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Article

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Controlled Crystallization of Lead-Free Cs₃Bi₂I₉ Perovskite Nanocrystals *via* Continuous-Flow Ligand-Assisted Re-precipitation

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Abstract

Wide band-gap Bismuth (Bi)-based perovskites, specially Cs₃Bi₂I₉ are getting much attention in lead (Pb)-free perovskite solar cells (PSCs) due to their tuneable bandgap. However, process optimization plays a key role in controlling the film quality and the performance of PSC. Hence, a new strategy to improve crystallization and thin film quality is equally important to developing efficient PSC. Herein, an attempt was made to prepare the Bi-based Cs₃Bi₂I₉ perovskites *via* the ligand-assisted re-precipitation approach (LARP) at controlled residence times using a flow reactor is carried out. The physical, structural, and optical properties of perovskite films deposited, and PSCs photovoltaics performance were investigated. The synthesized Cs₃Bi₂I₉ perovskites gives bandgap values of 1.8 eV. Cs₃Bi₂I₉-based PSCs fabricated based on the device architecture of FTO/TiO₂/Cs₃Bi₂I₉/Spiro-OMeTAD/Ag. The device exhibited the considerable power conversion efficiency (PCE) of 0.5% followed by a corresponding increase in fill factor (FF) of 77.6%, open circuit voltage (V_{oc}) of 0.73 V and current density (J_{sc}) of 4.9×10^{-2} mA cm⁻².

Keywords: *Cs₃Bi₂I₉, energy Conversion, flow reactor, ligand-assisted re-precipitation approach, perovskite solar cell*

1.0 Introduction

Third generation photovoltaic technology of perovskite solar cells (PSCs) is emerging due to its high efficiency, low-cost materials, and simple fabrication. The active layer of PSCs is typically composed of halide perovskites with the general formula ABX_3 [1, 2], in which A stands for a monovalent cation (such as methylammonium (CH_3NH_3^+), formamidium ($\text{NH}_2\text{CHNH}_2^+$), or cesium (Cs^+) ions), B is a divalent cation (such as lead (Pb^{2+}), tin (Sn^{2+}), or germanium (Ge^{2+}) ions), and X is a halide ion (chloride (Cl^-), bromide (Br^-), or iodide (I^-) ion) [3, 4]. Since first being introduced in 2009, PSCs have grown quickly, and as a result, power conversion efficiencies (PCEs) have increased from 3.8% to over 26% [2, 5-7], matching or even surpassing numerous thin-film alternatives and classic silicon-based solar cells. However, the commercialization of PSCs is hindered by the toxicity of Pb and the poor moisture stability of organic cations. Consequently, considerable research efforts have been directed toward the development of lead-free, stable light-harvesting materials that can provide both environmental sustainability and long-term device performance. [8-11]. Nevertheless, the substitution of Pb^{2+} with less hazardous metal ions, such as Sn^{2+} , Ge^{2+} , and Sb^{3+} pose hurdles due to the oxidation instability of Sn- and Ge-based perovskites (Sn^{2+} to Sn^{4+} and Ge^{2+} to Ge^{4+}) [12-16] and the high-temperature fabrication needs of Sb-based perovskites [17-19]. On the other hand, bismuth (Bi^{3+}) has been widely recognized as a promising substitute for Pb^{2+} in all-inorganic perovskite systems, owing to its comparable electronic configuration, similar ionic radius, and superior chemical stability [20]. In addition, the presence of a stereochemically active $6s^2$ lone pair plays a crucial role in stabilizing the crystal structure, thereby enhancing the overall structural integrity and long-term stability of Bi-based perovskite materials. [14, 21-23]. These halide perovskites also found a broad application in memory devices, photovoltaics [23] and photodetectors [23, 24], due to their strong light absorption, long carrier lifetimes, tuneable bandgaps, a varies different crystal shapes, and high chemical stability [25].

In previous report on all-inorganic Bi-based perovskites, including $\text{Rb}_3\text{Bi}_2\text{I}_9$, $\text{K}_3\text{Bi}_2\text{I}_9$, $\text{Cs}_3\text{Bi}_2\text{I}_9$, and $\text{CsBi}_3\text{I}_{10}$, the cesium bismuth iodide (CBI) family-based perovskites are the most promising candidates for PSC applications attributable to its better environmental stability, low toxicity, and significant optoelectronic properties [26-30]. The bandgap and charge transport properties of CBI-based perovskites, which are primarily categorized into zero-dimensional (0D) $\text{Cs}_3\text{Bi}_2\text{I}_9$ and two-dimensional (2D) $\text{CsBi}_3\text{I}_{10}$ structures, exhibit significant variation. In general,

these lower-dimensional perovskite systems demonstrate enhanced phase stability and improved resistance to environmental degradation. [30-32]. Since the first report of $\text{Cs}_3\text{Bi}_2\text{I}_9$ -based PSCs by Park et al. in 2015, which demonstrated a PCE of 1.09%, noticeably efforts have been devoted to enhance the performance of CBI-based PSCs [33]. These previous works focused on elucidating and engineering the perovskite crystal structure as well as optimizing its optoelectronic properties. Even with recent advancements, the PCEs of CBI-based PSCs are remain below theoretical limits due to several persistent challenges, including high defect concentrations [34], limited precursor solubility [35], rapid crystallization [36], energy-level mismatches [37], and inefficient light absorption [38, 39]. Hence, it is key to have a better knowledge of the mechanics underlying CBI-based PSC manufacturing and film formation.

Although synthesis techniques such as hot-injection and ligand-assisted reprecipitation (LARP) offer precise control over the size, morphology, and crystallinity of nanocrystals (NCs), the solution-phase synthesis of $\text{Cs}_3\text{Bi}_2\text{X}_9$ NCs remains relatively underexplored[40, 41]. In contrast to the hot-injection technique, which typically requires elevated temperatures and an inert atmosphere, the LARP method is simpler and more cost-effective, involving the dissolution of precursors in a polar solvent, such as dimethyl sulfoxide (DMSO) or dimethylformamide (DMF), followed by injection into a nonpolar solvent to induce NCs formation [41, 42]. Nevertheless, the LARP approach may result in particle aggregation and reduced product yields, which can adversely affect the quality and reproducibility of the synthesized NCs [43].

Previous studies have revealed that conventional batch reactors such as three-neck flask systems may have poor reproducibility and have irregular reaction conditions upon large-scale synthesis, thus poor crystal growth, particle uniformity and film quality control could be realized [44]. To address these limitations, microscale flow syntheses have gained interest as they allow for constant operation with high specificity for precursor mixing, residence time, nucleation, and reaction kinetics [45-49]. Collectively, these advantages in the scalable synthesis of high-quality $\text{Cs}_3\text{Bi}_2\text{I}_9$ nanocrystals with better reproducibility and optoelectronic performance which are essential for photovoltaic applications [50, 51]. However, there are a few limitations remain unresolved, such as low concentration of cesium precursor, at room temperature and its impact on precursor homogeneity, crystallization behavior and device performance.

Hence, this study investigates the photovoltaic performance of $\text{Cs}_3\text{Bi}_2\text{I}_9$ solar cells fabricated *via* the LARP method using a continuous flow reactor with precisely controlled

residence times, aiming to elucidate the impact of crystallization on film quality and optoelectronic properties. Bi-based $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskites were synthesized *via* ligand-assisted re-precipitation approach (LARP) at controlled residence times using a flow reactor is carried out. During the synthesis, DMF and DMSO at (8:2 v/v) mixed solvent ratio were used in step-I microchip reactor as dissolving solvents and toluene was used in the second step-II microchip reactor to precipitate the perovskites crystals under controlled process. These fabricated solar cell devices employed the architecture of FTO/TiO₂/perovskite/Spiro-OMeTAD/Ag.

2.0 Experimental

2.1 Chemicals and Regents

Bismuth iodide (BiI_3 , 99%), cesium iodide (CsI , 99.9%), *N,N*-dimethylformamide (DMF, anhydrous, 99.8%), dimethyl sulfoxide (DMSO), titanium diisopropoxide bis(acetylacetonate) (75% in isopropanol), and chlorobenzene (anhydrous, 99.8%), *n*-butanol (99.8%, anhydrous), bis(tri-fluoromethyl) sulfonimide lithium salt (*LiTFSI*, trace metal basis, 99.95%), *tert*-butylpyridine (*t*BP, 99%), Acetonitrile (ACN, 99%, anhydrous), and 2,2',7,7'-tetrakis(*N,N*-dimethoxyphenylamino)-9,9'-spirobifluorene (Spiro-OMeTAD). All chemicals were sourced from Sigma-Aldrich and used without additional purification.

2.2 Cesium Precursor Solution

Synthesis of $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite through LARP method using flow reactor is depicted in Figure 1. A precursor solution was prepared by dissolving 1.3 mmol of CsI and 0.87 mmol of BiI_3 in 5 mL of a DMF: DMSO mixed solvent (8:2 v/v). The mixture was stirred at 35 °C for 30 minutes in a clean vial until a clear and miscible solution was formed. The resulting precursor solution was then transferred to the inlet system of flow reactor. A continuous-flow synthesis process is carried out by two separate 5 mL precursor solutions, labeled A and B, containing CsI (1.3 mmol) and BiI_3 (0.87 mmol), respectively, were loaded into inlet 1 and inlet 2 using a Harvard syringe pump. PTFE tubing from both inlets was securely connected to entrances 1 and 2 of the microchip reactor. The outlet from the step-I microchip reactor was connected to inlet 3 of the step-II reactor, while toluene (solution C) was introduced through inlet 4 as the precipitation solvent. The synthesis was conducted at 70 °C with controlled residence times (t_R) of 20 s, 40 s, and 60 s. The resulting $\text{Cs}_3\text{Bi}_2\text{I}_9$ nanocrystals were collected from the product outlet of the reactor system. The collected

nanocrystals were centrifuged at 6000 rpm for 15 minutes and washed repeatedly with toluene until a clear supernatant was achieved. Finally, the purified precipitates were filtered and dried at 80 °C for 2 hours to obtain Cs₃Bi₂I₉ perovskite nanocrystal powder.

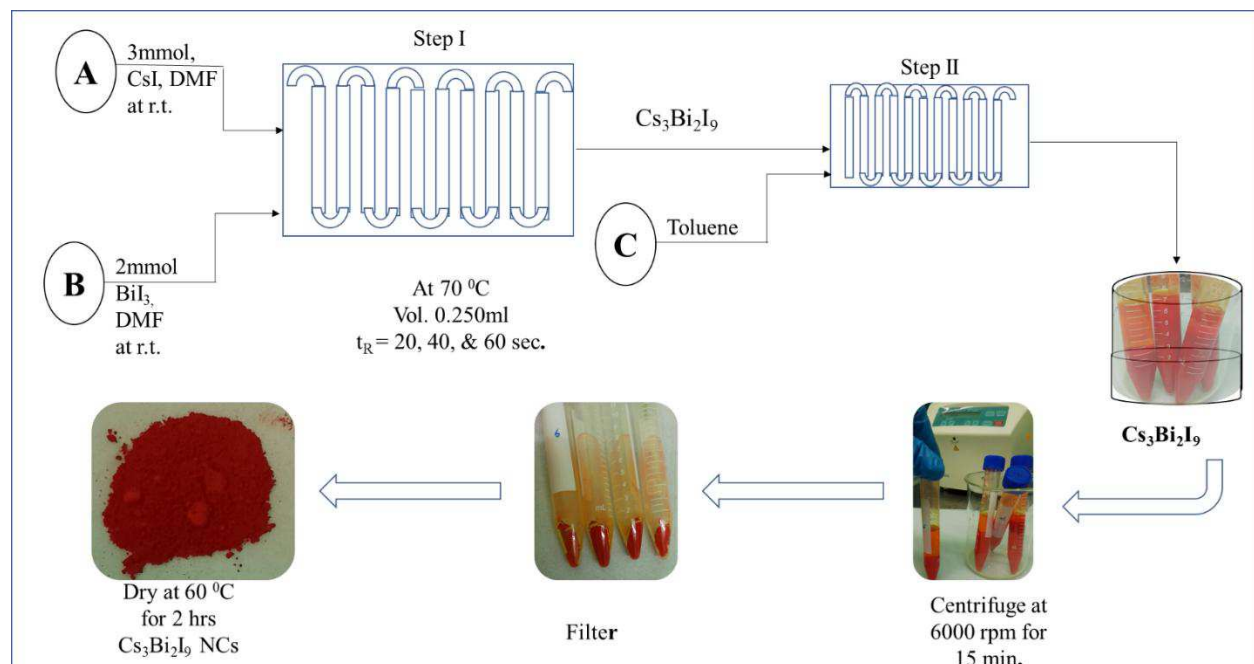


Figure 1. The schematic diagram for the synthesis process of Cs₃Bi₂I₉ perovskite through LARP method using flow reactor.

2.3 Fabrication of Perovskite Solar Cells

FTO glass substrates were cleaned with a 10% decon 90, rinsed with deionized water and ethanol for 15 min each using ultrasonic, and dried. Followed by ultraviolet-ozone (UVO) treatment for another 15 min. A homogeneous TiO₂ compact layer, functioning as the electron transport layer (ETL), was deposited onto the FTO substrate through a two-step spin-coating technique. A solution of 0.15 M titanium diisopropoxide bis(acetylacetonate) was applied, followed by spinning at 1000 rpm for 10 s, then 2000 rpm for 20 s. This spin-coating cycle was repeated twice, with a 10-min drying interval at 100°C after each cycle, ensuring a uniform film. Finally, the coated TiO₂ annealed at 500°C for 20 min to complete the sintering process and enhance film quality. The TiO₂-coated FTO was treated with UV/O₃ for an additional 15 minutes to remove organic materials and form a rough surface. The perovskite layer coated on ETL by spin-coating at 1000 rpm for 10 seconds and 5000 rpm for 20 s, followed by annealing at 120 °C for 30 min to crystallize Cs₃BiI₉. The hole transport layer (HTL) was prepared by dissolving 72.5 mg Spiro-OMeTAD in

chlorobenzene along with LiTFSI solution and *t*BP (25 μ L and 29 μ L). The HTL was spin-coated at 5000 rpm for 20 s, and finally, 80 nm silver electrode was deposited on top using thermal evaporation at 3×10^{-5} torr.

2.4 Characterization

Crystal structure of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ NCs was examined using powder X-ray diffraction (XRD) model D8 Advance diffractometer by Bruker, utilizing Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Thermal behavior of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ nanocrystals (NCs) was investigated by Jupiter simultaneous thermal analyzer (NETZSCH, STA 449 F3). Surface morphology and elemental composition of $\text{Cs}_3\text{Bi}_2\text{I}_9$ NCs were analyzed using field-emission scanning electron microscopy (FE-SEM; Quanta 250FEG). Elemental composition of the thin film was measured by using energy dispersive spectroscopy (EDS). UV–Visible–Near Infrared (UV–Vis–NIR) absorption spectra of the films were recorded with a Shimadzu UV-3600 spectrophotometer. Current-voltage (I-V) characteristics of the fabricated PSCs were measured under standard conditions using a Gamry potentiostat interface 1010 (Gamry, Warminster, PA, USA), with the effective cell area defined as 0.1 cm^2 and utilizing a non-reflective metal mask.

3.0 Result and discussion

X-ray diffraction (XRD) patterns of synthesized $\text{Cs}_3\text{Bi}_2\text{I}_9$ nanocrystal powders prepared under different residence times in a continuous flow microreactor which shown in Fig. 2(a). The diffraction peaks observed at $2\theta = 12.15^\circ, 12.8^\circ, 21.1^\circ, 24.3^\circ, 25.1^\circ, 25.8^\circ, 27.5^\circ, 29.7^\circ, 32.3^\circ, 42.1^\circ, 42.9^\circ, 45.8^\circ$, and 50.4° are corresponds to the (100), (101), (103), (105), (006), (202), (203), (204), (205), (220), (209), and (226) crystallographic planes, respectively. The diffraction pattern is in good agreement with the standard hexagonal $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite phase JCPDS card no. 97-041-0726 [52], confirming the formation of a hexagonal crystal system. The obtained peaks are belonging to the $P6_3/mmc$ space group, with lattice parameters $a = b = 8.40 \text{ \AA}$ and $c = 21.24 \text{ \AA}$. The absence of unindexed reflections in the XRD pattern confirms the phase purity of the synthesized $\text{Cs}_3\text{Bi}_2\text{I}_9$ nanocrystals, with no detectable secondary or impurity phases.

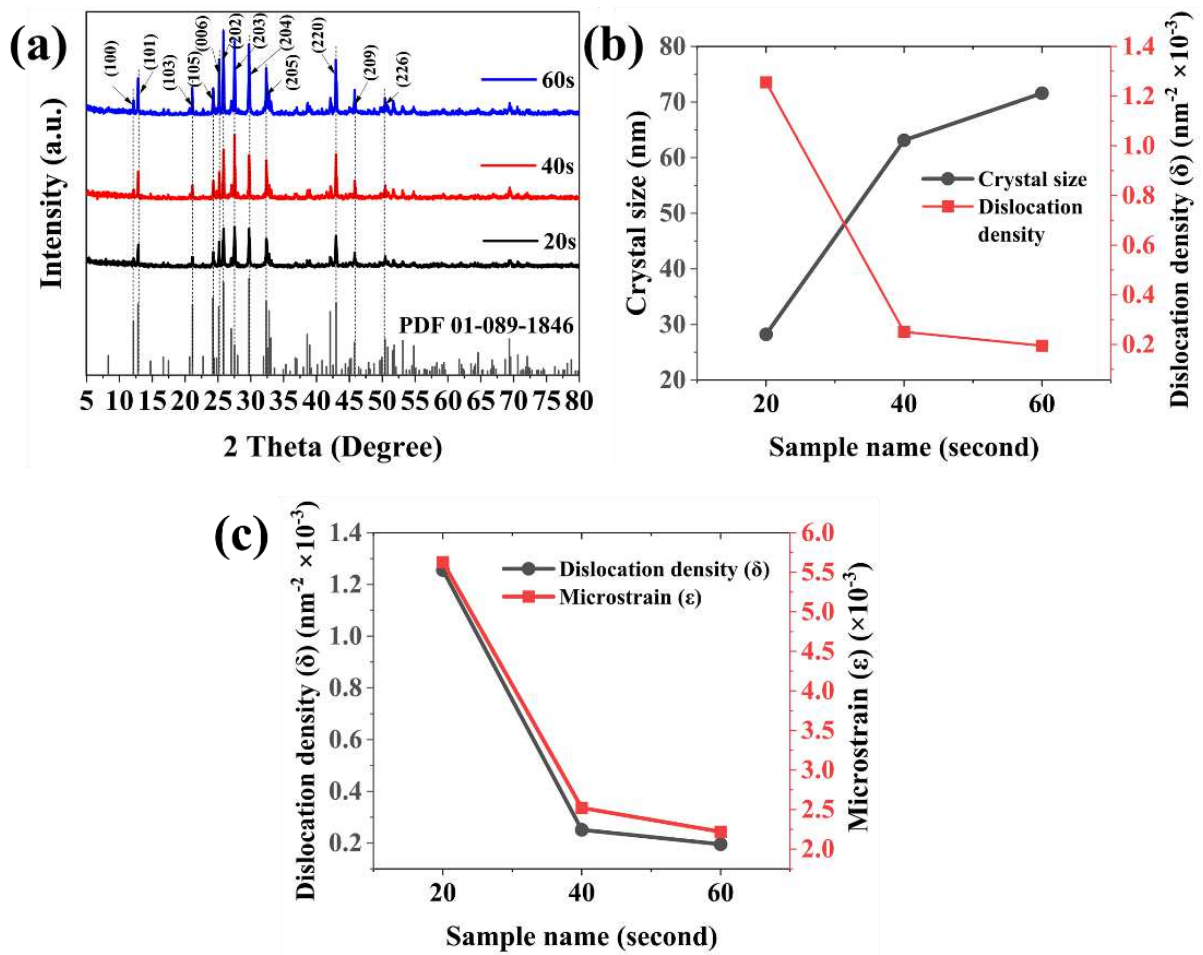


Figure 2. (a) XRD spectra of different $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite NCs powder from different residence time. (b) average size of crystals and dislocation density variation. (c) micro-strain and dislocation density.

Table 1. Comparative analysis of FWHM, crystallite size, dislocation density, and lattice strain in $\text{Cs}_3\text{Bi}_2\text{I}_9$ thin films prepared using different ink formulations.

Samples	FWHM	Crystallite size, D (nm)	Micro-strain, $\epsilon \times 10^{-3}$	Dislocation density, $\delta \times 10^{-3} (\text{nm}^{-2})$
20 s	0.29	28.22	5.63	1.26
40 s	0.13	63.11	2.52	0.25
60 s	0.11	71.58	2.22	0.20

Considering the $\text{Cs}_3\text{Bi}_2\text{I}_9$ which adopts a 0D perovskite framework composed of isolated $[\text{Bi}_2\text{I}_9]^{3-}$ bi-octahedral units formed by face-sharing $[\text{BiI}_6]^{3-}$ octahedra [53], which are separated by Cs^+ ions occupying the interstitial voids, thereby limiting electronic dimensionality and influencing charge transport characteristics. A comparative analysis of the XRD profiles reveals that residence time in the microreactor plays a decisive role in governing the crystallographic quality and microstructural evolution of $\text{Cs}_3\text{Bi}_2\text{I}_9$ nanocrystals. At the shortest residence time of 20 s, the diffraction peaks are noticeably broadened and exhibit reduced intensity, particularly for the (006) reflection at approximately $2\theta \approx 25.1^\circ$. Such pronounced peak broadening is indicative of reduced crystallite size and enhanced lattice disorder which shown Fig. 2(b), typically associated with rapid nucleation and insufficient growth time within the reaction channel. The diminished peak intensity further suggests weaker preferential orientation and incomplete structural ordering of the crystalline domains. Correspondingly, the elevated full width at half maximum (FWHM), micro-strain, and dislocation density values for the 20 s sample confirm the presence of significant lattice imperfections and internal structural distortion which shown in Fig. 2(c) and tabulated in Table 1, which are expected to adversely affect charge carrier transport and increase non-radiative recombination pathways [54].

With increasing residence time to 40 s, a noticeable sharpening of diffraction peaks is observed, accompanied by an increase in peak intensity, indicating improved crystallinity and enhanced crystal growth. This behavior suggests that extended residence time allows more complete precursor conversion and stabilizes nucleation and growth kinetics within the microreactor environment. However, despite this improvement in crystallinity, the 40 s sample still exhibits relatively higher defect-related parameters compared to the 60 s sample, implying the persistence of residual lattice strain and structural imperfections at intermediate growth conditions. The sample synthesized at 60 s residence time exhibits the most intense and sharply defined diffraction peaks, particularly for the (006) plane, reflecting good crystallinity, enhanced crystallite growth, and improved long-range periodic ordering. The significant reduction in peak broadening indicates minimized micro-strain and reduced dislocation density, confirming a substantial decrease in crystallographic defects. This structural refinement suggests that prolonged residence time facilitates more complete atomic arrangement and defect reduction within the growing lattice, leading to a more stable crystalline framework.

Although, the systematic evolution of peak broadening, intensity, micro-strain, and dislocation density with increasing residence time clearly demonstrates a transition from defect-rich, poorly ordered nanocrystals at short residence times toward highly crystalline and structurally stabilized $\text{Cs}_3\text{Bi}_2\text{I}_9$ at longer residence times. Among the studied conditions, the 60 s sample exhibits the highest structural quality, characterized by optimal crystallite growth and minimal defect concentration, which is expected to significantly enhance charge transport properties and suppress non-radiative recombination, thereby making it more suitable for high-performance optoelectronic applications [52].

Thermal behavior of $\text{Cs}_3\text{Bi}_2\text{I}_9$ was investigated using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and derivative thermogravimetry (DTG). The DSC thermogram of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite nano crystal exhibits two distinct endothermic transitions at approximately $\sim 85^\circ\text{C}$ and 271°C [55] as shown in Fig. 3(a). The first broad endothermic peak, with an enthalpy change of -7.72 J g^{-1} , is attributed to the removal of physically adsorbed moisture and residual solvent molecules weakly bound to the perovskite surface rather than a structural phase transition or decomposition. The relatively low enthalpy associated with this event suggests that only a small number of volatile species such as DMF/DMSO remains in the synthesized material, indicating effective precursor conversion during the continuous flow synthesis process. Importantly, no additional thermal transitions or decomposition-related peaks were observed up to 450°C , demonstrating that the $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite maintains good thermal stability over a broad temperature range as shown by TGA thermogram in Fig. 3(b). The absence of crystallographic phase transformations within the measured temperature window further indicates that the crystal structure remains stable under moderate heating conditions, which is advantageous for subsequent device fabrication and operation where thermal robustness is required [56].

A TGA thermogram in Fig. 3(b) shows mass of $\text{Cs}_3\text{Bi}_2\text{I}_9$ remains essentially constant up to approximately 450°C , confirming its excellent thermal stability. The absence of detectable weight loss below this temperature indicates that residual solvents, adsorbed moisture, and other volatile impurities were effectively removed during synthesis and purification of NCs, [57] consistent with the weak endothermic event observed in the DSC thermogram. These results demonstrate that the all-inorganic $\text{Cs}_3\text{Bi}_2\text{I}_9$ framework remains chemically stable under moderate thermal conditions, making it suitable for photovoltaic applications that require thermal robustness.

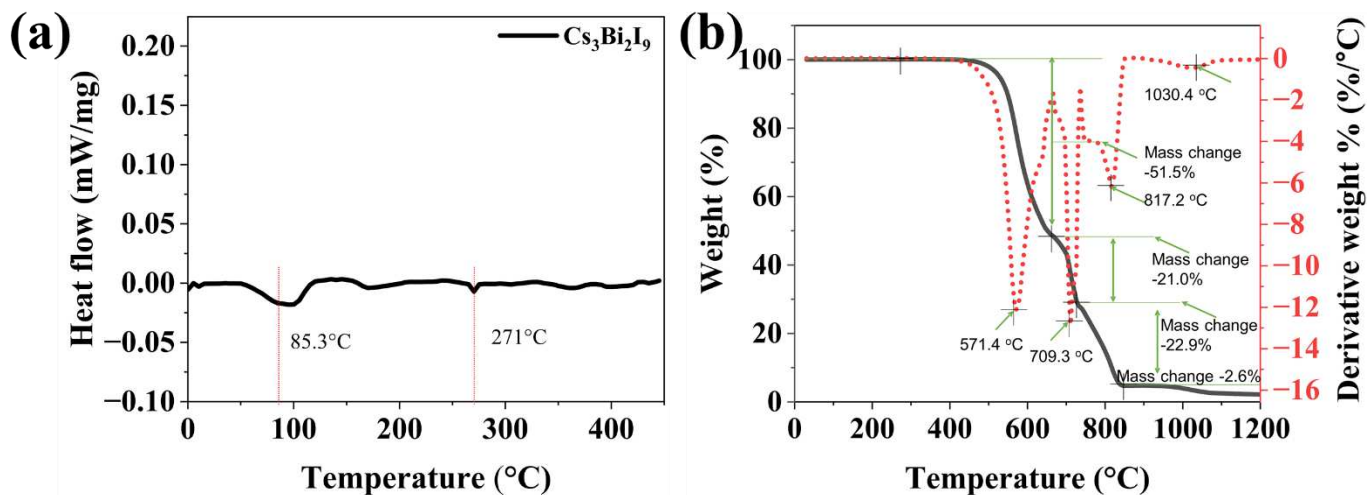
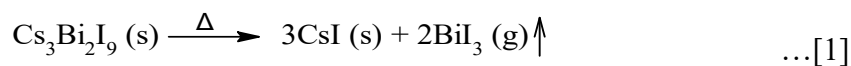


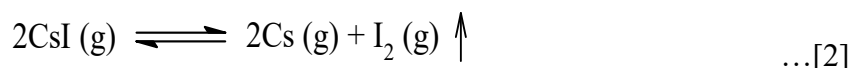
Figure 3. (a) DSC of $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite illustrating a low-enthalpy phase transition at 85.3 °C and (b) mass loss, wt.% (solid line) and obtained from thermogravimetry analysis and derivative of thermogravimetry (DTG), % min⁻¹ (dash line) illustrating the stepwise thermal decomposition pathways of $\text{Cs}_3\text{Bi}_2\text{I}_9$ up to 1200 °C.

Above 450 °C, the DTG profile reveals a multistep thermal decomposition process. The first and most significant decomposition stage occurs between approximately 450 and 660 °C, reaching a maximum decomposition rate at ~571 °C (T_{d1}) and a corresponding mass loss of ~52%. This stage is attributed to the thermal decomposition of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ lattice followed by volatilization of iodine-containing species, primarily BiI_3 , which possesses a relatively high vapor pressure at elevated temperatures. The observed mass loss suggest that decomposition proceeds progressively rather than through a single instantaneous reaction, as commonly reported for bismuth halide perovskites [58]. A convincing decomposition pathway [59] represented by chemical equation [1] below:



A second decomposition stage is observed between 660 - 750 °C, with a DTG maximum at ~709 °C (T_{d2}) and an additional mass loss of 21%. Following, the initial decomposition the perovskite framework, the remaining solid is expected to be enriched in CsI. The continued

decrease in mass is therefore attributed primarily to the volatilization of CsI as its vapor pressure increases at elevated temperatures. A third decomposition stage occurs between 750 and 860 °C, exhibiting a DTG peak at 817 °C (T_{d3}) with a further 22.9% mass loss. This stage is associated with continued evaporation of the remaining iodide-containing species and completion of the thermal decomposition process. extensive volatilization of CsI was accompanied by thermal dissociation of gaseous iodide species [60] according to the following chemical equation [2] below:



Beyond 900 °C, the TG curve gradually approaches a constant value, indicating that the major decomposition reactions have been completed. A weak DTG signal at approximately 1030 °C (T_{d4}) corresponds to only 2.6% additional mass loss, which is attributed to volatilization of trace residual inorganic species remaining after the principal decomposition steps. At 1200 °C, only approximately 2% of the initial mass remains, indicating that nearly all volatile iodide-containing constituents have been removed under the inert atmosphere.

The combined DSC, TGA, and DTG analyses demonstrate that $\text{Cs}_3\text{Bi}_2\text{I}_9$ exhibits excellent thermal stability up to approximately ~450 °C, before undergoing multistep decomposition involving breakdown of the perovskite framework and sequential volatilization of iodine-containing species. The relatively high decomposition temperatures confirmed the superior thermal robustness of $\text{Cs}_3\text{Bi}_2\text{I}_9$ compared with many hybrid organic–inorganic perovskites, highlighting its potential for photovoltaic and optoelectronic applications where long-term thermal stability is essential.

Residence time in a continuous-flow reactor governs the kinetics of nucleation and crystal growth, thereby affecting the structural and morphological characteristics of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite [58]. Field-emission scanning electron microscopy (FESEM) images of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ NCs powders synthesized at residence times of 20, 40, and 60 s are presented in Fig. 4. The sample synthesized at a residence time of 20 s Fig. 4(a) exhibited irregularly shaped particles with a broad size distribution and noticeable agglomeration, indicating that the short residence time was insufficient for complete precursor conversion and controlled crystal growth. These observations suggest incomplete crystallization and a non-uniform particle morphology. Increasing the

residence time to 40 s resulted in more uniformly distributed nanocrystals with improved particle definition and reduced agglomeration Fig. 4(b). The longer residence time allowed more complete nucleation and subsequent crystal growth, producing particles with greater morphological uniformity. At a residence time of 60 s, the $\text{Cs}_3\text{Bi}_2\text{I}_9$ NCs exhibited a well-defined nanosheet-like morphology with a more homogeneous particle distribution and reduced structural irregularities Fig. 4(c). The improved particle uniformity suggests that the longer residence time facilitated more complete crystal growth and structural ordering. These observations are consistent with the XRD results, which showed enhanced crystallinity for the sample synthesized at 60 s. Grain size analysis further confirmed the influence of residence time on crystal growth. The average particle sizes increased from 101.9 nm to 130.4 nm and 155.9 nm for the samples synthesized at 20 s, 40 s, and 60 s, respectively. This increase reflects the progressive growth and coalescence of nanocrystals with increasing residence time under continuous-flow conditions.

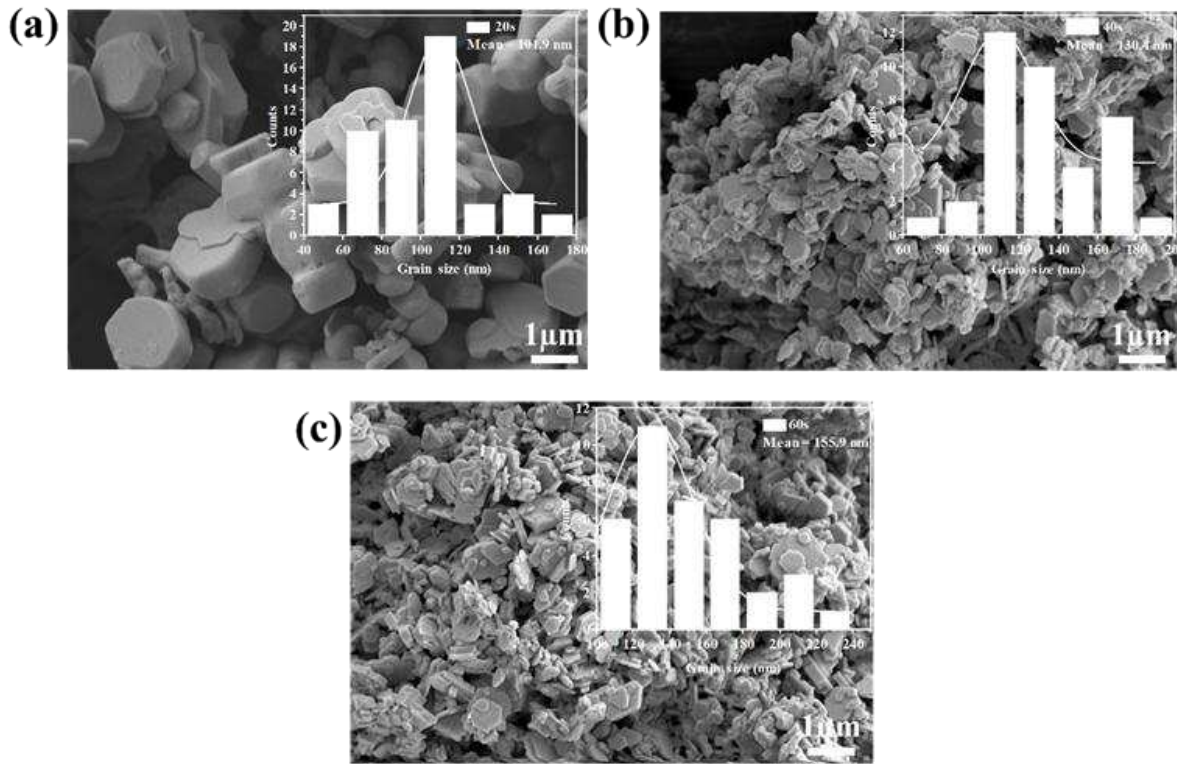


Figure 4. FESEM top-view image of perovskite $\text{Cs}_3\text{Bi}_2\text{I}_9$ nano-crystals and histogram produced with various residence (a) 20 s with residence time 20 seconds, (b) 40 s with residence time 40 seconds, and (c) 60 s with residence time 60 seconds.

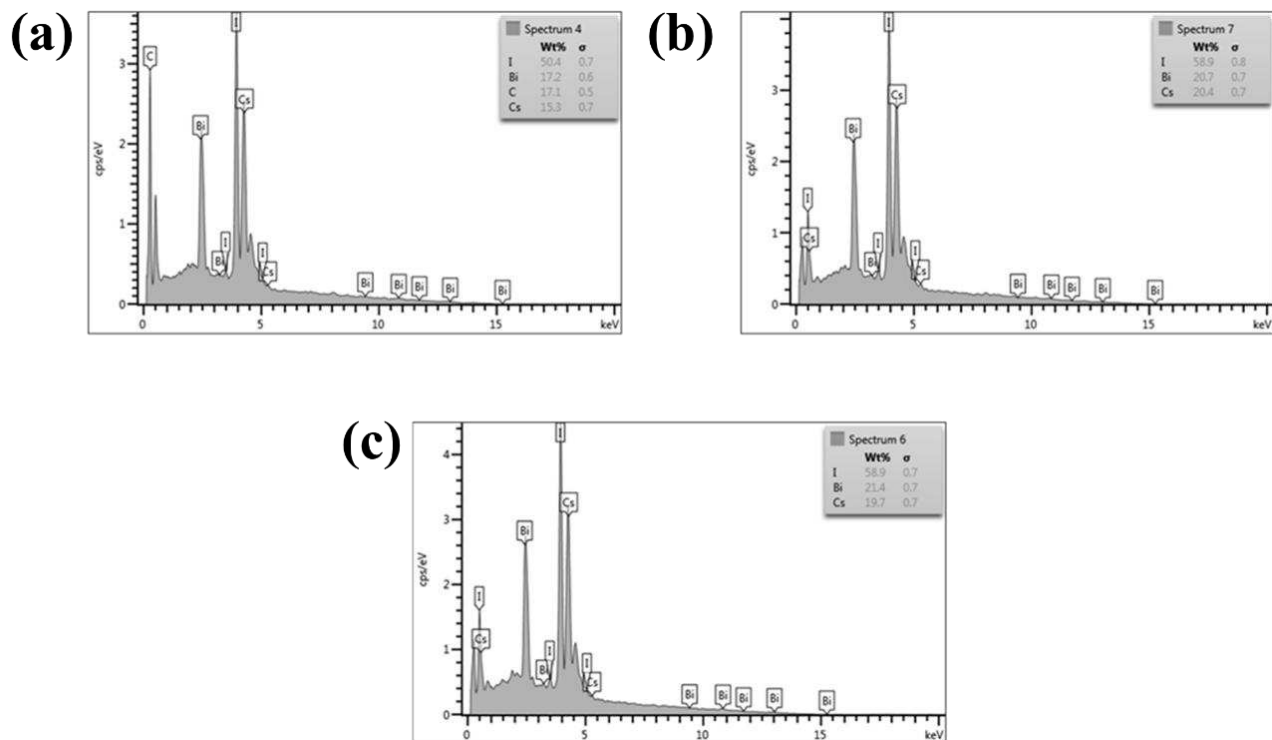


Figure 5. EDX analysis of perovskite NCs synthesized at (a) residence time of 20 seconds as 20 s, (b) residence time of 40 seconds as 40 s, and (c) residence time of 60 seconds as 60 s.

Table 2. EDX weight percentage and empirical formula analysis of $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite NCs prepared from 3 different samples.

Samples	Elements (weight %)			Empirical formula
	Cs	Bi	I	
20 s	15.3	17.2	50.4	$\text{Cs}_{1.4}\text{Bi}_1\text{I}_{4.83}$
40 s	24.4	20.7	58.9	$\text{Cs}_{1.85}\text{Bi}_1\text{I}_{4.69}$
60 s	19.7	21.4	58.9	$\text{Cs}_{1.45}\text{Bi}_1\text{I}_{4.53}$

Energy-dispersive X-ray (EDX) spectroscopy was employed to determine the elemental composition of the synthesized $\text{Cs}_3\text{Bi}_2\text{I}_9$ NCs. The theoretical elemental composition of $\text{Cs}_3\text{Bi}_2\text{I}_9$ is 20.36 wt.% Cs, 21.34 wt.% Bi, and 58.30 wt.% I. Among the synthesized samples, the composition of the 60 s sample showed in Fig. 5(c) the closest agreement with the theoretical stoichiometry, while larger deviations were observed for the 20 s and 40 s samples, which shown

in Fig 5(a) and Fig. 5(b) and tabulated in Table 2. These deviations are attributed to the semi-quantitative nature of EDX analysis and local compositional variations associated with particle morphology. Nevertheless, all samples exhibited only Cs, Bi, and I without detectable impurity elements, confirming the successful synthesis of $\text{Cs}_3\text{Bi}_2\text{I}_9$ nanocrystals

Overall, the FESEM and EDX results demonstrate that increasing the residence time from 20 s to 60 s promotes the formation of larger, more uniformly distributed, and better-crystallized $\text{Cs}_3\text{Bi}_2\text{I}_9$ nanocrystals while maintaining their chemical composition. The improved crystallinity and particle morphology of the NCs powders are expected to provide favorable starting materials for subsequent thin-film fabrication, although the morphology of the deposited thin films cannot be inferred directly from the powder FESEM observations.

Optical characteristics of perovskite $\text{Cs}_3\text{Bi}_2\text{I}_9$ thin film produced from synthesized NCs using a continuous-flow reactor at residence times of 20 s, 40 s, and 60 s, were analyzed by UV-visible spectroscopy as shown in Fig. 6(a) and the resulting Tauc plot shown in Fig. 6(b) were used to determine the optical bandgap energies and assess their optoelectronic properties. The nucleation, crystal growth, and film quality of the perovskite thin film were significantly affected by the residence time via flow reactor. As shown in Fig. 6(a) the thin film prepared at a residence time of 20 s exhibited relatively low absorbance, which indicated less precursor conversion and incomplete reaction conversion and crystallization due to the shorter reaction time inside the microchip reactor channel. As a result, leads to smaller crystal growth, suboptimal film uniformity, higher defect state density was produced, which negatively interfered the transfer of charge carriers and increased recombination losses. Moreover, the corresponding optical bandgap is relatively wide, at about 2.16 eV was observed, which indicating limited electronic delocalization effects. The absorbance intensity increased at 60 s of residence time across the visible region, near 500–530 nm, indicating improved better optical photon harvesting capabilities and improved film crystallinity. The increased time of interaction in the flow reactor leads to more extensive precursor reaction, controlled crystal growth, and improved grain connectivity, which enhanced electronic structure and decreased trap-state density. Moreover, in the 60 s sample, the lowest optical bandgap 1.90 eV showed increased electronic delocalization and more efficient charge carrier transport. The narrower bandgap and higher optical absorption indicated that a residence time of 60 s provided the optimum conditions for generation of better $\text{Cs}_3\text{Bi}_2\text{I}_9$ thin films with higher optoelectronic properties. Nevertheless, this behavior was attributed to excessive crystal growth,

grain agglomeration, and partial structural disorder at lower residence time 20 s and 40 s during the synthesis of $\text{Cs}_3\text{Bi}_2\text{I}_9$ in the microchip reactor that produced a non-uniform film, increased the recombination, decreased charge-transfer efficiency, and moderately deteriorated the optical performance as compared with the 60 s sample. Overall, the study showed that residence time in the continuous-flow reactor was a significantly influenced optical absorption, band structure, and optoelectronic properties of $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite thin film, and 60 s was most favorable condition for selective characteristics of $\text{Cs}_3\text{Bi}_2\text{I}_9$ PV thin films in the long term for optoelectronic and photovoltaic applications.

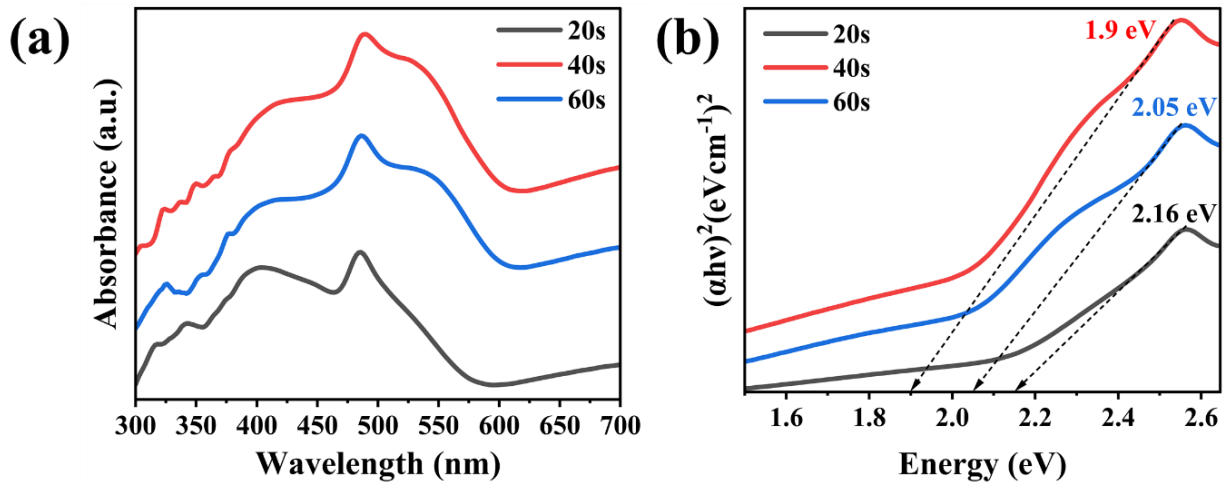


Figure 6. (a) UV-vis spectra of $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite films prepared from 20 s, 40 s, and 60 s perovskite. (b) Tauc plot of different perovskite thin film

The photovoltaic performance of $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite solar cells using Spiro-OMeTAD as hole transport material (HTM) was evaluated during various residence times 20, 40, and 60 s as shown in Fig. 7(b) and Fig 7(a) show device architecture of $\text{FTO}/\text{TiO}_2/\text{Cs}_3\text{Bi}_2\text{I}_9/\text{Spiro-OMeTAD}/\text{Ag}$. The $J-V$ characteristics indicated that the 60 s $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite absorber device displayed the best photovoltaic performance among the samples. As result, the 60 s shown an open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), and fill factor (FF) value 1.1 V, $5.22 \times 10^{-2} \text{ mA cm}^{-2}$, 64.9%, respectively along with the power conversion efficiency (PCE) of 0.52%. The optimized photovoltaic properties for the 60 s sample were due to increased recrystallization and increased film quality from the prolonged residence time of 60 s in the continuous-flow reactor. From the $J-V$ curves, the 60 s device had a better current density and a larger photocurrent

over a wider voltage range compared with the 20 s and 40 s devices. In contrast, the 20 s sample displayed a rapid decline in current density with increasing voltage which reflected poor transport charge and high recombination losses resulting from insufficient crystallization and high defect density. 40 s device exhibited intermediate photovoltaic performance indicating intermediate enhancement of crystal growth and charge transport properties. This improvement in device performance at 60 s was correlated with high crystallinity, better connectivity of the grains, a lower trap assisted recombination yielding more effective $\text{Cs}_3\text{Bi}_2\text{I}_9$ carrier formation and transfer. In addition, the above 60 s devices presented a better reproducibility coefficient and operational stability than the 20 s and 40 s devices showed, indicating that residence time was the most key factor for improving the optoelectronic and photovoltaic performance of $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite solar cells. Collectively, the result showed that 60 s of residence time improved film morphology and enhanced solar cell performance.

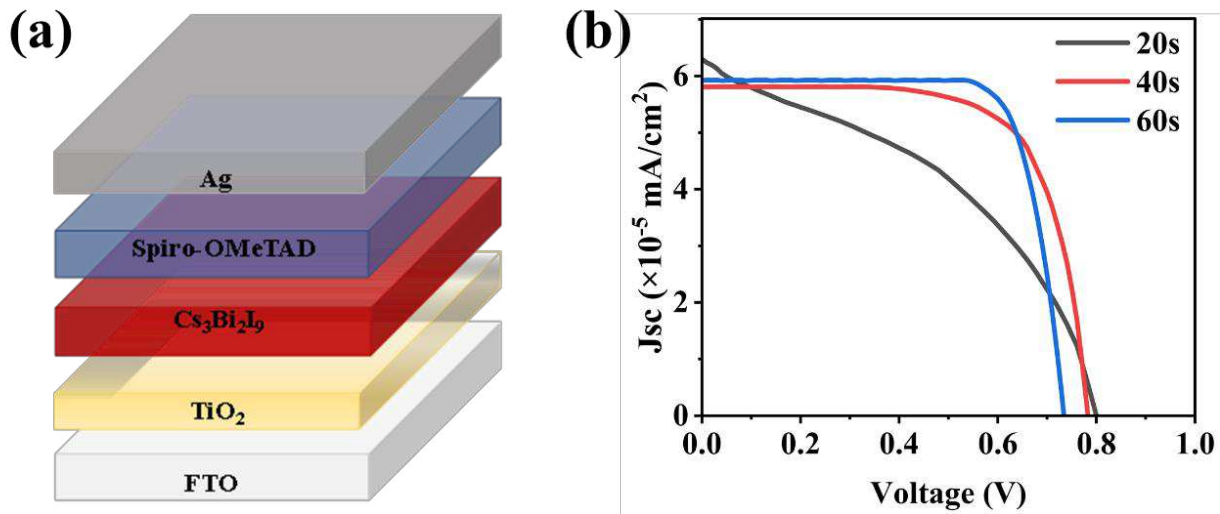


Figure 7. J - V curve of $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite solar cell of 20 s, 40 s, and 60 s.

Table 3. Tabulated of J - V curve of $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite solar cell of 20 s, 40 s, and 60 s.

Sample	Current density, J_{sc} (mA cm^{-2})	Voltage open circuit, V_{oc} (V)	Fill factor, FF (%)	Power conversion efficiency, PCE (%)
20 s	6.29×10^{-2}	0.79	41.02%	0.28
40 s	5.79×10^{-2}	0.78	69.80%	0.44
60 s	5.9×10^{-2}	0.73	77.65%	0.50

4.0 Conclusion

Cs₃Bi₂I₉ nanocrystals were successfully synthesized by continuous-flow processing under ambient conditions, and the effect of residence time on their structural evolution and subsequent thin-film photovoltaic performance was systematically investigated. Residence time was identified as a critical parameter governing crystallization, morphology, and thermal stability, which in turn influenced the quality of the deposited thin films. Among the investigated conditions, a residence time of 60 s produced nanocrystals with the most favorable structural characteristics, resulting in thin films with improved optical and electrical properties and the highest device performance. The corresponding photovoltaic device achieved a PCE of 0.50%, with an V_{oc} of 0.77 V, a J_{sc} of 5.9×10^{-2} mA cm⁻², and FF of 77.6%. These results demonstrate that controlling residence time during continuous-flow synthesis provides an effective means of tailoring the properties of Cs₃Bi₂I₉ nanocrystals and their derived thin films. This work highlights the potential of continuous-flow processing as a scalable and reproducible approach for the preparation of lead-free bismuth halide perovskite materials and provides a basis for further optimization of device architecture and film engineering to improve photovoltaic performance.

Credit authorship contribution statement

Gufran Umar Alam Shaikh: Writing– original draft, Visualization, Validation, Experiment, Methodology, Investigation, Formal analysis. **Fatin Farisha Alia Azmi:** Writing – review & Editing, Visualization, Validation. **Erra Natasha Rasul:** Writing – review & Editing, Experiment, Methodology, Data Curation. **Siti Naqiyah Sadikin:** Data Curation, **Jegadesan Subbiah:** Conceptualization, Supervision, **Akrajas Ali Umar:** Conceptualization, Supervision, Resources, Validation. **Suhaila Sepeai:** Writing – Review & Editing, Resources, **Puvaneswaran Chelvanathan:** Conceptualization, Writing – Review & Editing, Supervision, Resources, Validation. **Norasikin Ahmad Ludin:** Conceptualization, Supervision, Resources, Funding Acquisition, Project administration. **Mohd Sukor Su'ait:** Writing – review & Editing, Resources, Validation, Supervision.

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Data availability statement

All data that supports the findings of this study are included within the article.

Conflicts of interest

The authors declare no conflict of interest.

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