

Understanding the Methylammonium Chloride-Assisted Crystallization for Improved Performance of Lead-Free Tin Perovskite Solar Cells

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In the quest for perovskite materials with reduced toxicity, Sn perovskites are emerging. However, they suffer from material instability and rapid crystallization, leading to high defect densities in the films. In this work, the methylammonium chloride (MACl)-assisted crystallization as a route to improve stability and optoelectronic quality of quasi 2D/3D $\text{PEA}_{0.08}\text{FA}_{0.92}\text{SnI}_3$ perovskite is demonstrated. For an optimal additive amount (10 mol%), a 37% increase in power conversion efficiency is found. Notably, MACl enhances the films' stability, evidenced by temporal PL tracking. Understanding the effect of MACl addition in this system is interesting for the pursuit of efficient and stable tin-based devices. The investigations show that MACl addition causes a shift in the optical bandgap and improves morphology, indicating effects in the bulk crystal structure. X-ray photoelectron spectroscopy confirms the presence of Cl on the surface, but no indication of MA^+ is found. Intriguingly, UV photoelectron spectroscopy shows pronounced changes in the density of states. For the first time, it is shown that MACl promotes the formation of a two-dimensional layer via the surface accumulation of PEA^+ . The MACl additive lowers the absorber's ionization energy, possibly facilitating hole extraction. Overall, this work highlights a facile route to control the crystallization of Sn perovskites.

defect tolerance and a low defect density, and solution-based low-temperature compatible fabrication.^[6–8] The development of PSCs has so far been focused mainly on lead-based perovskites, which raise toxicity concerns and might hinder their commercial deployment.^[9–11] Although strategies for the leakage prevention of toxic Pb adducts have been explored,^[12,13] Pb-free alternatives are highly desirable due to environmental and regulatory concerns.^[14,15]


Various alternatives have been explored to replace toxic Pb such as germanium (Ge),^[16] antimony (Sb),^[17] bismuth (Bi),^[18] copper (Cu),^[19] and tin (Sn). Among these, Sn-perovskites are, to date, the most promising choice as they offer a narrow bandgap of 1.2–1.4 eV^[20] that renders them suitable as top cells in tandem cell configurations, low exciton binding energy, and a high electron mobility.^[21–24] Nonetheless, Sn-based PSCs have inherent critical issues that currently hamper their performance compared

to their Pb counterparts. First, the strong tendency of Sn^{2+} to oxidize to Sn^{4+} results in p-type doping, which contributes to a high defect density and instability for this class of perovskites. Second, the fast and difficult-to-control crystallization of Sn perovskite thin films that leads to pinholes in the film. Third, prompt material degradation is induced by atmospheric oxygen and water.^[25–27] Several strategies are currently being investigated to improve device performance and stability of Sn perovskites. These include the addition of reducing agents into the precursor solution or in

1. Introduction

Perovskite solar cells (PSCs) have reported a certified power conversion efficiency (PCE) of 26.1%, which is achieved by controlling composition and crystallization kinetics of the perovskite absorber layer and optimizing the device heterojunctions to ensure minimal losses during charge extraction.^[1–5] Perovskite materials offer strong absorption, tunable bandgaps from violet to the near-infrared part of the electromagnetic spectrum, high

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