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Effect of preparation rotation speed on structural properties of $CH_3NH_3PB1\text{-}xSnxCl_3$ using spin coating methods

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Abstract – *Perovskite-based hybrid organic-inorganic solar cells that use the methylammonium lead tri-iodide ($CH_3NH_3PbI_3$) have demonstrated ever-increasing energy conversion efficiency and low processing costs, comparable to that of high-efficiency silicon-based solar cells. However, it is suffuring from instability caused by material degradation. Recently, enhancing stability and hence decreasing the degradation process of $CH_3NH_3PbI_3$based solar cells is one of the main topics of research in photovoltaic field. The poor stability of these cells prevents their commercialization despite their huge potential that exceeds conventional solar cells. The energy efficiency and economic viability of Perovskite cells depend primarily on the rate of degradation caused by light, temperature, moisture, and oxygen. This paper presents a review of different degradation sources of $CH3NH3PbI_3$-based Perovskite solar cells (PSCs). In this work, a deposition of a $CH_3NH_3PB1\text{-}xSnxCl_3$ Perovskite layer using spin coating method has been investigated. Therefore, different rotation speed have been used in layer spin coating phase to find out their effects on structural parameters characteristics of the resulting $CH_3NH_3PB1\text{-}xSnxCl_3$ organic/inorganic Perovskite material.*

Keywords: Structural properties, Perovskite films, Spin coating, $CH_3NH_3PB1\text{-}xSnxCl_3$.

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I. Introduction

Renewable energy research is increasingly focused on developing cost-effective and efficient alternatives to traditional fuel sources. Perovskite materials, particularly the hybrid organic-inorganic methylammonium lead triiodide ($MAPbI_3$), have emerged as promising candidates for photovoltaic applications. Various deposition methods, such as spray pyrolysis, and the impact of processing conditions such as temperature on film properties are crucial to optimize solar cell performance. These studies explore the effects of these factors on the optical and morphological characteristics of $MAPbI_3$ films and their implications for improving power conversion efficiency. Additionally, simulation tools and alternative Perovskite materials, such as methylammonium tin triiodide ($MASnI_3$), are used to further improve the efficiency and stability of solar cells [1-5].

The study examines how humidity, annealing temperature, and deposition methods (single-step, sequential deposition, and hot casting) affect the morphology of Perovskite layers. Optimal deposition conditions are identified, revealing that humidity and annealing temperature significantly influence crystal shape and size. In the one-step method, increasing humidity from <10% to ~40% changes the fiber morphology from ribbon-like to hollow fibers, while higher annealing temperatures reduce the fiber diameter. The hot casting technique produces a compact, flat layer with fewer pinholes. Perovskite cells from sequentially deposited $CH_3NH_3PbI_3$ crystals show the highest efficiency (4.8%), but are less stable over time than those

from the one-step method due to humidity-induced degradation [6].

Other study compares brush coating and spin coating for deposition of 0.1 M precursor solution onto glass substrates in solar cell production. Brush coating used a fibril brush and thermal annealing at 180°C for 1 minute, while spin coating was performed at 1000 rpm for 10 seconds. EDAX confirmed the presence of stannic oxide and XRD revealed a tetragonal SnO_2 structure. SEM showed better surface morphology for the spin-coated films, but the brush-coated films had improved morphology and crystallinity compared to previous research. The optical and electronic properties were similar between the two methods, with slight differences in the bandgap and edge potentials. The main disadvantage of brush coating was the surface morphology, which can be addressed through optimized coating and heat treatment [7].

$CsPbI_2Br$ Perovskite solar cells face challenges related to rapid crystallization, small grain size, and poor light absorption due to their wide bandgap. This study presents a double spin coating (PTS) process incorporated with $PbAc_2$ to address these issues. The addition of $PbAc_2$ delays crystallization, leading to thicker, denser films with fewer defects. The $CsPbI_2Br$ PTS device achieved peak power conversion efficiency (PCE) of 16.19% and maintained 96.7% of its initial PCE for 1,500 hours at room temperature and 25% relative humidity without encapsulation [8].

Investigation explores the effects of precursor concentration, spin coating speed, and substrate temperature on $(BA)_2FA_2Pb_3I_{10}$ films. Using thiourea in the precursor solution, films and solar cells were fabricated with different spin deposition speeds (1000 rpm to 6000 rpm) at a constant concentration (0.25 M) and varying concentrations (0.1 M to 1 M) at a constant speed (4,000 rpm). The results showed that the optical properties and film morphology were stable with spin deposition speed, but higher concentrations of precursors improved the out-of-plane alignment and domain size. The best power conversion efficiency (PCE) of 7.5% was achieved with a 0.25 M solution at 4000 rpm on a room temperature substrate, demonstrating the high efficiency and robustness of $(BA)_2FA_2Pb_3I_{10}$ for solar cells [9].

Search evaluates brush and spin coating methods for SnO_2 electron transport layers using XRD, UV-Vis-NIR, and SCAPS-1D simulations. The results highlight that bandgap engineering significantly improves device efficiency. Simulations showed a 5% increase in bandgap with the synthesized material, improving efficiency. Physical and simulation analyzes indicate that brush coating is effective for large-scale perovskite solar cells. The simulated brush-coated device achieved a current density (Jsc) of 21.6 mA/cm² and an efficiency of 17.20%, approaching that of spin-coated devices [10].

This research improves the stability of $CsPbBr_3$ Perovskite solar cells using a modified multi-step spin-coating method. By adding low concentrations of CsBr and $PbBr_2$ in two additional steps, we create a $PbBr_2$ layer with fewer pinholes and better crystallinity, leading to a high-quality $CsPbBr_3$ film with larger grains and defects reduced interface. This process increases energy conversion efficiency from 5.43% to 9.36%, and unencapsulated devices remain stable for over 2,400 hours in ambient air [11].

Scientific article examines $CH_3NH_3PbI_{3-x}Br_x$ Perovskites deposited on FTO-coated glass by spin coating. We explored the effects of substituting PbI_3 for $PbBr_3$ on structural and optical properties, noting that increased Br content shifts the structure from tetragonal to cubic and widens the bandgap. Device simulations showed that the optimal Br composition resulted in a tandem solar cell with a short circuit current density (Jsc) of 38.81 mA/cm², an open circuit voltage (Voc) of 1 .54 V, a fill factor (FF) of 73.32 %, and power conversion efficiency (PCE) of 43.84% [12].

Scientific research presents a modified two-step sequential spin coating method for Perovskite solar cells, addressing the low solubility of Cs salts in isopropanol. Using a mixed ethanol/methanol solvent to dissolve CsI, FAI, and MACl, we optimized the solvent ratio to improve solubility. This approach produces high-quality $FA_{1-x}Cs_xPbI_3$ Perovskite films with large crystals, low defect density, and long carrier lifetime. The optimized cells achieved power conversion efficiencies of 21.17% (0.1 cm²) and 14.65% (0.25 cm²), providing a promising method for fabricating efficient FA/Cs mixed Perovskite solar cells [13].

Investigation examines the impact of precursor solution concentration on the formation of bromide-based Perovskite ($Cs_{0.05}MA_{0.10}FA_{0.85}PbBr_3$) thin films using in situ optical measurements during spin coating. We find that variation in concentration affects film morphology and optoelectronic quality. Higher concentrations result in delayed nucleation and slower growth kinetics, with the formation of more pre-organized colloids and higher coordination lead-bromide complexes. These results highlight the concentration of precursors as a key factor in optimizing the deposition of thin Perovskite films [14].

Efficient CsFAMAPbIBr Perovskite solar cells typically require controlled environments due to the instability of formamidinium (FA) ions in humidity. This study

explores the impact of static and dynamic spin-coating methods on the fabrication of ambient air-processed CsFAMAPbIBr films and their photovoltaic performance. Different coating methods result in variations in film composition and morphology, influencing Ostwald ripening and ion exchange. Dynamic spin-coated films achieve higher power conversion efficiency (PCE) of 19.70% compared to 16.01% for static spin-coated films, demonstrating the benefits of dynamic coating to improve performance and stability of solar cells [15].

In recent research on thin-film photovoltaics, Perovskite solar cells (PSCs) have become a major topic, achieving efficiencies of around 26%. However, commercialization is limited by lead toxicity, organic cation instability and structural problems. To address these challenges, various inorganic materials, including hole transport layers (HTL), have been explored. This study focuses on MoO3 thin films as a potential HTL for lead-free PSCs. We fabricated MoO3 thin films and characterized them using XRD, FESEM, EDX, UV-Vis, and Hall Effect measurements. We designed a lead-free PSC structure with FTO/MoO3/PTAA/(FA)2BiCuI6/ZnO/Ag and performed numerical simulations using SCAPS-1D. Our simulations, based on the optoelectric properties of MoO3, predict a maximum efficiency of approximately 22.28% for lead-free PSC [16].

In this work, a deposition of a $CH_3NH_3PB_{1-x}Sn_xCl_3$ Perovskite layer using spin coating method has been investigated. Therefore, different rotation speed have been used in layer spin coating phase to find out their effects on structural parameters characteristics of the resulting $CH_3NH_3PB_{1-x}Sn_xCl_3$ organic/inorganic Perovskite material.

II. Methodology and Experimental details

II.1. Materials synthesis

Figure 1 shows the preparation steps for **$CH_3NH_3PB_{1-x}Sn_xCl_3$**.

Step 1: Precursor Solution Preparation

1. Mixing of Salts:
   - Materials Needed:
     - Lead(II) chloride ($PbCl_2$)
     - Tin(II) chloride ($SnCl_2$)
     - Solvents: Dimethylformamide (DMF), isopropanol, and Dimethylsulfoxide (DMSO)
   - Procedure:
     1. Dissolve the desired amounts of $PbCl_2$ and $SnCl_2$ in a mixture of DMF, isopropanol, and DMSO. The exact volumes and ratios will depend on the target concentration and the desired Pb/Sn ratio.
     2. Stir the solution at 70°C for 3 hours to ensure complete dissolution and formation of a homogeneous precursor solution. This step helps to fully dissolve the salts and integrate them into the solvent mixture.
3. Formation of CH_3NH_3Cl:
   - Addition of Methylammonium Chloride:
     - Dissolve methylammonium chloride (CH_3NH_3Cl) in a suitable solvent (often the same solvent mix as above) and then combine it with the lead/tin chloride solution.
     - Stir this combined solution at 70°C to allow complete reaction and mixing.

Step 2: Solution Homogenization

1. Agitation:
   - Temperature:
     - Maintain the solution at 60°C.
   - Duration:
     - Agitate the solution for 2 hours.
   - Purpose:
     - This step ensures that the solution is homogeneous and that all the components are well-mixed, resulting in a consistent precursor solution suitable for spin coating.

Step 3: Spin Coating

1. Spin Coating Process:
   - Application:
     - Dispense the homogeneous precursor solution onto the center of the substrate (e.g., glass or ITO-coated glass).
   - Spin Speeds:
     - Perform spin coating at different speeds (2000 rpm, 2500 rpm, 3000 rpm). Each speed will affect the thickness and uniformity of the deposited film.
   - Spin Time:
     - Typically, spin-coating is done for about 30-60 seconds.
2. Thermal Processing:
   - Annealing:
     - After spin coating, the film is subjected to thermal processing.
     - Heat the coated substrate at 150°C for thermal annealing. This step helps in forming a uniform Perovskite layer and improving the film's crystallinity and morphology.
     - Annealing time can vary, but it is usually around 10-30 minutes.

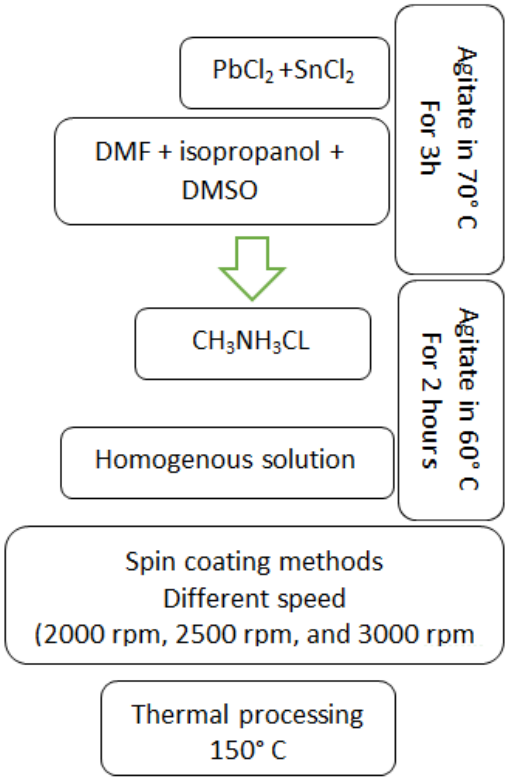

Figure 1. Solar still during the experiment

III. Results and discussion

III.1. Structural analysis

Figure 2 shows the XRD diffraction patterns of **$CH_3NH_3PB_{1-x}Sn_xCl_3$**. Films prepared at different speed ration. We have observed the appearance of both many from peaks (101), (110), (111), (310), (200), (221), (311) and (312) of Perovskite films, respectively. These peaks indicate the formation of cubic Perovskite structure as illustrated in literature. The intensity of the tow (Pbcl2 +Sncl2) peaks show ((311) and (312)) at all spectrum range at (2000 rp) films as shown in Figure 3.

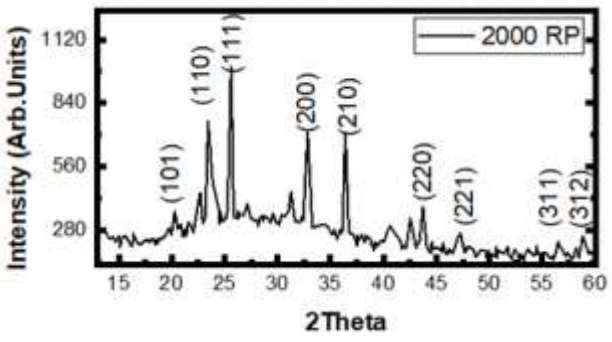

Figure 2. XRD diffraction patterns of **$CH_3NH_3PB_{1-x}Sn_xCl_3$** (2000 rp)

While the (311) and (312) intensity disappears completely from the film at (2500rp and 3000rp) due to the decreases of rotation speed which may react with residual from mix (Pbcl2 +Sncl2) as shown in Figure 4. The strongest peaks manifested in the case of the Prepared Perovskite film sample are sharp, indicating its high crystallinity. Also, peaks of (tin +chloride) become very weak at a deposition when films (2500rp and 3000rp) is heated at 150°C, which may be considered an adequate way to form high- CH3NH3PB1-xSnxCl3 stability and the best crystallization

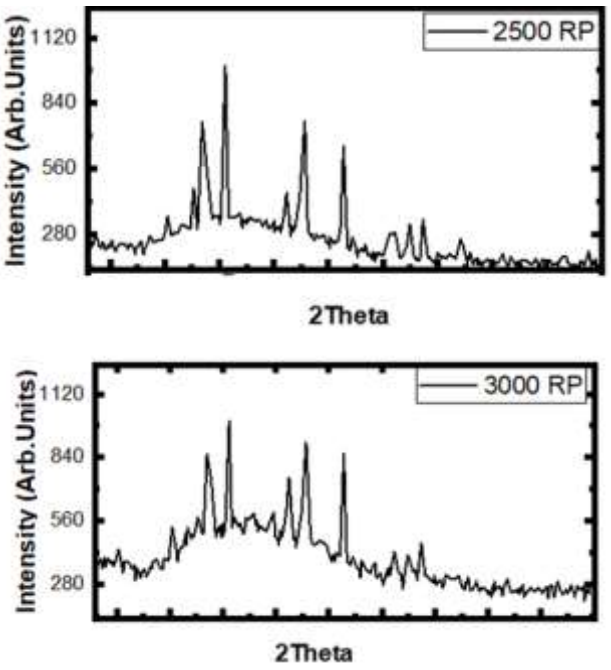

Figure 3. XRD diffraction patterns of **$CH_3NH_3PB_{1-x}Sn_xCl_3$** (2500 and 3000rp)

Table 2 summarizes various parameters including d_{hkl}, 2θ, lattice parameters, and crystallite size for all different substrates types of Perovskite films. The inter-reticular distance d_{hkl}, lattice parameters (*a* and *c*), crystallites size *D*, stress *μ*, and Miller indices (*hkl*) of the Perovskite product at different rotation speed was determined from the obtained most intense peaks (101), (110), (111), (310), (200), (221), (311) and (312) For the diffraction lines of weaker intensity, we can say that this is due to the preferential orientation, which is a factor that influences the intensity of certain peaks. There are also many other factors, such as crystal size and deformation, and the extinction of peaks in some special directions due to coherent subtraction.

Table 2. Various parameters

Perovskite $CH3NH3PB_{1-x}Sn_xCl_3$	(hkl)	2θ (°)	Calculated d(Å)	Lattice parameters a=b=c(Å)	Crystallite size (nm) from XRD D_{nm}
2000rpm	101	20.295	4.372	5.738	35.8133411
	110	23.445	3.791		
	111	25.595	3.477		
	200	32.835	2.725		
	210	36.395	2.467		
	220	43.715	2.069		
	221	47.265	1.922		
2500rpm	101	20.265	4.378	5.7417	38.33831652
	110	23.445	3.791		
	111	25.565	3.481		
	200	32.835	2.725		
	210	36.375	2.468		
	220	43.655	2.072		
	221	47.105	1.928		
3000rpm	101	20.235	4.385	5.7379	38.9744227
	110	23.505	3.782		
	111	25.585	3.479		
	200	32.845	2.725		
	210	36.395	2.467		
	220	43.695	2.07		
	221	47.235	1.923		

For the cubic Perovskite, the inter-reticular distance d_{hkl} and the lattice constants a and c, are determined by the following expressions:

$$2d\sin(\theta) = n\lambda \tag{1}$$

and

$$\frac{1}{d_{hkl}^2} = \frac{1}{a^2}(h^2 + k^2) + \frac{l^2}{c^2} \tag{2}$$

Where λ = 1.054 Å is the wavelength of cooper K_α, β is the full width at half medium in (rd), and θ is the diffraction angle in (°), whereas k is taken 0.9. a and c are the lattice parameters, (hkl) are the Miller indices of the planes and d_{hkl} is the inter-planar spacing. The crystallite size can be calculated using the Scherer's equation given by:

$$D = \frac{k\lambda}{\beta\cos\theta} \tag{3}$$

IV. Conclusion

The study investigates the impact of spin-coating speed on the crystallinity and stability of CH3_33NH3_33 Pb1−x_{1-x}1−xSnx_xxCl3_33 Perovskite films, as evidenced by XRD diffraction patterns. The films prepared at 2000 rpm exhibit prominent peaks corresponding to the Perovskite structure, specifically (101), (110), (111), (310), (200), (221), (311), and (312), confirming the formation of a cubic Perovskite phase. However, as the spin-coating speed increases to 2500 rpm and 3000 rpm, the intensity of the (311) and (312) peaks decreases, suggesting a reaction with residual PbCl2_22 + SnCl2_22 and a potential alteration in film composition. Despite this, the films prepared at higher speeds show sharper and more intense peaks overall, indicating improved crystallinity. Heating the films at 150°C further reduces the intensity of tin chloride peaks, suggesting enhanced stability and better crystallization of the Perovskite phase. The analysis of crystallographic parameters, such as inter-reticular distances, lattice constants, and crystallite sizes, reveals that the spin-coating speed significantly influences these properties, thereby affecting film quality. Overall, optimizing spin-coating parameters is crucial for achieving high-quality, stable Perovskite films with desirable crystallographic properties.

Declaration

- The authors declare that they have no known financial or non-financial competing interests in any material discussed in this paper.
- The authors declare that this article has not been published before and is not in the process of being published in any other journal.
- The authors confirmed that the paper was free of plagiarism.

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