

Short Communication

Preparation of Air Stable Lead-free CsSnI₃ Perovskites: Synthesis Based on CsI and SnCl₂ Solutions

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Abstract

Objective: This study focuses on the synthesis and analysis of the morphology of CsSnI₃ crystals and films based on CsI (Cesium Iodide) and Tin(II) chloride (SnCl₂) solutions. The aim of this approach is to synthesize air-stable perovskites and prevent phase transitions of tin-containing perovskite, where previous studies have often reported its rapid oxidation when dissolved in dimethyl sulfoxide.

Methods: CsSnI₃ crystalline films were obtained from CsI and SnCl₂ solutions, in which deionized water and ultrapure ethanol were used for their dissolution. Dissolution and mixing were performed at room temperature. High-purity CsI (99.99%) and SnCl₂ (99.99%) powders were used to obtain solutions. To obtain a homogeneous CsSnI₃ solution, the SnCl₂ solution was added dropwise to the CsI solution and stirred on a magnetic stirrer at 900rpm. The resulting solution was then applied to Fluorine-doped Tin Oxide (FTO) substrates heated on a hotplate without spin coating. The samples were heated to temperatures from 60°C to 130°C, where, depending on the rate of evaporation of the liquid, the process of formation of crystalline and thin-film structures was controlled.

Results: Stable CsSnI₃ films were obtained. Scanning electron microscope (SEM) and X-ray diffraction analyses of the obtained cesium tin triiodide films deposited on conventional FTO glass substrates were performed. X-ray diffraction patterns of synthesized perovskite crystals and films were obtained.

Conclusion: The synthesized CsSnI₃ perovskite thin films retained their black perovskite phase for more than 4 months, indicating their long-term stability. Based on the results and long-term stability performance, it can be concluded that the black phases of CsSnI₃ are suitable for various applications such as photovoltaic devices.

Keywords: lead-free perovskites, perovskite stabilization, stability, band gap, solar cells, perovskite solar cells, photovoltaic technology

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1 INTRODUCTION

In recent years, solar photovoltaic technology has been developing rapidly, and to advance in this field, it is always necessary to develop high-efficiency devices based on affordable and cost-effective materials^[1]. Including CdTe, CIGS, amorphous Si, monocrystalline Si, GaAs, organic photovoltaic cells, graphene solar cells and other functional materials have found wide applications in the field of photovoltaics, but each particular material is characterized by its own disadvantages, including toxicity, shortcomings of the original site, disadvantages technological process of panel fabrication, etc^[2]. As is known, the 21st century has acquired the name of the century of silicon, but all such despite the laudable characteristics of this material there are some shortcomings. For example, silicon-based solar cells have been found to have a number of drawbacks including cost, correlation of efficiency with weather conditions, space requirements, pollution problems, rigidity and high manufacturing costs^[3]. In addition, pure silicon-based materials have long since reached the theoretical limit of Schottky efficiency^[4]. Therefore, in current technologies, new types of photovoltaic devices are associated with sensitized solar cells such as quantum dots and perovskite solar cells. Among them, perovskite solar cells have the advantage of low manufacturing cost and structurally regulated materials. Recently, perovskite solar cells, called “third generation solar cells”, have emerged and have been widely promoted as economically and environmentally viable and renewable technologies compared to conventional solar cell technologies to solve global energy, safety and environmental problems^[5]. Moreover, the latest perovskite solar cells can convert energy with up to 26.7% efficiency^[6]. Recently, a theoretical achievement of over 46% efficiency of solar inverters based on perovskite materials by focusing with a light lens in a small photovoltaic cell has been reported^[3]. Among materials with perovskite structure (ABX₃, where A is an organic or inorganic cation that coordinates with 12X anions, B is a divalent metal that coordinates with 6X anions, and X is a halide ion^[7]), FAPbI₃, MAPbI₃, CsPbI₃, and other lead-containing perovskites have shown good efficiency as it is committed in recent studies. However, the presence of toxic lead makes us think about replacing the B position with another element that does not strongly affect on the perovskites bandgap. The conversion efficiency of solar cells depends on the optical properties of materials, the so-called ability to absorb light, which, in turn, strongly depends on the bandgap width of the materials. It is known that halide perovskites of the CsSnX₃ family can be a suitable candidate to maximize the absorption ability. However, the presence of tin in the perovskite matrix makes them thermally unstable at temperatures closer to normal conditions. The most stable perovskites with tin content, such as CsSnCl₃ and CsSnF₃ have large band gaps, so the actual task is to develop new

methods of synthesis and stabilization of CsSnI₃, CsSnBr₃ or Sn-containing stable perovskites with shifted halogen compositions with optimal bandgap.

In this work, we report the preparation of stable crystals and thin films with perovskite structure by solution reaction of Cesium Iodide (CsI) (99.99%) and Tin(II) chloride (SnCl₂) (99.99%) containing salts.

2 EXPERIMENTAL METHODOLOGY

To obtain clean surfaces, the substrates were cleaned in 4 steps using an ultrasonic bath. Washed glass substrates of 2.5×2.5cm were used for perovskite coating. The first washing step is carried out for 10 minutes using distilled water (with the addition of liquid soap). The process is then repeated with distilled water without soap (10min). The substrates are then washed in ultrapure acetone (99.99%) and isopropanol (99.99%), each of which also takes 10min. After evaporation of the residual isopropanol, the substrates are cleaned by Ultraviolet (UV) light in a UV-OZONE cleaning device for 30min. After sufficient cleaning of the substrate, the preparation of thin film coating solutions was proceeded. A method for forming a CsSnI₃ film on a substrate, comprising the following steps:

(a) providing a substrate → (b) providing a homogeneous solution of CsSnI₃ → (c) depositing droplets of the homogeneous CsSnI₃ solution on the substrate → (d) heating the substrate after step (c) to remove the solvent in the homogeneous CsSnI₃ solution until the substrate is dry → (e) forming a CsSnI₃ film on the substrate.

The method of claim 1, wherein steps (a)-(c) are performed under ambient conditions; steps (d) and (e) is performed at a temperature in the range of from about 50°C to about 90°C in a heating plate.

In the first step, a CsI solution is prepared, which is a CsI solution with a concentration from about 40% by weight obtained by completely dissolving CsI powder in deionized water (Figure 1). A SnCl₂ solution containing from about 30% by weight of SnCl₂ solution is then prepared by completely dissolving SnCl₂ powder in ethyl alcohol (Figure 1). During the reaction, HCl is released from the solution as a gas. We then prepared a homogeneous CsSnI₃ solution by adding the SnCl₂ solution dropwise to the CsI solution. The CsSnI₃ solution was then stirred in a magnetic stirrer at a speed of 900revolutions/min to obtain the homogeneous CsSnI₃ solution. During the mixing process, the color of the clear SnCl₂ and CsI solutions first turns black and then yellow. Then, the obtained yellow solution was deposited directly on glass substrates heated in a hot plate without performing spin-coating procedure.

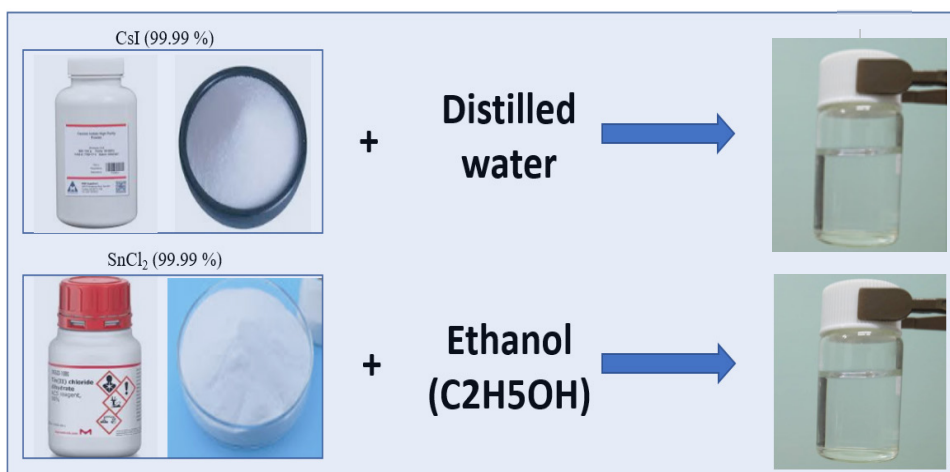


Figure 1. Scheme of preparation of CsI and SnCl₂ solutions.

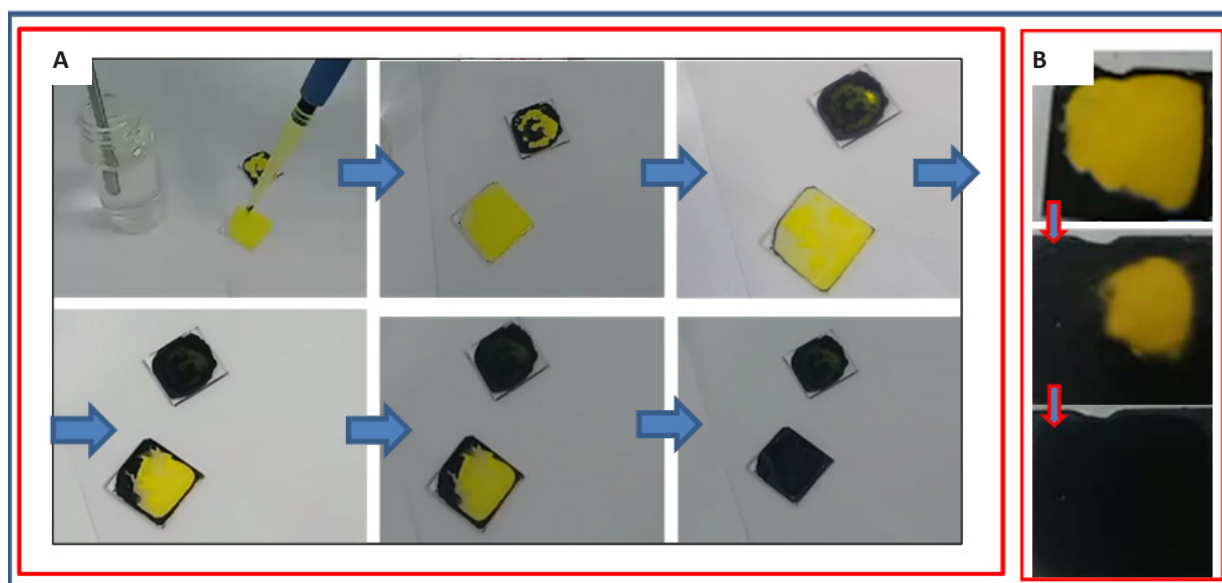


Figure 2. Snapshots of the process of formation of perovskite crystalline films at 60°C (A) and thin films at the 130°C (B).

3 RESULTS AND DISCUSSION

After obtaining a homogeneous solution, the films were deposited on glass substrates directly on the heating plate without the spin coating procedure. Figure 2 shows snapshots of the sintering process of CsSnI₃ films and their color change upon heating at a constant temperature of 60°C.

It can be seen that after heating, a black film with a mesoporous morphology with an ordered internal structure and rhombic crystallites is formed on the surface of the glass substrate (Figure 3A-3E). The results of X-ray diffraction (XRD) analysis of the obtained samples using a Dron 2 diffractometer are shown in Figure 3E.

However, when the temperature was increased to 130°C, a radical change was noted (Figure 2B): the resulting crystals became more agglomerated, forming a thin-film structure, the results of SEM analysis of which are shown in Figure 4A and 4B at magnifications of 3,500 and 7,500 times. Despite the fact that in all previous works the authors report about instability of this perovskite structure, the samples obtained by us retain the black phase of perovskite for more than 4

months and only some samples partially change color to yellow. However, for many samples obtained using this methodology, no changes have yet been detected.

It should be noted that since we did not have an XRD machine, X-ray structural analysis of the obtained samples was carried out only after 2 days.

4 CONCLUSIONS

We successfully synthesized crystalline thin films of perovskite CsSnI₃ by a simple method of mixing CsI and SnCl₂ solutions. According to the results, it can be seen that this technique can be used to obtain very stable structures of CsSnI₃, however, it is necessary to repeated experiments with different ratios of salts and solvents, with step-by-step temperature adjustments to optimize the morphology and thickness of the initial thin film.

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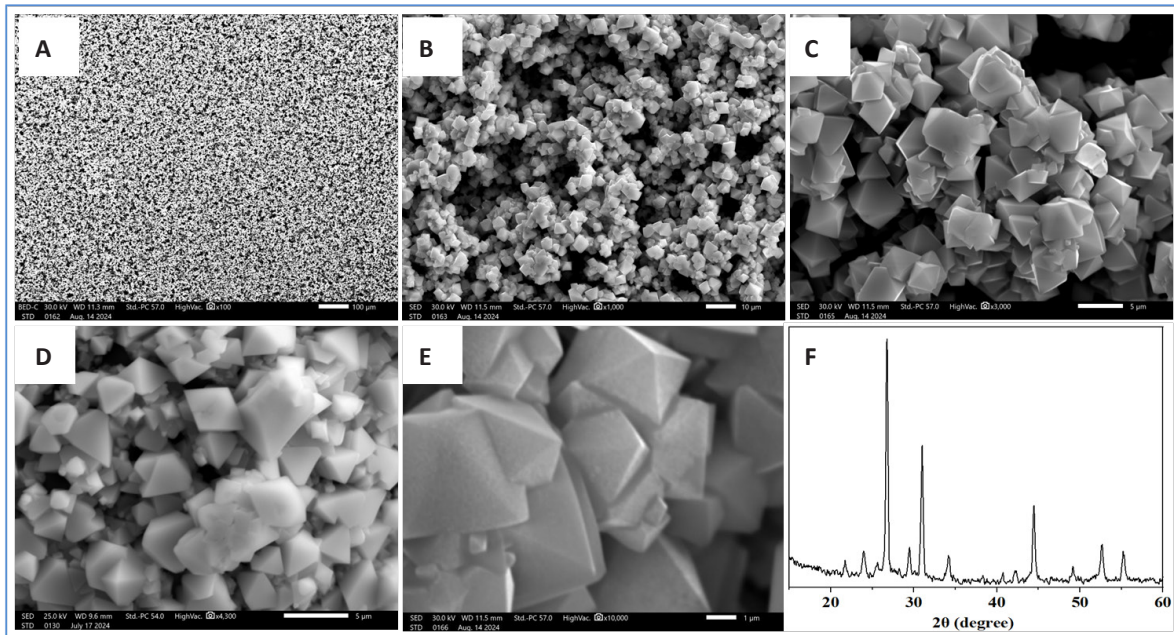


Figure 3. SEM images of the obtained samples after (A) 100, (B) 1,000, (C) 3,000, (D) 5,000 and (E) 11,000 times magnification.

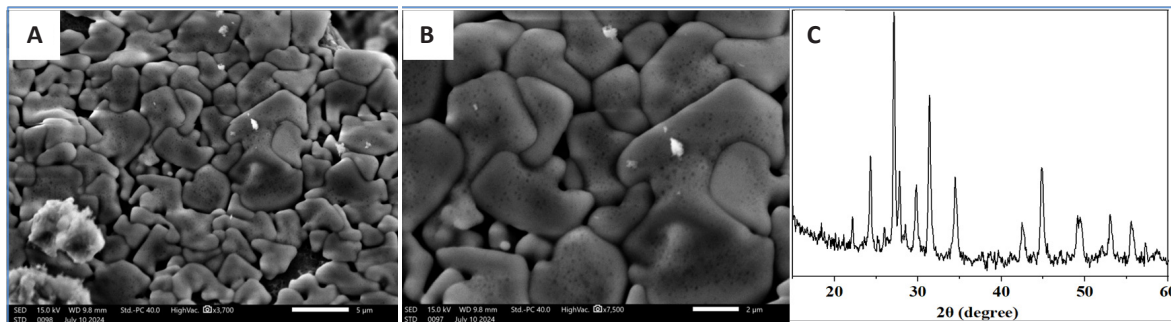


Figure 4. SEM images of crystalline perovskite films (A, B) and their X-ray diffraction patterns (C).

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Conflicts of Interest

The author declared no conflict of interest.

Author Contribution

Dilshod N was responsible for the project management, funding acquisition, supervision and resources. Amondulloi B was responsible for curating data and software. Dilshod N and Amondulloi B was responsible for the method and investigation. Kholmurodov K was responsible for the validation. Anushervon A was responsible for formal analysis. Dilshod N and Kholmurodov K was responsible for writing-review and editing. All authors have read and agreed to the published version of the manuscript.

Abbreviation List

CsI, Cesium Iodide
FTO, Fluorine-doped Tin Oxide
SEM, Scanning electron microscope

SnCl₂, Tin(II) chloride
UV, Ultraviolet
XRD, X-ray diffraction

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