

## Article

# Dual Light Emission of CsSnI<sub>3</sub>-Based Powders Synthesized via a Mechanochemical Process

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**Abstract:** Lead toxicity has hindered the wide applications of lead halide perovskites in optoelectronics and bioimaging. A significant amount of effort has been made to synthesize lead-free halide perovskites as alternatives to lead halide perovskites. In this work, we demonstrate the feasibility of synthesizing CsSnI<sub>3</sub>-based powders mechanochemically with dual light emissions under ambient conditions from CsI and SnI<sub>2</sub> powders. The formed CsSnI<sub>3</sub>-based powders are divided into CsSnI<sub>3</sub>-dominated powders and CsSnI<sub>3</sub>-contained powders. Under the excitation of ultraviolet light of 365 nm in wavelength, the CsSnI<sub>3</sub>-dominated powders emit green light with a wavelength centered at 540 nm, and the CsSnI<sub>3</sub>-contained powders emit orange light with a wavelength centered at 608 nm. Both the CsSnI<sub>3</sub>-dominated and CsSnI<sub>3</sub>-contained powders exhibit infrared emission with the peak emission wavelengths centered at 916 nm and 925 nm, respectively, under a laser of 785 nm in wavelength. From the absorbance spectra, we obtain bandgaps of 2.32 eV and 2.08 eV for the CsSnI<sub>3</sub>-dominated and CsSnI<sub>3</sub>-contained powders, respectively. The CsSnI<sub>3</sub>-contained powders exhibit the characteristics of thermal quenching and photoelectrical response under white light.

**Keywords:** mechanochemical synthesis; lead-free perovskites; CsSnI<sub>3</sub>; dual light emission



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## 1. Introduction

The success in the synthesis of lead halide perovskites at low cost has opened active research fields for the applications of lead halide perovskites in photovoltaics and sensing and light-emitting devices and systems [1,2]. One of the challenges for the applications of lead halide perovskites is the lead toxicity, which has hindered the commercialization of lead halide perovskites. This has stimulated extensive work to explore the replacement of lead halide perovskites with lead-free halide perovskites and lead-free halide double perovskites. Sn-based halide perovskites represent one important group of lead-free halide perovskites.

There are various methods available to synthesize Sn-based halide perovskites, including spin-coating [3], vapor-assisted deposition [4], solid-phase sintering [5], hot injection [6], and mechanochemical processing [7,8]. Weiß et al. [9] used atomic layer deposition and pulsed chemical vapor deposition to form γ-CsSnI<sub>3</sub> film on patterned silicon substrates and obtained a bandgap of 1.20 eV from the Tauc plot. Shum et al. [10] used a two-step method to obtain CsSnI<sub>3</sub> films on three different substrates of glass, ceramics, and silicon with thermal and electron-beam evaporators in a vacuum chamber (~10<sup>5</sup> Torr). Kim and Kang [11] combined spin-cast with drop cast to form CsSnI<sub>3</sub> crystals in a glove box with nitrogen. Wang et al. [12] used a one-pot process to synthesize CsSnI<sub>3</sub> nanocrystals with and without the use of an antioxidant solvent additive (TPPi) and the prepared CsSnI<sub>3</sub> nanocrystals to form CsSnI<sub>3</sub> films. Kapil et al. [3] used a spray-deposition method to

prepare  $\text{Cs}_2\text{SnI}_6$  films and obtained a bandgap of 1.54 eV. Murshed and Bansal [13] applied drop-coating to construct  $\text{Cs}(\text{Sn,Pb})\text{I}_3$  films with a bandgap of 1.5 eV for the applications in perovskite-based solar cells. Nairui et al. [14] synthesized  $\text{Cs}_2\text{SnI}_6$  powders via a one-step method and studied dependence of the optical characteristics of the  $\text{Cs}_2\text{SnI}_6$  powders on the process parameters, including reactant type and solvent type. Jiang et al. [15] used a chemical bath method to prepare  $\text{Cs}_2\text{SnI}_6$  powders and reported the long-term stability of the  $\text{Cs}_2\text{SnI}_6$  powders over a period of one month. Lee et al. [16] used electrospraying to form  $\text{Cs}_2\text{SnI}_{6-x}\text{Br}_x$  layers and evaluated the Br effect on the bandgaps of the  $\text{Cs}_2\text{SnI}_{6-x}\text{Br}_x$  layers. Saparov et al. [17] prepared  $\text{Cs}_2\text{SnI}_6$  films via a two-step process and obtained a bandgap of 1.60 eV. Tang et al. [18] obtained  $\text{Cs}_2\text{SnI}_6$  with a size-dependent light emission via an aqueous process. It is worth noting that extensive work has been conducted on the applications of Cs-, Sn-, and Sn-Pb-based perovskites in the field of solar cells. There are few works on infrared emission and green emission of Sn-based halide perovskites. Also, most processes reported in the literature to prepare Sn-based halide perovskites are much more complex than the mechanochemical process used in this work.

Currently, few studies [8,19] are on the use of mechanochemical processing to synthesize Sn-based halide perovskites. To realize the potential applications of Sn-based halide perovskites in solar cells and bioimaging, we used a mechanochemical method to synthesize  $\text{CsSnI}_3$ -based powders under ambient conditions from CsI and  $\text{SnI}_2$  powders. In contrast to the work reported in the literature, the temporal evolution of the optical characteristics of the prepared  $\text{CsSnI}_3$ -based powders were characterized. The prepared  $\text{CsSnI}_3$ -based powders were divided into two groups—one is  $\text{CsSnI}_3$ -dominated powders, which emit green light under the excitation of UV light of 365 nm, and the other is  $\text{CsSnI}_3$ -contained powders, which emit orange light under the excitation of UV light of 365 nm. Both the  $\text{CsSnI}_3$ -dominated powders and  $\text{CsSnI}_3$ -contained powders exhibit infrared emission with the emission wavelengths centered at 916 nm and 925 nm, respectively, under a laser of 785 nm in wavelength.

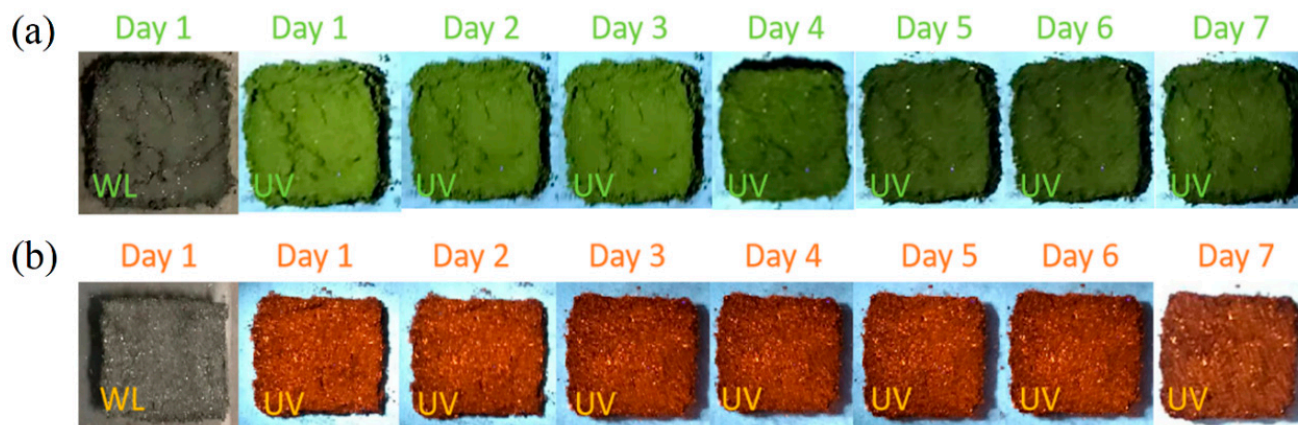
## 2. Experimental Details

The materials used to prepare Sn-based halide perovskites are cesium iodide (CsI, 99.9%, Alfa Aesar, Ward Hill, MA, USA), tin (II) iodide ( $\text{SnI}_2$ , 99%, Strem Chemical, Newburyport, MA, USA), and deionized (DI) water. The as-received materials were used directly in the experiments without pre-purification.

For the synthesis of  $\text{CsSnI}_3$ -dominated powders, 0.4 mmol (103.92 mg) CsI was mixed with 0.4 mmol (149 mg)  $\text{SnI}_2$  to form a mixture without any additives and water. The mixture was put in a ceramic mortar and ground mechanically at  $\sim 18.4^\circ\text{C}$  and with a humidity of  $\sim 22\%$  for 5 min initially. Twenty milliliters of DI water was then added to the ground material, which was further ground mechanically for 5 min, leading to the formation of black powders ( $\text{CsSnI}_3$ -dominated powders) under white light, as shown in Figure 1a. The as-prepared black powders were stored in a vacuum chamber (Napco 5831) at 44.7 KPa for one week.

For the synthesis of  $\text{CsSnI}_3$ -contained powders, 0.2 mmol (51.96 mg) CsI was mixed with 0.2 mmol (74.5 mg)  $\text{SnI}_2$  with 200  $\mu\text{L}$  of DI water. The mixture was put in a ceramic mortar and ground mechanically at  $\sim 18.4^\circ\text{C}$  and with a humidity of  $\sim 22\%$  until the color of the mixture became light black. The ground mixture was dried naturally to form light black powders ( $\text{CsSnI}_3$ -contained powders) in the mortar under white light, as shown in Figure 1b.

The crystal structures of the prepared  $\text{CsSnI}_3$ -based powders were analyzed on an X-ray analyzer (Bruker D8 Discover, Bruker, Billerica, MA, USA) with a scintillation counter detector under the  $\text{CuK}\alpha$  radiation of  $\lambda = 1.5406 \text{ \AA}$ . The chemical compositions and morphologies of the prepared  $\text{CsSnI}_3$ -based powders were characterized on a scanning electron microscope (SEM) (JEOL JSM-5900ILV, JEOL, Tokyo, Japan) equipped with an EDS micro-analysis system.



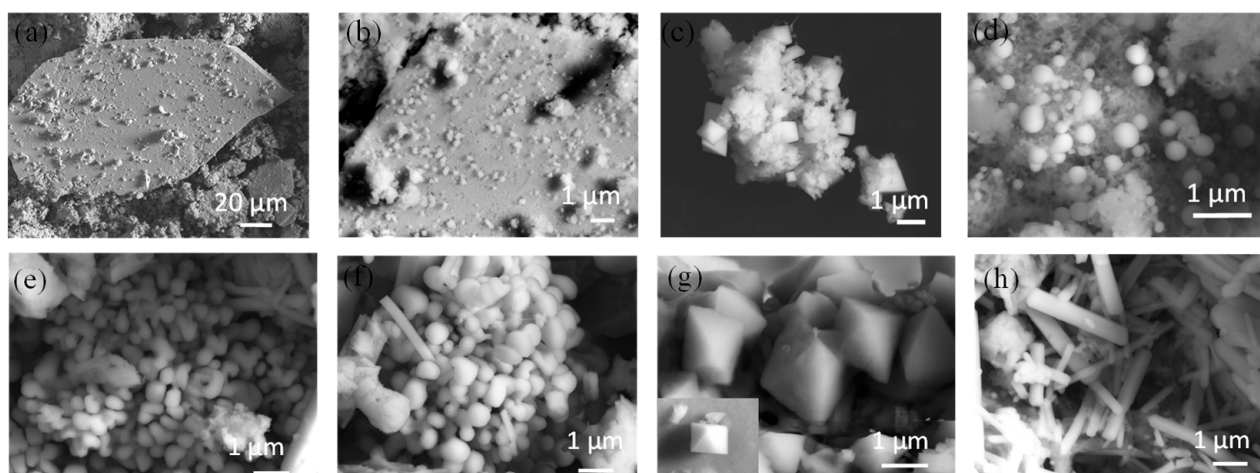
**Figure 1.** Optical images of the prepared powders under white light and UV light of 365 nm in wavelength: (a)  $\text{CsSnI}_3$ -dominated powders, and (b)  $\text{CsSnI}_3$ -contained powders.

A spectrometer (Ocean Optics, FLAME-S-VIS-NIR-ES, Ocean Optics, Orlando, FL, USA) was used to characterize the photoluminescence (PL) of the synthesized  $\text{CsSnI}_3$ -based powders under the excitation of UV light of 365 nm in wavelength and a laser of 785 nm in wavelength, respectively. The absorbance of the synthesized  $\text{CsSnI}_3$ -based powders was analyzed on a UV-Visible spectrophotometer (EVOLUTION 201, Thermo Fisher scientific, Waltham, MA, USA). The photoconduction of the prepared  $\text{CsSnI}_3$ -based powders was examined on a power meter (Keithley 2400, Keithley, Solon, OH, USA) under white light.

### 3. Results and Discussion

Figure 1 depicts optical images of the synthesized  $\text{CsSnI}_3$ -dominated powders, which were stored in a vacuum chamber, and the prepared  $\text{CsSnI}_3$ -contained powders, which were placed under ambient conditions, under UV light of 365 nm in wavelength over a period of 7 days. It is evident that the color of the  $\text{CsSnI}_3$ -based powders under the UV light experienced gradual changes from light green to dark green for the  $\text{CsSnI}_3$ -dominated powders and from light orange to dark orange for the  $\text{CsSnI}_3$ -contained powders over the period of 7 days. The green emission of  $\text{CsSnI}_3$ -based powders under UV light of 365 nm in wavelength has not been reported in the literature to our knowledge. Note that Bharti et al. [20] recently reported the formation of green  $\text{CsSnI}_3$  via solid state reaction under mechanical grinding and sintering at 280 K. The orange emission of the  $\text{CsSnI}_3$ -contained powders is qualitatively in accord with the light emission of  $\text{Cs}_2\text{SnI}_6$  nanobelts/nanocrystals in mother liquor reported by Wang et al. [21]. Note that the  $\text{Cs}_2\text{SnI}_6$  nanobelts/nanocrystals reported in the work of Wang et al. [21] were synthesized by a hot injection method with the use of octadecene, oleylamine, and oleic acid, which is significantly different from the method used in this work.

Figure 2a–d depicts SEM images of green-emitting powders. There are plate-like structures formed from the grinding of the mixture, as shown in Figure 2a,b, which can be attributed to the combinational effect of the shear and compression deformation. There are small particles on the surfaces of the plate-like structures. The SEM images in Figure 2c,d show the formation of aggregates of particles in a nearly octahedral shape and in a nearly spherical shape, respectively. The size of the particles in a nearly octahedral shape is in a range of 100 nm to 300 nm, and the size of the particles in a nearly spherical shape is in a range of 380 nm to 880 nm. The EDS analyses, as shown in Figures S1–S3 in Supplementary Information, yield atomic ratios of nearly 1:1:3 of Cs:Sn:I, 1:1:3 of Cs:Sn:I, 2:1:6 of Cs:Sn:I, and 1:1 of Cs:I for the plate-like structures, the particles on the surface of the plate-like structures, the particles in a nearly octahedral shape, and the particles in a nearly spherical shape, respectively. This result indicates that the prepared green-emitting powders consist of  $\text{CsSnI}_3$ ,  $\text{Cs}_2\text{SnI}_6$ , and  $\text{CsI}$  crystals. Note that the octahedral shape of  $\text{Cs}_2\text{SnI}_6$  crystal is consistent with the observation reported in the literature [18,22,23].



**Figure 2.** SEM images of green-emitting powders: (a,b) plate-like structure, (c)  $\text{Cs}_2\text{SnI}_6$  octahedral microcrystals, and (d) spherical nanocrystals; SEM images of orange-emitting powders: (e,f) spherical nanocrystals, (g) octahedral microcrystals, and (h) rod-like microcrystal.

Figure 2e–h depicts SEM images of the orange-emitting powders. There are many particles presented in a bean-like or sphere-like shape from the grinding of the mixture, as shown in Figure 2e,f, in contrast to the plate-like structures for the green-emitting powders. The SEM images in Figure 2g,h show particles in an octahedral shape and in a rod shape, respectively. The size of the particles in a bean-like or sphere-like shape is in a range of 250 nm to 880 nm, and the size of the particles in an octahedral shape is in a range of 500 nm to 1  $\mu\text{m}$ . The dimensions of the rod-like particles are 500 nm to 4  $\mu\text{m}$  in length and 157 nm to 587 nm in diameter. The EDS analyses, as shown in Figures S4–S6 in Supplementary Information, yield atomic ratios of nearly 1:1 of Cs:I, 2:1:6 of Cs:Sn:I, and 1:1:3 of Cs:Sn:I for the particles in a bean-like or sphere-like shape, the particles in an octahedral shape, and the rod-like particles, respectively. This result indicates that the prepared orange-emitting powders consist of  $\text{CsSnI}_3$ ,  $\text{Cs}_2\text{SnI}_6$ , and CsI crystals.

Figure 3 presents the XRD patterns of the freshly prepared  $\text{CsSnI}_3$ -dominated powders and  $\text{CsSnI}_3$ -contained powders and the corresponding ones stored for one week. According to Figure 3a, there are diffraction peaks corresponding to  $\text{CsSnI}_3$ ,  $\text{Cs}_2\text{SnI}_6$ ,  $\text{SnI}_2$ , and CsI for the freshly prepared  $\text{CsSnI}_3$ -dominated powders, which are in accord with the EDS results presented in the supplementary information. Specifically, the diffraction peaks centered at  $25.52^\circ$ ,  $25.90^\circ$ ,  $31.48^\circ$ ,  $37.73^\circ$ ,  $41.36^\circ$ , and  $46.78^\circ$  correspond to the crystal planes of (131), (211), (221), (051), (002), (171), and (152) of orthorhombic  $\text{CsSnI}_3$  (PDF#97-001-4070); the diffraction peaks centered at  $26.53^\circ$ ,  $30.73^\circ$ , and  $44.02^\circ$  correspond to the crystal planes of (222), (400), and (440) of cubic  $\text{Cs}_2\text{SnI}_6$  (PDF#97-025-0743); the peak centered at  $48.80^\circ$  corresponds to the crystal plane of (211) of cubic CsI (PDF#97-004-4938); and the diffraction peak centered at  $28.67^\circ$  corresponds to the crystal plane of (311) of monoclinic  $\text{SnI}_2$  (PDF#97-000-2831). Using the XRD peaks, the molar fractions of individual compounds in the freshly prepared  $\text{CsSnI}_3$ -dominated powders are calculated and listed in Table 1. It is evident that  $\text{CsSnI}_3$  has the largest molar fraction of 32.80%. Thus, the green-emitting powders are referred to as  $\text{CsSnI}_3$ -dominated powders. The larger molar fraction of  $\text{SnI}_2$  than CsI in the freshly prepared powders indicates that more CsI reacted to form  $\text{CsSnI}_3$  and  $\text{Cs}_2\text{SnI}_6$  than  $\text{SnI}_2$  during the grinding. It is speculated that the green emission of the powders may be associated with the doping in  $\text{SnI}_2$ .





The XRD pattern of the freshly prepared CsSnI<sub>3</sub>-contained powders is depicted in Figure 3b. The peaks centered at 26.54°, 30.90°, 44.31°, 52.44°, and 54.99° correspond to the crystal planes of (222), (400), (440), (622), and (444) of cubic Cs<sub>2</sub>SnI<sub>6</sub> (PDF#97-025-0743); the peaks centered at 25.49° and 25.96° correspond to the crystal planes of (131) and (211) of orthorhombic CsSnI<sub>3</sub> (PDF#97-001-4070); the peaks centered at 39.48°, 48.85°, and 57.02° correspond to the crystal planes of (200), (211), and (220) of cubic CsI (PDF#97-004-4938); and the peaks centered at 31.50°, 32.75°, 37.88°, 41.04°, 46.68°, and 56.18° correspond to crystal planes of (312), (113), (511), (602), (115), and (515) of monoclinic SnI<sub>2</sub> (PDF#97-000-2831). This result indicates that the freshly prepared CsSnI<sub>3</sub>-contained powders consist of four phases of Cs<sub>2</sub>SnI<sub>6</sub>, CsSnI<sub>3</sub>, CsI, and SnI<sub>2</sub>. Using the XRD peaks, the molar fractions of individual compounds in the freshly prepared CsSnI<sub>3</sub>-contained powders are calculated and listed in Table 2. It is evident that CsI has the largest molar fraction of 73.63%. Thus, the orange-emission powders are referred to as CsSnI<sub>3</sub>-contained powders.

**Table 2.** Molar ratios of four compounds in the CsSnI<sub>3</sub>-contained powders.

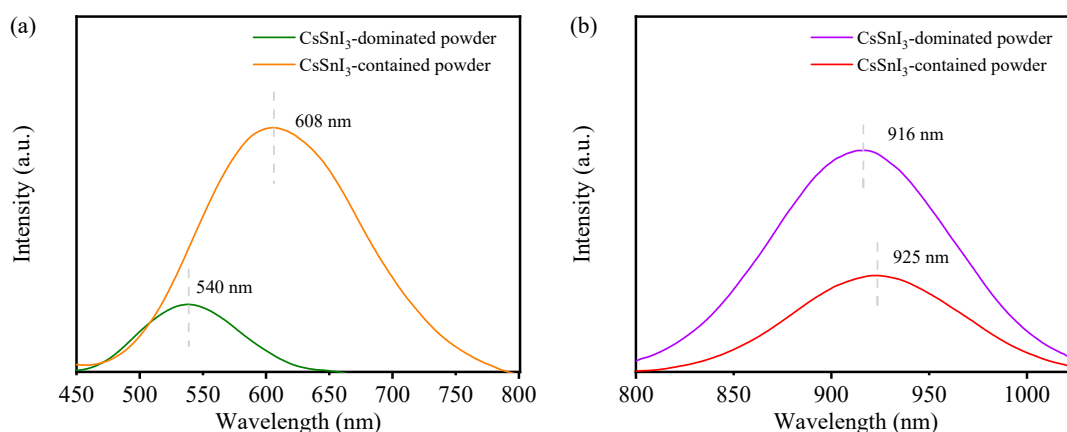
|        | CsI    | SnI <sub>2</sub> | CsSnI <sub>3</sub> | Cs <sub>2</sub> SnI <sub>6</sub> |
|--------|--------|------------------|--------------------|----------------------------------|
| Fresh  | 74.11% | 10.59%           | 7.68%              | 7.62%                            |
| Week 1 | 56.82% | 8.65%            | 6.38%              | 28.16%                           |

Figure 3b also shows the XRD pattern of the CsSnI<sub>3</sub>-contained powders stored under ambient conditions for one week. The peaks centered at 13.08°, 21.54°, 26.41°, 30.69°, 43.91°, 52.10°, and 54.49° correspond to the crystal planes of (111), (220), (222), (400), (440), (622), and (444) of cubic Cs<sub>2</sub>SnI<sub>6</sub> (PDF#97-025-0743); the peaks centered at 27.44° and 48.64° correspond to the crystal planes of (110) and (211) of cubic CsI (PDF#97-004-4938); the peak centered at 25.52° corresponds to the crystal plane of (131) of orthorhombic CsSnI<sub>3</sub> (PDF#97-001-4070); and the peak centered at 28.39° corresponds to the crystal plane of (311) of monoclinic SnI<sub>2</sub> (PDF#97-000-2831). There are no diffraction peaks of new phases presented in the figure in comparison with the freshly prepared one. Using the XRD peaks, the molar fractions of individual compounds in the CsSnI<sub>3</sub>-contained powders stored under ambient conditions for one week are calculated and listed in Table 2. It is evident that there are slight decreases in the molar fractions of both CsSnI<sub>3</sub> and SnI<sub>2</sub>, a large decrease in the molar fraction of CsI, and a large increase in the molar fraction of Cs<sub>2</sub>SnI<sub>6</sub>. There are reactions that lead to the increase of Cs<sub>2</sub>SnI<sub>6</sub> and the decrease in CsI in the CsSnI<sub>3</sub>-contained powders.

From Table 2, we note a large molar fraction of CsI in the CsSnI<sub>3</sub>-contained powders. The orange-emission of the CsSnI<sub>3</sub>-contained powders is likely associated with the doping of Sn in CsI, as illustrated in Figures S7–S9 in Supplementary Information.

The larger molar fraction of CsI compared to SnI<sub>2</sub> in the CsSnI<sub>3</sub>-contained powders indicates that more SnI<sub>2</sub> reacted to form CsSnI<sub>3</sub> and Cs<sub>2</sub>SnI<sub>6</sub> than CsI. The orange emission of the powders can be attributed to the doping in CsI. After one week, the molar fraction of Cs<sub>2</sub>SnI<sub>6</sub> increases, while the molar fractions of SnI<sub>2</sub>, CsSnI<sub>3</sub>, and CsI decrease, suggesting that the Cs<sub>2</sub>SnI<sub>6</sub> comes from CsSnI<sub>3</sub> and SnI<sub>2</sub> through the reactions illustrated in Equations (1) and (2). The decrease in the molar fraction of CsI means the doping effect is weaker as indicated by the optical images in Figure 1b.

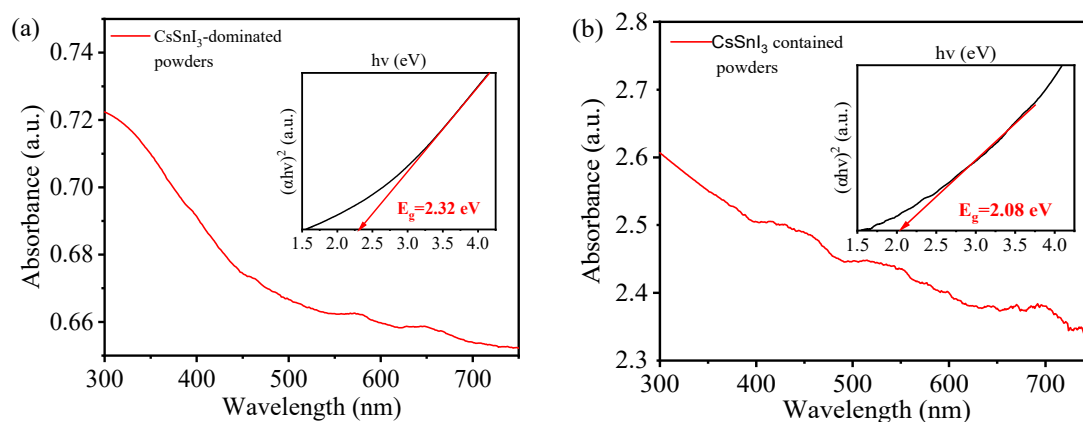
Figure 4a,b presents PL spectra of the freshly prepared CsSnI<sub>3</sub>-based powders under UV light of 365 nm and a laser of 785 nm, respectively. It is interesting to observe that the CsSnI<sub>3</sub>-dominated powders emit both green light centered at 540 nm in wavelength under the UV light and infrared light centered at 916 nm in wavelength under the 785 nm laser. The emission of the green light centered at 540 nm has not been reported in the literature, and the emission of the infrared light centered at 916 nm corresponds to a bandgap of 1.35 eV in accord with 1.31 eV reported by Chung et al. [25].



**Figure 4.** PL spectra of (a) freshly prepared  $\text{CsSnI}_3$ -dominated and  $\text{CsSnI}_3$ -contained powders under UV light of 365 nm in wavelength, and (b) freshly prepared  $\text{CsSnI}_3$ -dominated and  $\text{CsSnI}_3$ -contained powders under a laser of 785 nm in wavelength.

According to Figure 4a,b, the  $\text{CsSnI}_3$ -contained powders emit orange light centered at 608 nm in wavelength under the UV light and infrared light centered at 925 nm in wavelength under the laser. The emission of the orange light centered at 608 nm is close to the PL emission of  $\text{Cs}_2\text{SnI}_6$  centered at 620 nm reported by Wang et al. [21], who prepared  $\text{Cs}_2\text{SnI}_6$  nanocrystals with a hot-injection process. The emission of the infrared light centered at 925 nm corresponds to a bandgap of 1.34 eV in accord with 1.32 eV reported by Wang et al. [26]. The PL peak intensity for the green emission is significantly lower than that for the orange emission, and the PL peak intensity for the infrared emission centered at 916 nm is higher than that for the infrared emission centered at 925 nm. Such differences suggest that the  $\text{CsSnI}_3$ -dominated powders (green emission) and  $\text{CsSnI}_3$ -contained powders (orange emission) possess different characteristics in terms of photoluminescence in the visible and infrared regimes, which can be attributed to the differences in compositions.

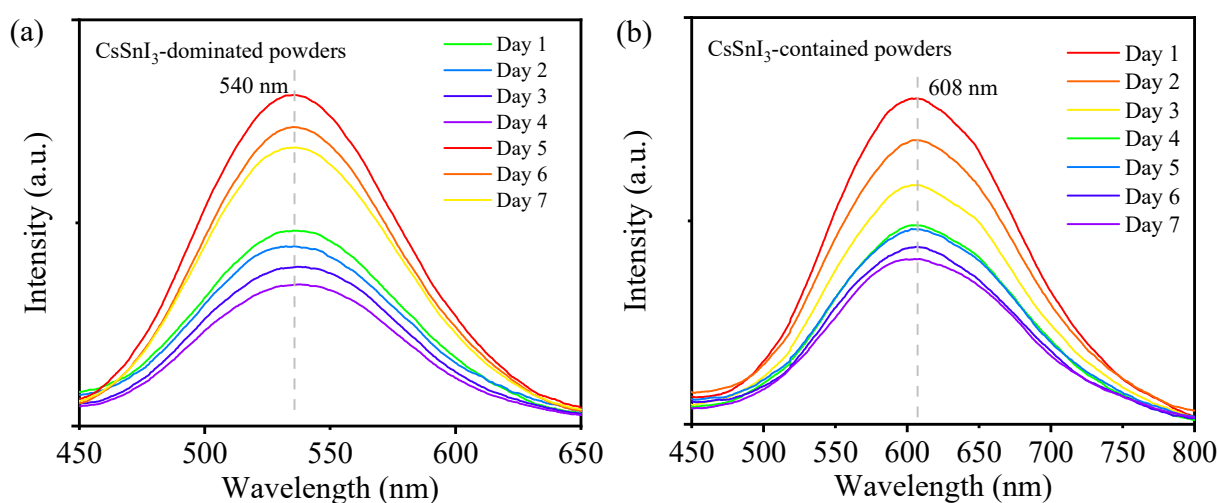
Figure 5a depicts the absorbance spectrum of the  $\text{CsSnI}_3$ -dominated powders. There is no distinct band-edge absorption peak, which might be due to the contributions from four different compounds and the wide range of crystal sizes. Using the absorbance spectrum, the corresponding Tauc plot is constructed and shown as an inset in Figure 5a. From the Tauc plot, we obtain a bandgap of 2.32 eV, which is slightly larger than 2.29 eV from the PL spectrum of the  $\text{CsSnI}_3$ -dominated powders under UV light of 365 nm and less than 2.55 eV reported by Chung et al. [25],



**Figure 5.** Absorbance spectra and Tauc plots (insets) of freshly prepared (a)  $\text{CsSnI}_3$ -dominated powders and (b)  $\text{CsSnI}_3$ -contained powders.

Figure 5b depicts the absorbance spectrum of the  $\text{CsSnI}_3$ -contained powders. There is no distinct band-edge absorption peak, which is similar to the  $\text{CsSnI}_3$ -dominated powders. Such behavior again might be due to the contributions from four different compounds and the wide range of crystal sizes. Using the absorbance spectrum, the corresponding Tauc plot is constructed and shown as an inset in Figure 5b. From the Tauc plot, we obtain a bandgap of 2.08 eV, which is slightly larger than 2.04 eV from the PL spectrum of the  $\text{CsSnI}_3$ -contained powders under the excitation of UV light of 365 nm.

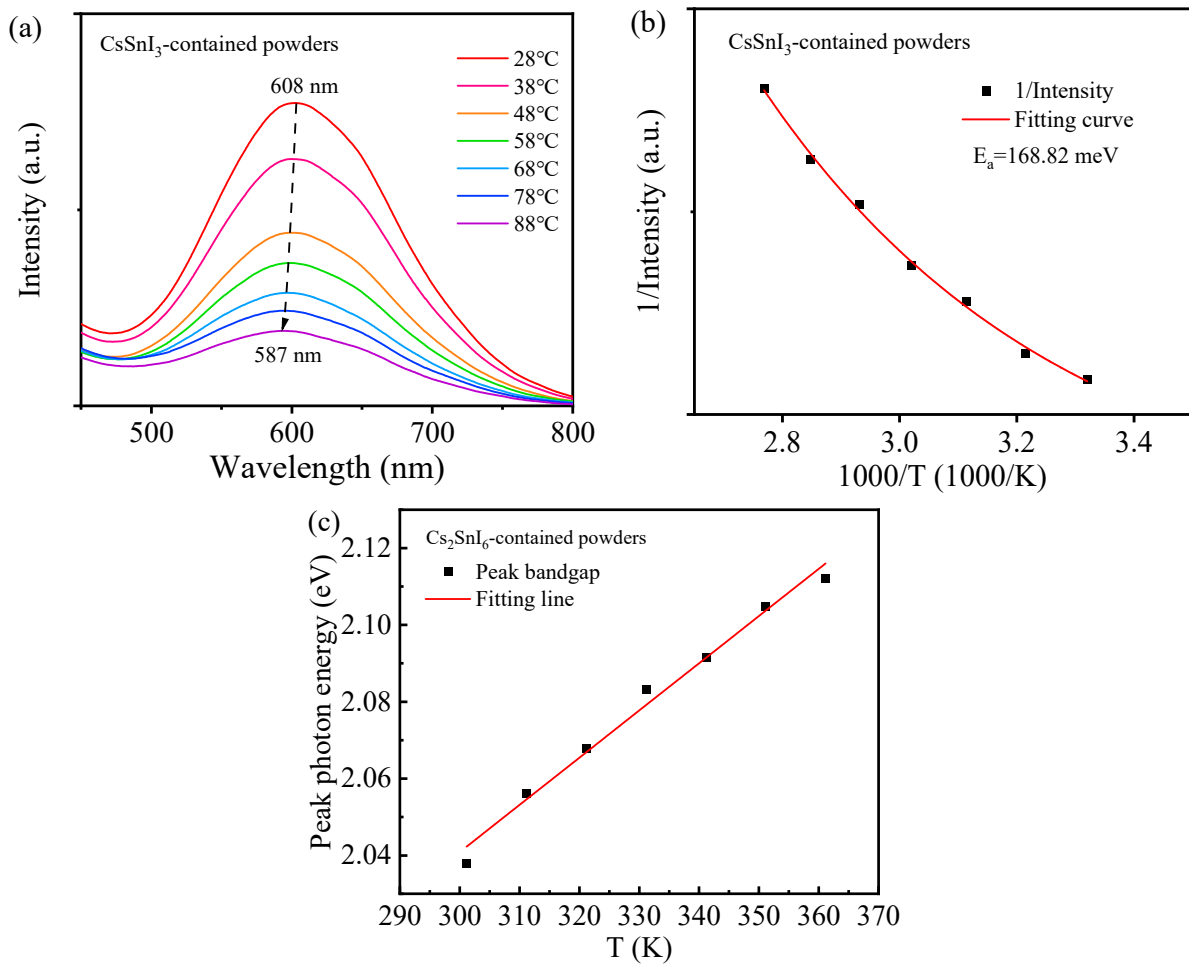
The long-term stability of the  $\text{CsSnI}_3$ -based powders was examined over a period of 7 days. Figure 6a,b depicts the PL spectra of the  $\text{CsSnI}_3$ -dominated powders and  $\text{CsSnI}_3$ -contained powders, respectively. The emission wavelengths of both the powders remain unchanged. The peak intensity decreases continuously, which is consistent with the color change, as shown in Figure 1. Such a trend implies that the prepared  $\text{CsSnI}_3$ -based powders are not at a “stable” state. There exist chemical reactions occurring in the  $\text{CsSnI}_3$ -based powders over the period of 7 days, as supported by the changes in the molar fractions shown in Tables 1 and 2. The chemical reactions lead to the evolution of individual compounds and result in the decrease in the PL peak intensity. Note that the oxidation of Sn occurred in the vacuum chamber and under ambient conditions, which caused the degradation of the  $\text{CsSnI}_3$ -based powders responsible for the decrease in the PL peak intensity. The decreasing trend in the PL peak intensity with respect to time is similar to the decreasing trend for  $\text{MAPbI}_3$  films reported by Mahon et al. [27]. However, there exist differences in the observed behavior. Mahon et al. [27] used a continuous-wave laser as the excitation source and focused their study on a short time period of 250 s. It is also noted that continuous illumination of a laser can cause the variation of the concentration of charger carriers and local temperature [28], leading to the change of the PL peak intensity.



**Figure 6.** Long-term stability of the  $\text{CsSnI}_3$ -based powders over a period of 7 days: (a)  $\text{CsSnI}_3$ -dominated powders in a vacuum chamber, and (b)  $\text{CsSnI}_3$ -contained powder under ambient conditions.

Figure 7a depicts the PL spectra of the  $\text{CsSnI}_3$ -contained powders at different temperatures, from which we determine the peak wavelength and peak intensity at different temperatures. The PL peak wavelength experiences a blue shift from 608 nm to 587 nm when the temperature was increased from 28 °C to 88 °C, and increasing the temperature causes the decrease of the peak intensity. Figure 7b,c shows the temperature dependence of the peak intensity and peak wavelength, respectively.





**Figure 7.** Temperature effects on the PL characteristics of the CsSnI<sub>3</sub>-contained powders: (a) PL spectra at different temperatures, (b) PL intensity vs. temperature, and (c) photon energy vs. temperature.

In general, the variation of the peak intensity of the emission light with temperature can be expressed as [29]

$$I(T) = \frac{I_0}{Ae^{(-E_a/k_B T)} + 1} \quad (3)$$

where  $I_0$  is the peak intensity at 0 K,  $E_a$  is the activation energy,  $k_B T$  is the thermal energy, and  $A$  is a constant. Using Equation (3) to fit the data in Figure 7b yields the activation energy of 168.82 meV. For comparison, we include the fitting curve in Figure 7b. Such a large value of the activation energy suggests that the decrease in the PL peak intensity is ascribed to thermal quenching.

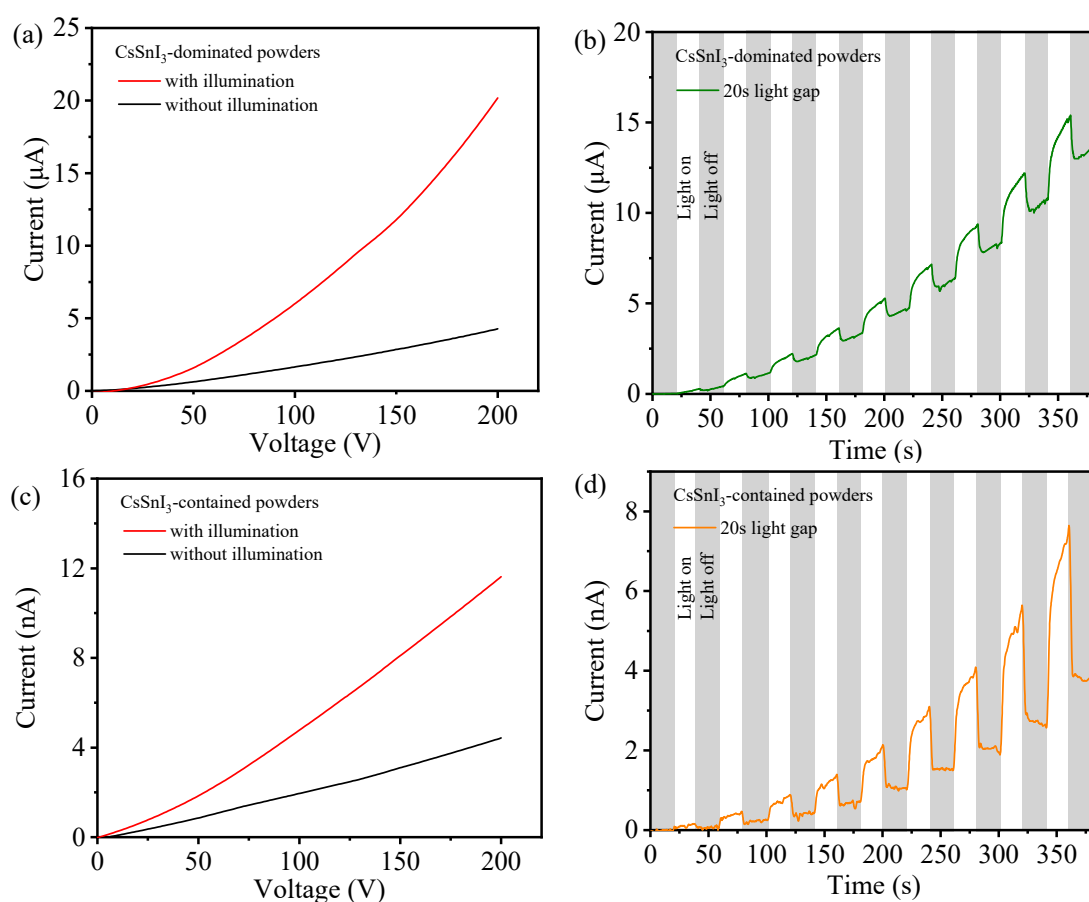
According to Yang [30] and Tang et al. [31], the relation between temperature,  $T$ , and the bandgap of a semiconductor,  $E$ , for  $|\Delta T| \ll T_0$  can be formulated to the first-order approximation as

$$E(T) = E(T_0) + \alpha(T - T_0) \quad (4)$$

with  $T_0$  as a reference temperature, and  $\alpha$  as a constant representing the temperature dependence of the bandgap. According to Figure 7c, the bandgap increases linearly with increasing temperature, supporting Equation (4) with  $\alpha > 0$ . The positive value of  $\alpha$  implies that there exists electron–phonon interaction, which widens the bandgap of the CsSnI<sub>3</sub>-contained powders [31].

It must be pointed out that the CsSnI<sub>3</sub>-dominated powders are unstable after being exposed to the air for a short period. Thus, no experiments were conducted on the thermal stability of the CsSnI<sub>3</sub>-dominated powders.

The photo-responses of the  $\text{CsSnI}_3$ -dominated powders and  $\text{CsSnI}_3$ -contained powders were investigated using a Keithley 2400 sourcemeter. A total of 0.4 mmol of the prepared powders was placed onto a glass substrate. The powders were then shaped to a  $1 \times 1 \text{ cm}^2$  shape and connected to a pair of copper electrodes. The photo-response of the powders was evaluated under a voltage sweeping at an increment of 84 mV. Figure 8a presents the I-V curve of the  $\text{CsSnI}_3$ -dominated powder with and without the illumination of white light. Increasing the voltage leads to a nonlinear increase of the current. The illumination of white light significantly increases the current through the powders, revealing the presence of optoelectrical response under the illumination of white light. Figure 8b presents the I-V curve of the  $\text{CsSnI}_3$ -dominated powders under the periodic on-and-off of white light at a time interval of 20 s. It is evident that the illumination of white light reduced the resistance to the current consistent with the results in Figure 8a. The  $\text{CsSnI}_3$ -dominated powders exhibit lucrative photoconductive characteristics, suggesting the potential application in perovskite-based solar cells.



**Figure 8.** Photo-response of the  $\text{CsSnI}_3$ -dominated powders during a voltage sweeping from 0 V to 200 V (a) with and without the illumination of white light and (b) under a 20 s light on-and-off cycle for 385 s; photo-response of the  $\text{CsSnI}_3$ -contained powders during a voltage sweeping from 0 V to 200 V, (c) with and without the illumination of white light and (d) under a 20 s light on-and-off cycle for 385 s.

Figure 8c,d presents the I-V curve of the  $\text{CsSnI}_3$ -contained powder with and without the illumination of white light and the I-V curve of the  $\text{CsSnI}_3$ -contained powders under the periodic on-and-off of white light at a time interval of 20 s, respectively. Similarly, the  $\text{CsSnI}_3$ -contained powders also exhibit photoconductive characteristics. Comparing Figure 8c,d to Figure 8a,b, we can conclude that the  $\text{CsSnI}_3$ -dominated powders have significantly higher photoconductivity than the  $\text{CsSnI}_3$ -contained powders, indicating a

higher photon-generated carrier concentration in the CsSnI<sub>3</sub>-dominated powders than the CsSnI<sub>3</sub>-contained powders. Note that similar photoconductive behavior was also observed in MAPbI<sub>3</sub> by Khenkin et al. [32], who suggested that the variation of dark conductivity is attributed to the phase change and photoconductivity has a non-monotonic dependence on temperature.

#### 4. Conclusions

Producing lead-free halide perovskites is of practical importance for their applications in solar cells and bioimaging to avoid the detrimental effects of lead to the planet and human health. We have demonstrated that the mechanical grounding of CsI and SnI<sub>2</sub> under two different conditions can produce CsSnI<sub>3</sub>-based powders, which can exhibit dual light emission under two different lights of 365 nm and 785 nm in wavelength. Such a process avoids the use of toxic, organic solvents and can be scaled up to produce Sn-based halide perovskites for industrial applications. The prepared CsSnI<sub>3</sub>-based powders were divided into two groups—one is the CsSnI<sub>3</sub>-dominated powders, and the other is the CsSnI<sub>3</sub>-contained powders. Both powders consist of four different chemical compounds of CsI, SnI<sub>2</sub>, CsSnI<sub>3</sub>, and Cs<sub>2</sub>SnI<sub>6</sub>. Under the excitation of UV light of 365 nm, the CsSnI<sub>3</sub>-dominated powders exhibit green emission with the wavelength centered at 540 nm, and the CsSnI<sub>3</sub>-contained powders exhibit orange emission with the wavelength centered at 608 nm. Such a large difference in the emission wavelength is likely due to the differences in the molar fractions of the four different chemical compounds. Under a laser of 785 nm, the CsSnI<sub>3</sub>-dominated powders exhibit infrared emission with the wavelength centered at 916 nm, and the CsSnI<sub>3</sub>-contained powders exhibit infrared emission with the wavelength centered at 925 nm. However, the lower emission intensity and stability of the prepared Sn-based halide perovskites than lead-based perovskites likely hinder their applications in solar cells.

The analysis of the thermal stability of the CsSnI<sub>3</sub>-contained powders yielded an activation energy of 168.82 meV. Thermal quenching plays a crucial role in determining the stability of the CsSnI<sub>3</sub>-contained powders at elevated temperatures. Both the CsSnI<sub>3</sub>-dominated powders and the CsSnI<sub>3</sub>-contained powders exhibit photoconductive characteristics with a decrease in the resistance of the powders under white light. The CsSnI<sub>3</sub>-dominated powders have significantly higher photoconductivity than the CsSnI<sub>3</sub>-contained powders.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/ma17143577/s1>, Figure S1: EDS spectrum of CsSnI<sub>3</sub> plate. (In Spectrum 14, atomic ratio of Cs: Sn: I = 21.73%: 19.96%: 58.31%); Figure S2: EDS spectrum of Cs<sub>2</sub>SnI<sub>6</sub> plate. (In Spectrum 21, atomic ratio of Cs: Sn: I = 24.1%: 12.6%: 63.3%); Figure S3: EDS spectrum of CsI crystals. (In Spectrum 15, atomic ratio of Cs: I = 49.80%: 45.90%); Figure S4: EDS spectrum of CsI crystals. (In Spectrum 9, atomic ratio of Cs: I = 50.40%: 44.90%); Figure S5: EDS spectrum of CsI crystals. (In Spectrum 1, atomic ratio of Cs: Sn: I = 23.34%: 14.46%: 62.20%); Figure S6: EDS spectrum of CsI crystals. (In Spectrum 11, atomic ratio of Cs: Sn: I = 21.7%: 20.9%: 57.4%); Figure S7: Optical image of SnI<sub>2</sub>-doped CsI under white light and UV lamp (365 nm); Figure S8: Photoluminescence of SnI<sub>2</sub>-doped CsI by mechanical synthesis excited under: (a) UV lamp (365 nm); (b) 785 nm laser at 0.75 V; Figure S9: XRD pattern of SnI<sub>2</sub>-doped CsI by mechanical synthesis. Table S1: Lattice constants of freshly prepared and stored CsSnI<sub>3</sub>-based powders.

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