation. This approach could improve both the stability and performance of Sn-based perovskite solar cells (Sn-PSCs).

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Disclosure of Interests.

The authors declare no competing interests.

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