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Master's Thesis of Engineering

High-Brightness Light-Emitting Diodes based on Pb-free Perovskite

환경 친화적인 비납 기반의 고휘도
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Abstract

Metal halide perovskites (MHPs) have attracted much attention in the field of light emitting diode (LEDs) because of their unique properties such as color tunability, high photoluminescence, and high color purity. However, most perovskite light-emitting diodes (PeLEDs) have used lead (Pb)-based perovskites which are toxic. Recently, many researchers have studied tin (Sn)-based perovskites to replace Pb-based perovskites. Among the Sn-based emitters in PeLEDs, cesium tin bromide (CsSnBr_3) is the most promising emitters due to its structural stability compared to that of methylammonium tin bromide (MASnBr_3), and formamidinium tin bromide (FASnBr_3). However, PeLEDs using CsSnBr_3 still exhibited low luminous efficiency because of the several critical problems (i.e., poor film morphology, poor film coverage, self-oxidation of Sn^{2+} , and large grain-size of CsSnBr_3). Herein, we employed two kinds of additives, tin fluoride (SnF_2) and 1,3,5-tris(N-phenylbenzimidazole-2-yl) benzene (TPBI), in CsSnBr_3 to achieve improvement of film morphology, prevention of Sn^{2+} oxidation, and reduction of grain size in the perovskite layers. We introduced SnF_2 as an additive to improve perovskite film coverage by increasing the number of nucleation site. Additionally, we introduced SnF_2 & TPBI treatment in CsSnBr_3 to achieve reduced grain size of CsSnBr_3 with further prevention of Sn^{2+} oxidation. Moreover, the grain size of

perovskite film was successfully reduced and modified the energy level of CsSnBr₃ film, which induced the effective hole blocking at the perovskite|electron transport layer interface. Finally, we employed the SnF₂ & TPBI treated CsSnBr₃ layer as an emitter in PeLEDs, and it exhibited highest luminescence (55 cd/m²) in solution-based Pb-free PeLEDs.

Keyword : perovskite, Pb-free, eco-friendly, PeLEDs, SnF₂, TPBI

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Chapter 1. Introduction

Metal halide perovskites (MHPs) material is having an enormous impact in optoelectronic research field in past decades because of their superior optical and electrical properties. MHPs generally compose of three component ABX_3 , in which A is an alkali metal cation (e.g., Cs^+ and Rb^+) or organic ammonium (e.g., methylammonium (MA; $CH_3NH_3^+$), formamidinium (FA; $CH(NH_2)_2^+$), B is a divalent metal cation (e.g., Zn^{2+} , Ge^{2+} , Sn^{2+} , Pb^{2+} , Fe^{2+} , and Mn^{2+}) and X is a halogen anion (F^- , I^- , Br^- , and Cl^-). These cations and anions can be combined with diverse combination.

MHPs are regarded as promising light-emitting materials due to several inherent traits: i) MHPs have higher color purity (full width at half maximum (FWHM) ≤ 20 nm) than organic emitters (FWHM ≥ 40 nm) and inorganic quantum dots (QDs) (FWHM ~ 30 nm), ii) easy emission wavelength tunability (from 380 nm to 1000 nm), iii) high charge carrier mobility, iv) similar energy level with organic semiconductor that are used in organic light-emitting diodes (OLEDs), and v) low energy disorder.[1] Therefore, MHPs are good alternative for light emitters for vivid color display.

In spite of these attractive advantages of using MHPs in optoelectronics applications, one of the key challenges is the toxicity of Pb. The toxicity issue of

Pb must be overcome due to not only for health problems on humans, but commercial sales market restriction due to RoHS (Restriction of the use of Hazardous Substances in electrical and electronic equipment), which is harmful materials (Cd, Pb, Hg, Cr⁶⁺, PBBs (Polybrominated biphenyls), and, PBDEs(Polybrominated diphenyl ethers)) prevention treaty. Meanwhile, there is an ongoing debate on the effect of Pb in the device on the human health. Some researchers argue that the amount of lead contained in MHPs devices are very small, so that it can prevent the risk of lead exposure by proper encapsulation techniques. However, Pb exposure during the fabrication process are huge, so it cannot be ignored. Therefore, studies on environmentally friendly MHPs are essential. For this reason, a lot of researcher studied on Pb-free perovskite materials such as Sn, Bi, and Cu.[2]–[8]; these are promising elements to reduce the environmental toxicity, which would substantially increase the application of PeLEDs in wearable and disposable devices.

Among the several metallic elements, Sn is considered as the most promising alternative to Pb because Sn and Pb are in the same group 14 in the periodic table. However, Sn-based MHPs are very unstable because of self-oxidation of Sn²⁺ to Sn⁴⁺. Especially, Sn⁴⁺ acts as a p-type dopant in the perovskite structure, which is called self-doping process that severely alters perovskites which intrinsically have semiconducting properties to have metallic behavior and increases hole

concentration. Huang group get Pb-free PeSCs with a PCE of 8.12% using mixed cation system ($\text{Fa}_{0.75}\text{MA}_{0.25}\text{SnI}_3$) as light absorber. Recently, introducing large ammonium cation such as phenylethylammonium (PEA^+) or butylammonium (BA^+) in 3D Sn-based perovskite (e.g., FASnI_3) to make a quasi-2D[6] or hybrid 2D/3D[9] like Pb-analog. Since tin fluoride (SnF_2) has been employed to modulate the Sn^{2+} vacancy and thus, prevent self-oxidation of Sn^{2+} [3]. Several studies have attempted to introduce SnF_2 in Sn-based perovskite solar cells (PeSCs) and achieved high power conversion efficiency (PCE) with stable operation. More recently, Seok's group fabricated stable Sn-based PeSCs using formamidinium tin iodide (FASnI_3) using SnF_2 -pyrazine complex.[10] as already mentioned, self p-doping of Sn-based MHPs have an obstacle to demonstrate high efficiency Pb-free devices.

Contrary to lead-free PSCs, only few research has reported Pb-free PeLEDs. Luis and co-workers demonstrated the visible lead-free PeLED using low-dimensional perovskite materials as an emitter ($(\text{PEA})_2\text{SnI}_x\text{Br}_{4-x}$), because 2D $(\text{PEA})_2\text{SnI}_4$ not only showed higher photoluminescence properties than 3D MASnI_3 , but also have visible light spectrum (~ 630 nm).[11] PeLEDs using this 2D $(\text{PEA})_2\text{SnI}_4$ emitter showed luminance of 0.15 cd/m^2 and current efficiency (CE) of 0.029 cd/A . recently, Fang and co-worker reported the Pb-free PeLEDs that have vacuum-deposited Sn-based perovskite layer, which showed 172 cd/m^2 of

luminance with 0.65 cd/A of CE. They got smooth and uniform lead-free MHP films with very small grain size (~60 nm).[12] Especially, previous solution-processed PeLEDs showed poor luminous properties. To practically replace the toxic Pb to non-toxic in PeLEDs, it is essential to study solution-processed Pb-free PeLEDs. Herein, we introduced TPBI & SnF₂ treatment for highly bright lead-free PeLEDs using CsSnBr₃ as an emitter. To demonstrate lead-free PeLEDs successfully, two strategies are introduced. Firstly, SnF₂ are used as a reducing agent to overcome Sn vacancy and perovskite film morphologies. Secondly, we introduced the TPBI & SnF₂ treatment for smaller grain size and energy level alignment. With these methods, bright Pb-free PeLEDs are fabricated.

Chapter 2. The effect of SnF₂ treatment on the CsSnBr₃ for Pb-free PeLEDs

2.1. Morphology of perovskite film

Inorganic metal halide perovskite is known to have low surface coverage due to non-uniform crystal formation from rapid crystallization during solution process and island crystal growth. Especially in the case of CsSnBr₃, uniform crystal formation is more difficult due to spontaneous oxidation of Sn²⁺ and formation of Sn²⁺ vacancy. To solve this problem, we used SnF₂ additive which can prevent vacancy modulation and oxidation.

SnF₂ has the lowest binding energy (476 kJ/mol) compared to other Sn-halide (Sn-Br: 337 kJ/mol and Sn-I: 235 kJ/mol), thus SnF₂ precipitated first. Since precipitated SnF₂ acts as a heterogeneous nucleation site, excess SnF₂ contributes to the increase of nucleation density and helps to improve the coverage of CsSnBr₃ perovskite film [13] (**Figure 2.1**).

SEM analysis was carried out to observe morphology change with addition of SnF₂. Morphology change of CsSnBr₃ perovskite film is showed according to SnF₂ addition ratio. Until the addition of 20% SnF₂, we can see that the coverage and

morphology are improved according to the heterogeneous nucleation (**Figure 2.2 A~C**). Since then, however, too many nucleation sites have been formed and aggregation has occurred between them, resulting in a phenomenon in which morphology and coverage do not improve (**Figure 2.2 D~F**). These changes in coverage would have significant influence on implementing Pb-free PeLEDs devices.

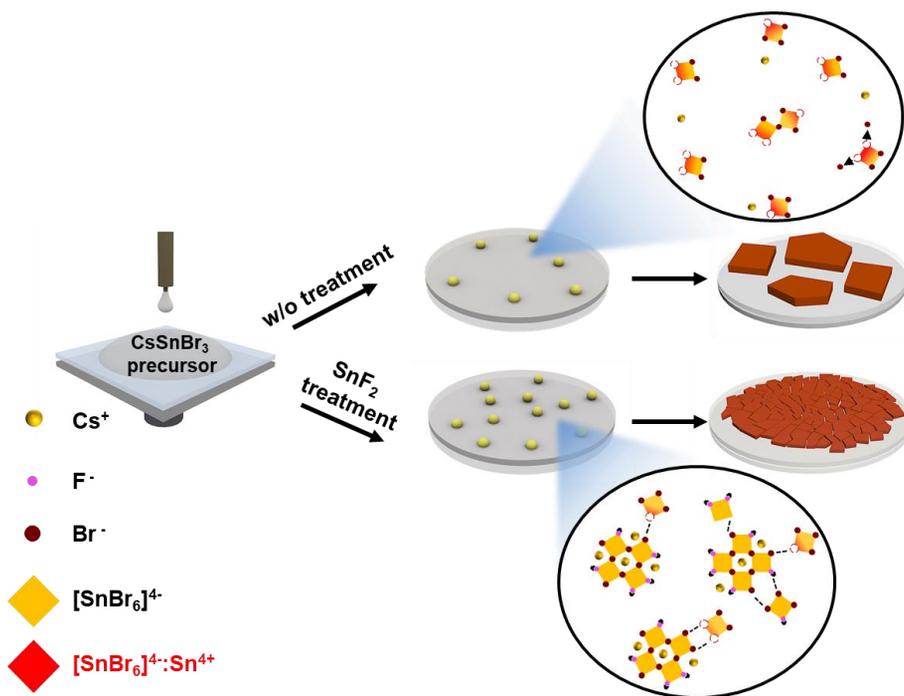


Figure 2.1 Schematic illustration of morphology modulation of CsSnBr₃ with SnF₂ treatment

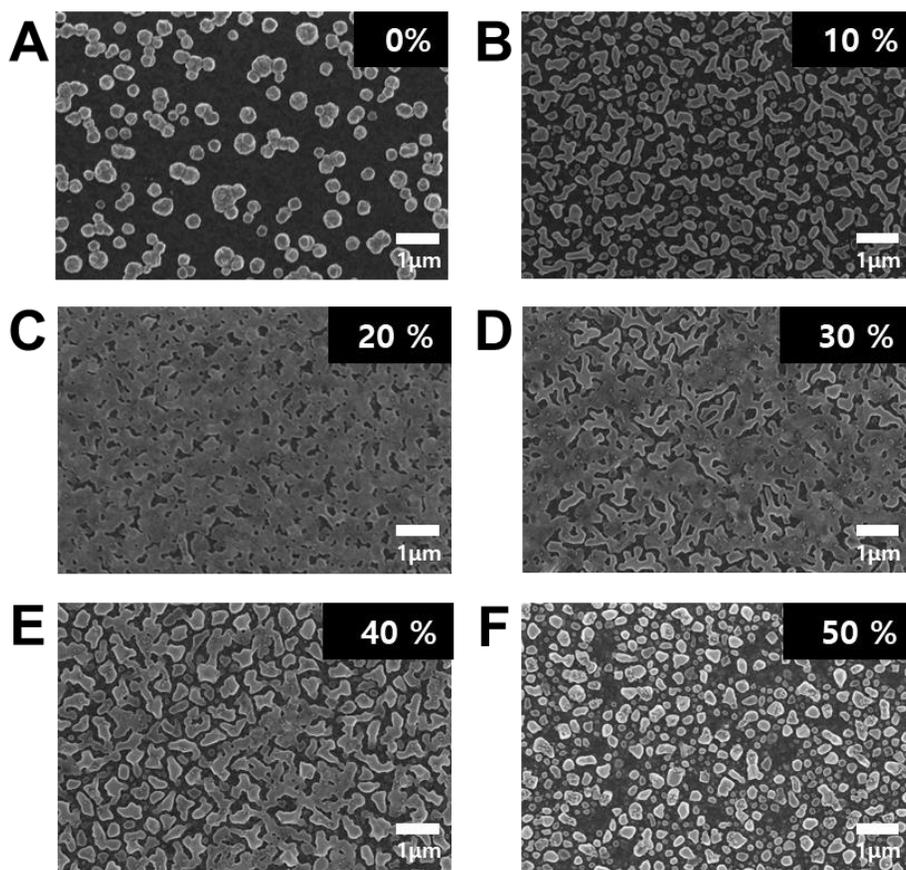


Figure 2.2 SEM (Scanning Electron Microscopy) image of CsSnBr₃ films with different amount of SnF₂ mol% A) 0%, B) 10%, C) 20%, D) 30%, E) 40%, F) 50%

2.2. Structure and optical properties of perovskite film

Here, we analyze the crystal structure of perovskite and optical properties of the perovskite to investigate the device characteristics of Perovskite LEDs.

First, the absorption spectrum of CsSnBr_3 was measured to determine crystal formation and electronic structure (**Figure 2.3 A**). At low SnF_2 ratios, the crystal structure is not completely formed and the crystallinity is low and the absorption peak is not clearly observed. However, it can be seen that the absorption edge at the band gap (1.8 eV) is clearly observed with SnF_2 . However, at high concentration (50%), the absorption edge is again blurred, which can be confirmed in SEM as well. Also, absorbance in long wavelength region can be attributed to the scattering cause by severely rough surface and non-uniform film of the perovskite.

X-ray diffraction (XRD) was measured to analyze the crystal structure. First, all samples have XRD peaks corresponding to the cubic structure of CsSnBr_3 (100) at 15, (110) at 23, (111) at 27, (002) at 31, (112) at 38, (022) at 44 which indicates that all the perovskite film shows cubic structure [14](**Figure 2.3 B**). In addition, it can be inferred that SnF_2 addition modulate the morphology without breaking the inherent cubic structure of perovskite.

In the PL characteristics, it was confirmed that the PL intensity was highest when SnF₂ was added at 20%, similar to the tendency of the morphology analysis results (**Figure 2.3 C**). As the surface coverage increases, the non-radiative recombination is suppressed and the PL intensity is considered to be improved. After that, the surface coverage does not improve again according to the aggregation of the perovskite film, and there are many pinholes and non-radiative recombination is increased again. In addition, it can be confirmed that there is no change in peak position when normalized PL is analyzed (**Figure 2.3 D**). This is interpreted as the absence of change in crystal structure or chemical bonding even when SnF₂ is added, as confirmed by the results of the absorption and XRD.

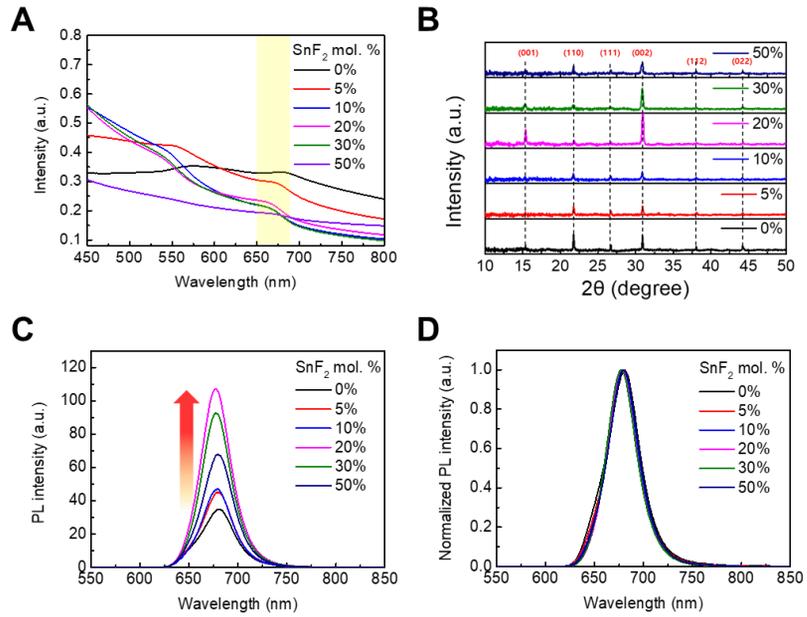


Figure 2.3 A) UV-Vis absorption spectrum, B) XRD patterns, C) steady-state PL spectra, D) normalized PL spectra of CsSnBr₃ thin film with different amount of SnF₂ molar ratio.

2.3. Device characteristics

Based on the optical structural features and surface analysis of the perovskite film, a perovskite LED device was fabricated. **(Figure 2.4 A~F)**. In pristine CsSnBr₃, even diode characteristics could not be shown due to poor morphology. However, improvement of morphology by SnF₂ addition is the most critical factor, so that diode is formed without leakage current in SnF₂ 20% device and shows red emission. Notably, in pure CsSnBr₃, leakage current flows and blue emission occurs in TPBI. However, after SnF₂ addition, only red emission is observed in CsSnBr₃ luminescent layer due to morphology improvement. (luminescence = 10 cd m⁻²), which is significantly higher than the currently reported solution process lead-free PeLED. [11] (luminescence = 0.15 cd/m²)

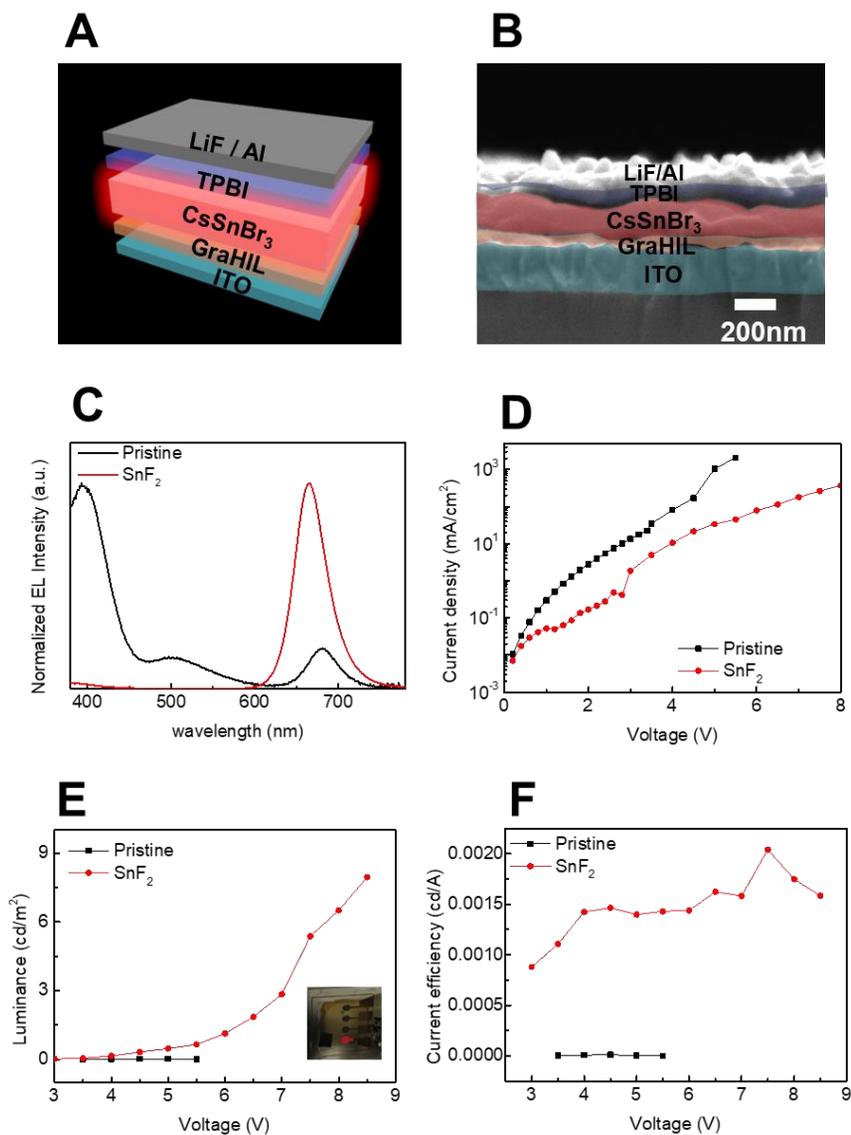


Figure 2.4 A) Schematic diagram of device structure of CsSnBr₃ PeLEDs. B) SEM image of a cross-section of a CsSnBr₃ PeLEDs. C) Normalized EL spectra, D) current density, E) luminance, F) current efficiency of CsSnBr₃ PeLEDs with and without SnF₂ treatment.

Chapter 3. The effect of SnF₂ & TPBI treatment on the CsSnBr₃ for Pb-free PeLEDs

3.1. Morphology of perovskite film

In chapter 2, we have studied Pb-free PeLEDs using SnF₂ as an additive, but there are many problems that have not been solved. Therefore, TPBI, an ETL material commonly used in OLEDs or PeLEDs fields, is used as an additive with SnF₂. TPBI could be act as a hinder during crystallization of CsSnBr₃.^[15] For this mechanism, it is possible to increase the number of nucleation sites by adding more SnF₂ and prevent the aggregation which is a disadvantage when we used SnF₂ as an additive, so that a perovskite film having a small grain can be obtained (**Figure 3.1**). SEM analysis was performed to see the morphology difference in perovskite film between TPBI & SnF₂ treatment and TPBI treatment. When TPBI was used as an only additive for CsSnBr₃ film (we call TPBI treatment), there was almost no change in surface coverage of perovskite film. We suggest that it comes from not enough nucleation sites because of absence of SnF₂ (**Figure 3.2 C**). On the other hand, when SnF₂ and TPBI are simultaneously used as an additive (we call SnF₂ & TPBI treatment) for making perovskite film, the huge difference of film coverage was observed. Also, the grain size was significantly decreased. (**Figure 3.2 D**).

We have confirmed the distribution of the grain size in order to see the change of the size of the grain size. We observed that the average grain size is down to 52 nm when we did TPBI & SnF₂ treatment (**Figure 3.3B**). It is much smaller grain size at the average grain size of 125 nm when the only SnF₂ treatment is performed (**Figure 3.3 A**).

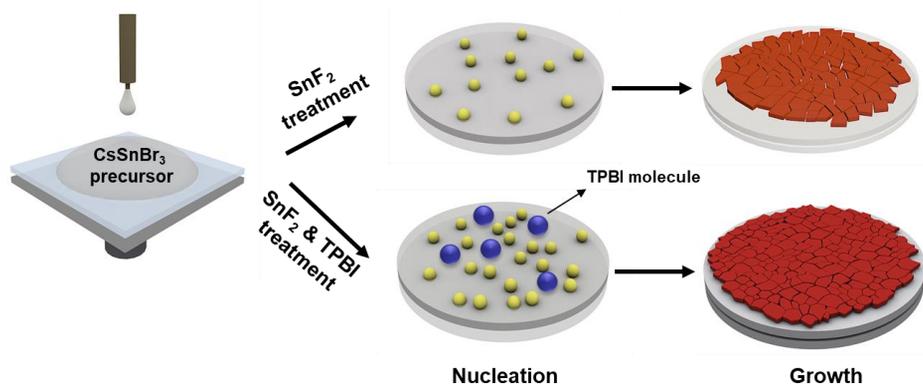


Figure 3.1 Schematic illustration of grain growth mechanism of CsSnBr₃ thin film with SnF₂ and SnF₂ & TPBI treatment.

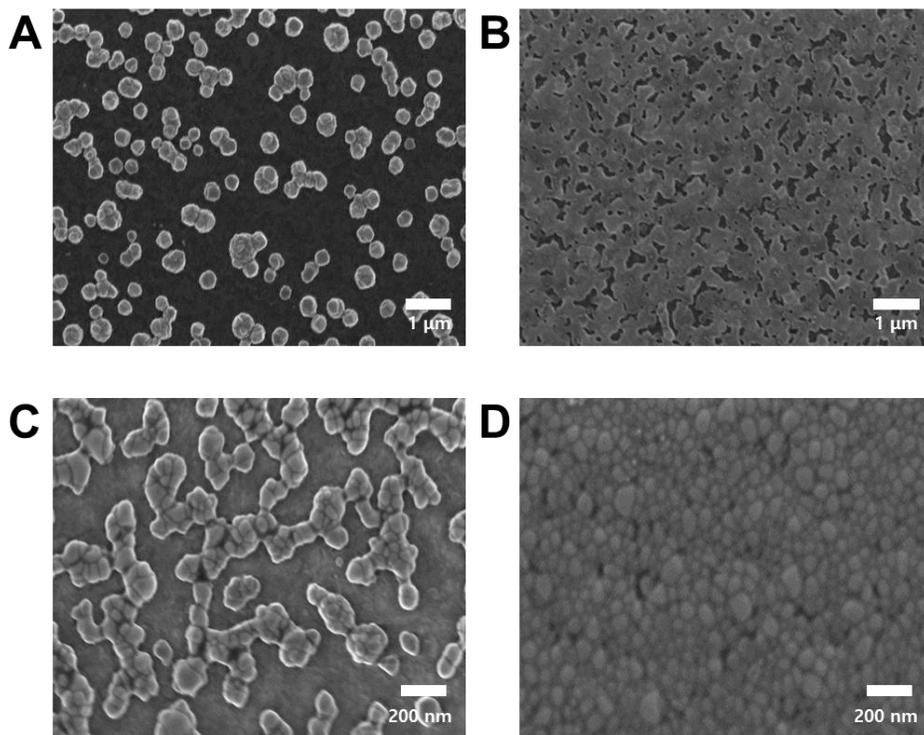


Figure 3.2 SEM image of CsSnBr₃ films with A) no additional treatment, B) SnF₂ treatment, C) TPBI treatment, D) SnF₂ & TPBI treatment.

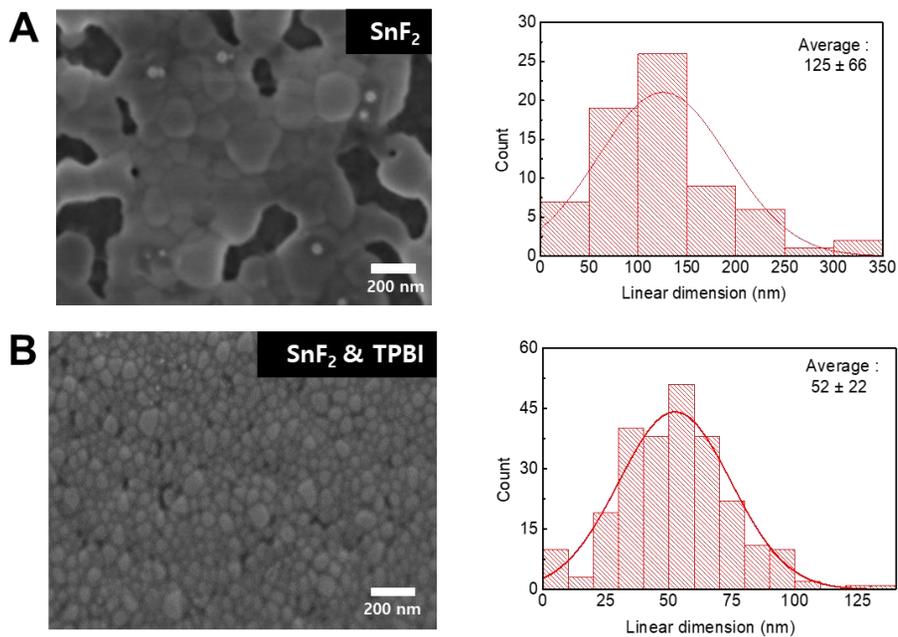


Figure 3.3 Distribution of calculated perovskite grain size for CsSnBr₃ films with A) SnF₂ treatment and B) SnF₂ & TPBI treatment.

3.2. Structure and optical properties of perovskite film

Here, we analyze the crystal structure of perovskite and optical properties of the perovskite to investigate the device characteristics of PeLEDs.

First, when TPBI was used as an additive, the absorption spectrum was measured to determine the crystal structure and electronic structure of CsSnBr₃ (**Figure 3.4 A**). By observing clear absorption edge, the structure is well formed even after TPBI was added. XRD was also measured to analyze the crystal structure (**Figure 3.4 B**). All the samples are observed to have a cubic structure by observing peaks corresponding to the cubic structure of CsSnBr₃ mentioned above. TPBI also showed grain size modulation without breaking the cubic crystal of CsSnBr₃ with luminescence properties like SnF₂. We can calculate the crystallite sizes of perovskite film from Scherrer equation by using the XRD results. Calculated crystallite size are 36.8 nm and 27.3 nm in SnF₂ treatment and SnF₂ & TPBI treatment respectively. It is much different with grain size distribution because crystallite size and grain size are different, but it has same tendency with grain size distribution. PL characteristics showed that PL luminescence was improved by TPBI & SnF₂ treatment (**Figure 3.4 C**). As described above with the addition of SnF₂, it is believed that PL intensity is improved by suppressing non-radiative recombination when the surface coverage was increased.

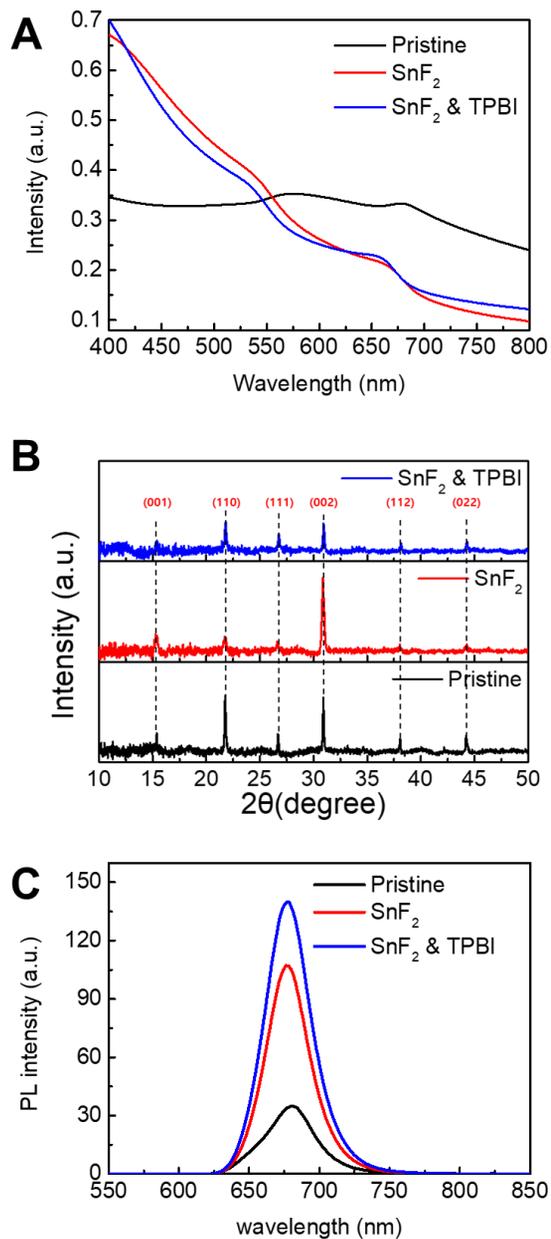


Figure 3.4 A) UV-Vis absorption spectrum, B) XRD patterns, C) steady-state PL spectra of CsSnBr₃ films after SnF₂ treatment, SnF₂ & TPBI treatment

3.3. Photo-electron spectroscopy analysis

We conducted X-ray photoelectron spectroscopy (XPS) to investigate the prevention behavior of Sn^{2+} by SnF_2 , and TPBI addition (**Figure 3.5 A**). All of the XPS spectra exhibit peaks at ~ 487 eV, and ~ 496 eV, indicating that $\text{Sn}3d_{5/2}$, and $\text{Sn}3d_{3/2}$, respectively. Interestingly, addition of SnF_2 cause downshift of XPS spectrum of pristine CsSnBr_3 ; it clearly shows the prevention of Sn^{2+} oxidation to Sn^{4+} because binding energy of Sn^{2+} is less than that of Sn^{4+} . XPS spectrum of SnF_2 and TPBI added CsSnBr_3 did not show upshift behavior compared with that of SnF_2 added CsSnBr_3 , which implies that additional TPBI does not degrade oxidation prevention by SnF_2 addition.

In order to investigate the energy level change of CsSnBr_3 film for fine the device structure, the UPS analysis were observed (**Figure 3.5 B, C**). As a result, it was found that the VBM level shallower when SnF_2 & TPBI treatment was performed (**Table 3.1**). This is presumably due to the lone pair electron in TPBI. This energy level changes make ETL layer (TPBI) to block hole effectively. It is expected that the rate of recombination at TPBI would be reduced and then, the rate of recombination at EML would be increased.

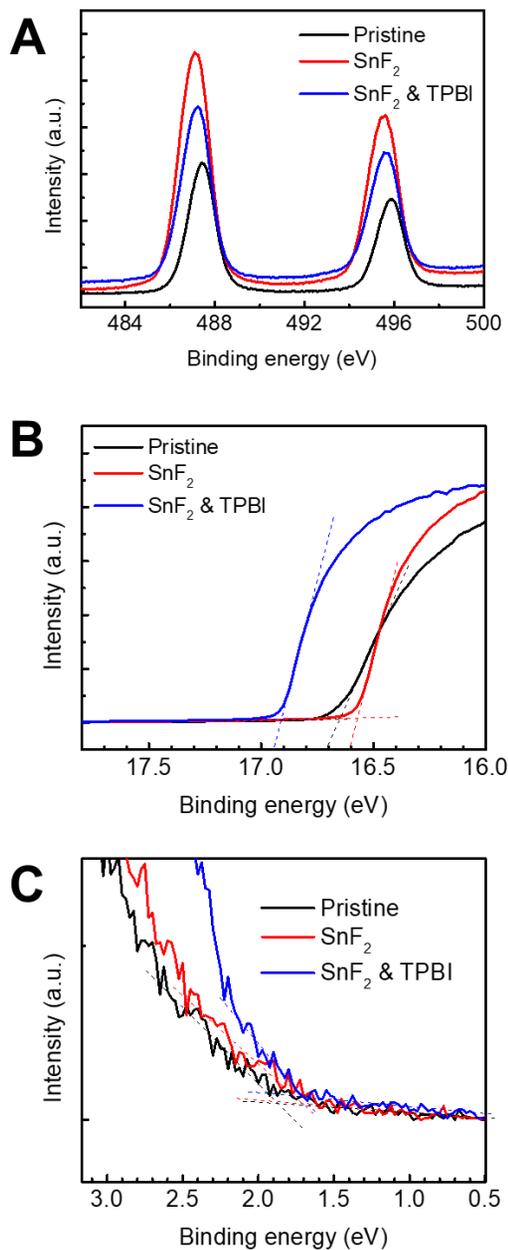


Figure 3.5 A) XPS Sn 3d spectra of CsSnBr₃ thin films after SnF₂ and SnF₂ & TPBI treatment, UPS spectra of CsSnBr₃ films after SnF₂ and SnF₂ & TPBI treatment showing B) secondary cutoff and C) VBM.

	WF (eV)	E _{offset} (eV)	VBM (eV)
CsSnBr₃	4.5	1.87	6.37
SnF₂	4.6	1.7	6.3
SnF₂ & TPBI	4.258	1.71	5.968

Table 3.1 WF, the offset and VBM of CsSnBr₃ thin films after SnF₂ and TPBI treatment.

3.4. Device characteristics

Based on the optical structural features and surface analysis of the perovskite film, a perovskite LED devices were fabricated. (**Figure 3.6 A-C**), the luminescence of SnF₂ & TPBI treatment Pb-free PeLEDs have five times better than SnF₂ treated one, (luminescence = 55 cd/m²) which is best result in solution processed Pb-free PeLEDs. Diode characteristics are also more clear than SnF₂ treatment one. We already show the possible three reasons of this enhancement of device performances: i) better surface coverage and smaller grain size of CsSnBr₃ film, ii) hindrance the oxidation of Sn²⁺ to Sn⁴⁺, and iii) effective hole blocking of ETL by introducing shallow energy level.

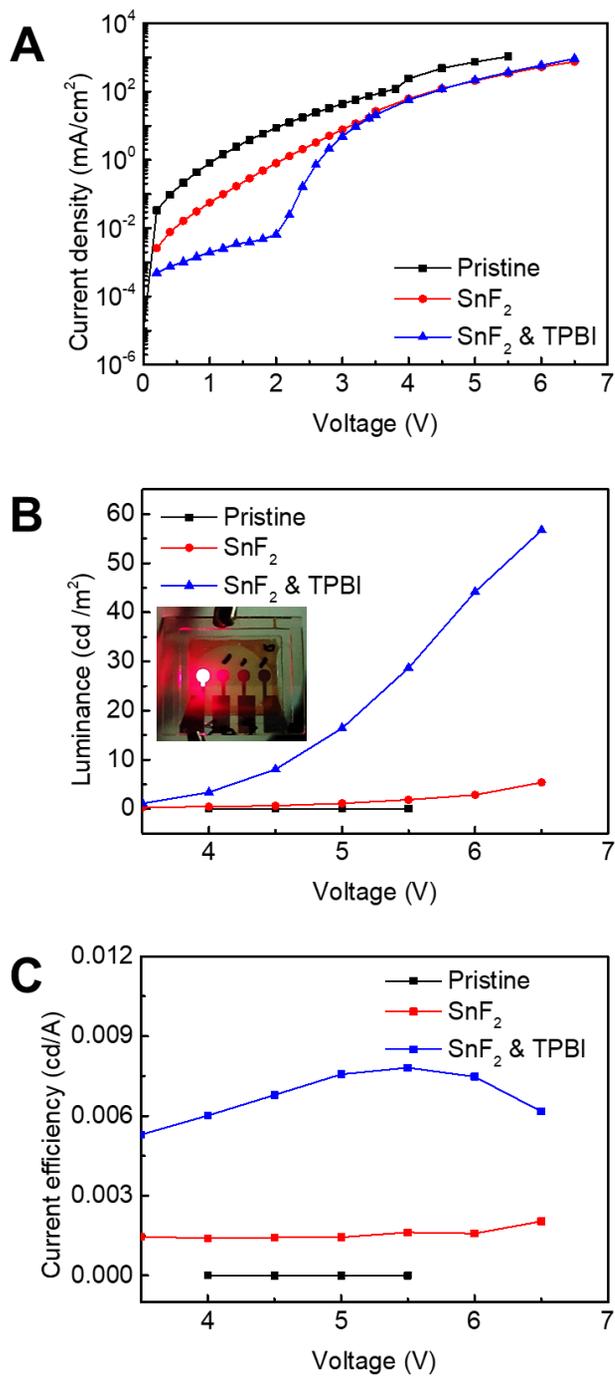


Figure 3.6 A) Current density, B) luminance, C) current efficiency of CsSnBr₃ PeLEDs with SnF₂ and SnF₂ & TPBI treatment.

Chapter 4. Experimental

Materials.

All reagents were as received without any purification: 1,3,5-Tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBI, OSM) was purchased from OSM. Cesium bromide (CsBr), tin (II) bromide (PbBr₂, 99.99%), tin (II) fluoride (SnF₂ 99.99%), chlorobenzene (CB, 99.8%, anhydrous), lithium fluoride (LiF, 99.99% trace metal basis), dimethyl sulfoxide (DMSO, 99.8%, anhydrous) were purchased from Sigma-Aldrich.

Fabrication of MHP films.

The initial CsSnBr₃ solutions (14.5 wt. %) were prepared by dissolving CsBr and SnBr₂ in DMSO with CsBr : SnBr₂ molar ratio of 1:1, and the solution was then stirred overnight. Right before spin-coating of the solution, TPBI solution (3 wt. %) in CB mixed with CsSnBr₃ solutions with volume ratio of 7 (perovskite precursor):1(TPBI solution). The mixed solutions were used as prepared without any further process.

The GraHIL layers were formed on cleaned glass, FTO or Si native wafer substrates as previously reported.[16] As-prepared CsSnBr₃ solutions were spin-coated with rotating speed of 3000 rpm, 70s. Then the films were baked on a hot plate at 170 °C for 10 min.

PeLED Fabrication.

Glass/ FTO/ GraHIL/ CsSnBr₃ was fabricated as mentioned above. On the CsSnBr₃ layers, 50 nm of TPBI, 1 nm of LiF, and 100 nm of Al were thermally deposited in sequence in a high-vacuum chamber, defining the device are of 4.8 mm². The devices were encapsulated in N₂ atmosphere.

Characterizations of MHP films.

Ultraviolet/visible absorption spectra of the Glass/GraHIL/MHP films with glass encapsulation under N₂ atmosphere were obtained using UV-Vis spectrophotometer (Cary-5000).

Steady-state PL of glass/ GraHIL/ MHP film samples was measured using a spectrofluorometer (JASCO FP8500). Xenon arc lamp with continuous-output power of 150 W was used as an excitation source, and the excitation

wavelength was 365 nm. The light was incident toward the glass side that is opposite to the MHP/N₂ interface.

X- The X-ray diffraction (XRD) measurements were performed by an X-ray diffractometer (BRUKER MILLER Co., D8-Advance) with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). XRD data were gained in the 2θ range of 10° - 50° at room temperature. Top-view and cross-sectional scanning electron microscopy (SEM) images of Si wafer/ GraHIL/MHP films were measured using field emission SEM (MERLIN compact, ZEISS) at the Research Institute of Advanced Materials, Seoul National University.

TCSPC measurement of Glass/ GraHIL/ CsSnBr₃ samples were conducted using the same equipment and procedure described elsewhere,[16] except a different TCSPC module was used (FluoTime 300, PicoQuant). Instrument response function (IRF) was ignored because the PL lifetime curves were much very longer than the temporal width of the IRF. The excitation power density was $\sim 25 \text{ mW cm}^{-2}$, and the excitation wavelength was fixed at 405 nm.

Ultraviolet Photoemission Spectroscopy (UPS) spectra of ITO /GraHIL /MHP films were measured using a photoelectron spectrometer (Kratos Inc.,

AXIS-Ultra DLD). He I radiation (21.2 eV) was used for UPS measurement, in collaboration with Korea Basic Science Institute (KBSI).

Characterization of PeLED Devices.

The fabricated devices were measured in N₂ atmosphere by glass encapsulation. The current-voltage-luminance characteristics of PeLEDs were measured by using a source-measurement unit (Keithley 236), a spectroradiometer (Minolta CS-2000), and control computer.

Chapter 5. Conclusion

Here, we employed SnF₂ and TPBI additives on CsSnBr₃, which is one of the most promising candidate to replace toxic Pb-based perovskite emitters and achieved substantially improved coverages with prevention of Sn²⁺ oxidation. Since SnF₂ can functions as heterogeneous nucleation site during the crystal growth of CsSnBr₃, it can improve the surface coverage of CsSnBr₃ film without any pinhole formation. Also, SnF₂ addition prevented the spontaneous oxidation of Sn²⁺ which is critical obstacles for Sn-based perovskite materials to be used in optoelectronics. Using this method, we could achieve Pb-free PeLEDs that have ~10 cd/m² of luminance. To induce further improvement in Pb-free PeLEDs, we employed TPBI additive in CsSnBr₃ & SnF₂ system. Even though SnF₂-added CsSnBr₃ have sufficient film coverage to be used in PeLEDs, its grain size is still large to achieve PeLEDs with strong carrier confinement in crystal and following high luminance. Further, use of TPBI additives impeded crystal growth during the spin-coating of perovskite; it could effectively reduce the grain size of CsSnBr₃ down to 52 nm to have uniform morphology and strong carrier confinement in perovskite crystal. Moreover, TPBI addition modified the energy level of CsSnBr₃ film, which induced the effective hole blocking at the perovskite|electron transport layer interface. Employing further addition of TPBI in PeLEDs, we achieved

PeLEDs that have high luminance (55 cd/m^2). This work has proved that additive strategy in eco-friendly Sn-based perovskite emitters can be a promising alternative to replace toxic Pb-based perovskite emitters.

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Abstract

금속 할라이드계 페로브스카이트는 그들의 고유한 특성인 색 가변성, 높은 광발광, 높은 색순도로 인해 발광 다이오드 분야에서 각광받고 있는 물질이다. 하지만, 대부분의 페로브스카이트 발광 다이오드는 독성이 있는 납 기반 페로브스카이트를 사용하고 있어 상업화가 힘든 상황이다. 최근, 많은 연구자들이 납 기반 페로브스카이트를 대체하기 위해 주석 기반 페로브스카이트를 연구 하고 있다. 발광 물질로서의 주석 기반 페로브스카이트 중에서, CsSnBr_3 는 MASnBr_3 및 FASnBr_3 와 비교하여 구조적 안정성으로 인해 가장 유망한 발광 물질 이다. 그러나, CsSnBr_3 를 사용하는 페로브스카이트 발광 다이오드는 박막 상태 및 Sn^{2+} 의 자발적인 산화 같은 문제로 인해 여전히 낮은 발광 효율만이 보고 되고 있다. 여기서 우리는 CsSnBr_3 에 첨가제인 SnF_2 와 TPBI를 사용하여 막 형태 개선, 자발적 산화방지, 및 페로브스카이트 결정립 크기의 감소 등을 이루어 냈다. 우리는 핵 생성 사이트의 수를 증가시킴으로써 페로브스카이트 박막질을 향상시키는 효과를 위해 SnF_2 를 첨가제로 도입하였다. 또한, SnF_2 와 TPBI를 동시에 첨가하여 페로브스카이트의 결정립 크기를 효과적으로 줄였으며 발광층의 에너지레벨을 변화시켜 정

공 저지층인 TPBI가 정공 수송을 효과적으로 방어 하도록 도와주었다.
마침내, 두가지 첨가제를 동시에 활용하여 휘도 55 cd/m^2 의 페로브스카이트 발광 다이오드를 구현하였으며 이는 용액공정 비납기반 페로브스카이트 중에서 가장 높은 값이다.

주요어 : 페로브스카이트, 비납 기반, 친환경적인, 페로브스카이트 발광 다이오드, 주석불화물

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