Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting Information

Highly Efficient Orange Luminescence in Sn^{2+}-doped $Cs_2AgInCl_6$ Double Perovskite with Large Stokes Shift

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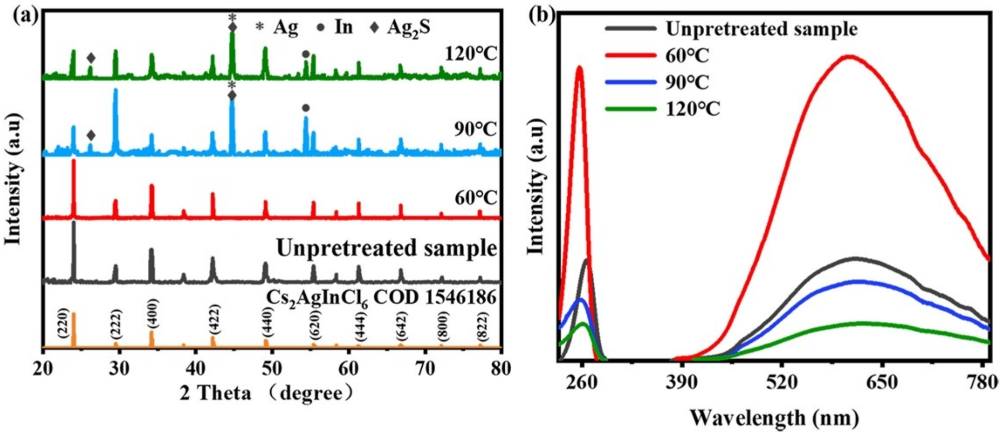

Figure S1. (a) XRD pattern of $Cs_2AgInCl_6$ prepared under different temperatures. (b) PL and PLE spectra of $Cs_2AgInCl_6$ corresponding to (a).

Peaks belongs to Ag_2S appears while treated temperature is 90 °C and 120 °C. As for how Ag_2S is produced, we infer that the reaction process maybe like this:

Firstly, DMSO could decompose under acid condition over 80 °C

$$(CH_3)_2SO \overset{\Delta, H^+}{\rightarrow} CH_2O + CH_4S \tag{S1}$$

The CH_4S produced by decomposition can react with DMSO continually:

$$2CH_4S + (CH_3)_2SO \overset{\Delta, H^+}{\rightarrow} CH_3S_2CH_3 + CH_3SCH_3 + H_2O \tag{S2}$$

The CH_3SCH_3 in this process will react with H_2O and obtain H_2S:

$$CH_3SCH_3 + 2H_2O \overset{\Delta, H^+}{\rightarrow} 2CH_3OH + H_2S \tag{S3}$$

Due to the solubility of Ag_2S is less than that of AgCl and finally produced Ag_2S in the samples prepared at 90 °C and 120 °C.

$$2AgCl + H_2S \overset{\Delta, H^+}{\rightarrow} Ag_2S\downarrow + 2HCl \tag{S4}$$

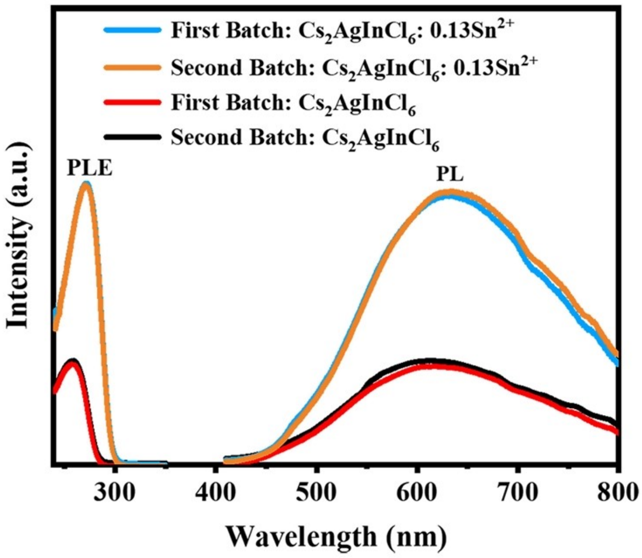

Figure S2. Spectral comparison of $Cs_2AgInCl_6$ and $Cs_2AgInCl_6$: $0.13Sn^{2+}$ prepared in two different batches.

Reproducibility is very important for sample preparation. Take $Cs_2AgInCl_6$ and $Cs_2AgInCl_6$: $0.13Sn^{2+}$ prepared in two batches as an example, the PLE and PL spectra of them in figure S2 shows the same shape, the excitation and emission wavelength of $Cs_2AgInCl_6$ are 257 nm and 612 nm while $Cs_2AgInCl_6$: $0.13Sn^{2+}$ are 257nm and 619 nm, respectively. Importantly, the intensity of peaks in different batches is closely, indicating the well reproducibility of synthesis method. The important point needs to be emphasized in $Cs_2AgInCl_6$: xSn^{2+} fabrication is the dissolution process. The solution must be transparent and clear when transferred to the autoclave, after chemicals added into DMSO and HCl under vigorously stirring at room temperature (25 ^{o}C) for 2 h.

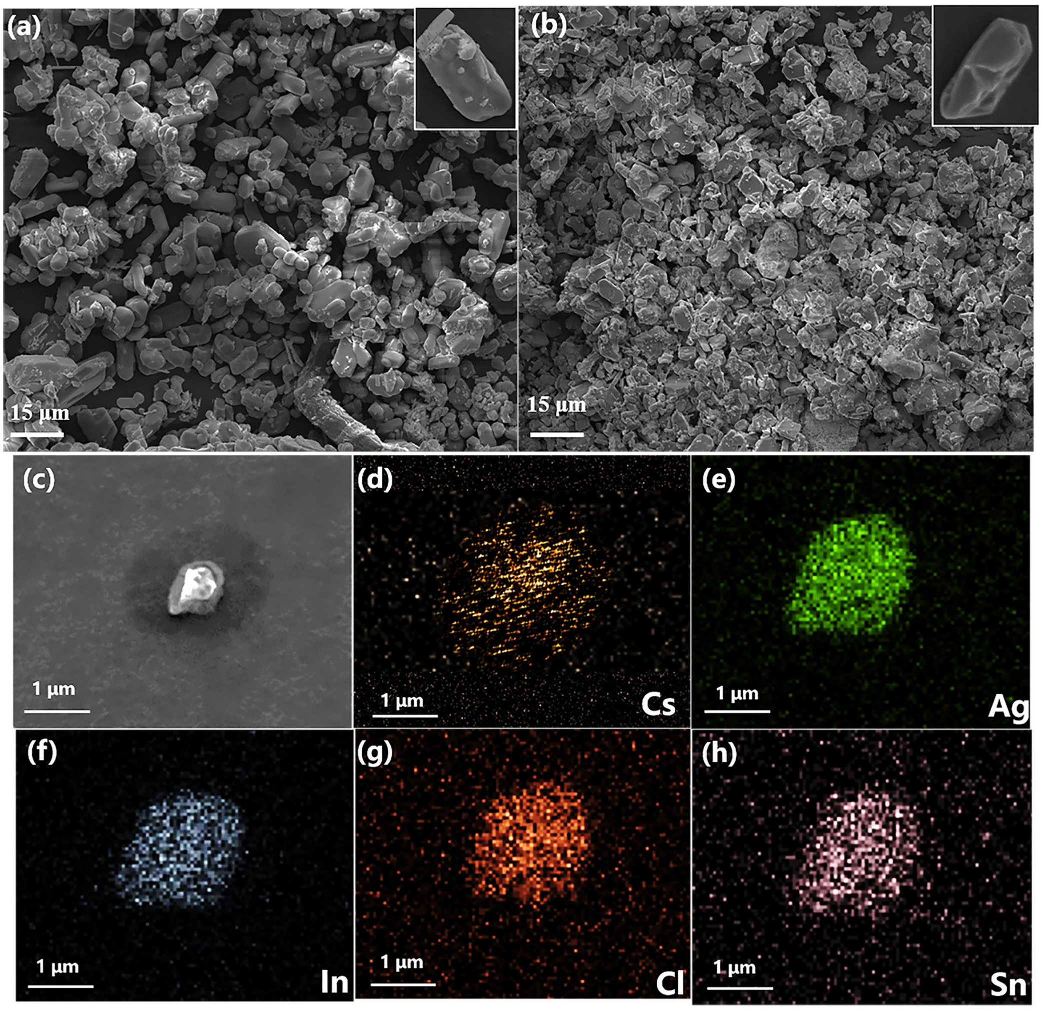

Figure S3. SEM images of $Cs_2AgInCl_6$: $x$$Sn^{2+}$, (a) x=0, (b) x=0.13. (c) $Cs_2AgInCl_6$: 0.13Sn^{2+} particle in (b). (d)-(h) are elemental mapping of (c).

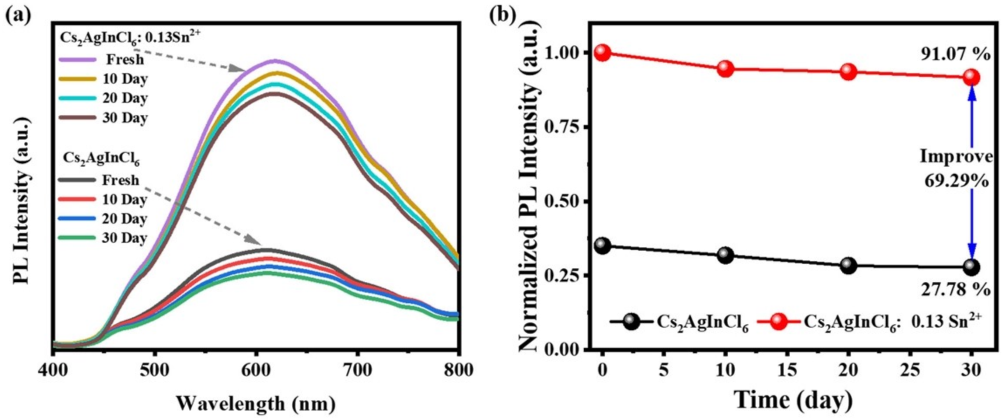

Figure S4. (a) PL spectra of $Cs_2AgInCl_6$ and $Cs_2AgInCl_6$: $0.13Sn^{2+}$ after stored for different time. (b) PL peak change corresponding to (a).

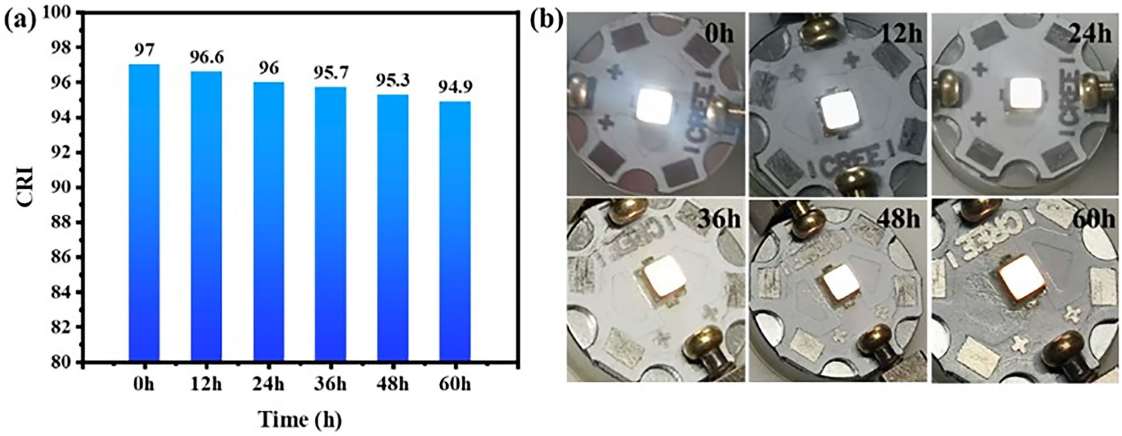

Figure S5. (a) The CRI of WLED after exposed to air for 60 h in 12 h increments. (b) Pictures of package WLED corresponding to (a).

The CRI of the packaged WLED was tested in 12 h increments while the device is directly exposed to the air, as shown in figure S5. 60 h later, the CRI of the WLED is 94.9, which is 97.8% remained compared to the initial value, also is much higher than all of the samples in table S4.

Table S1. The position of PL and PLE peaks of $Cs_2AgInCl_6$ under different hydrothermal treatment temperatures.

Preparation conditions of samples	PLE peak /nm	PL peak /nm	Stokes shift /nm
Unpretreated	266	617	351
60 °C	257	611	354
90 °C	259	616	357
120 °C	261	624	363

Table S2. ICP-OES results of $Cs_2AgInCl_6$: $x$$Sn^{2+}$ (x represents the mass concentration ratios between Sn^{2+} and In^{3+}).

Sample	**ICP-OES**		
	In(mg/L)	**Sn(mg/L)**	***x***
$Cs_2AgInCl_6$: $x$$Sn^{2+}$	465.98	61.02	0.13
	424.48	108.60	0.26
	310.53	115.88	0.37

Table S3. Photoluminescence spectroscopic analysis for $Cs_2AgInCl_6$: $x$$Sn^{2+}$.

Samples	**PLE peak /nm**	**PL peak /nm**	**Stokes shift /nm**
$\mathbf{Cs_2AgInCl_6}$	257	612	355
$\mathbf{Cs_2AgInCl_6}$**: 0.13**$\mathbf{Sn^{2+}}$	257	619	362
$\mathbf{Cs_2AgInCl_6}$**: 0.26**$\mathbf{Sn^{2+}}$	257	618	361
$\mathbf{Cs_2AgInCl_6}$**: 0.37**$\mathbf{Sn^{2+}}$	257	617	360

Table S4. Comparison between different ions doped $Cs_2AgInCl_6$ and this work.

	Materials	**Stokes shift /nm**	**PLQY /%**	**CIE**	**CCT /K**	**Ra**	**Ref**
Single element doping	$Cs_2AgInCl_6$:30%Bi^{3+}	-	4	(0.36,0.35)	4443	91	S1
	$Cs_2AgInCl_6$: Bi	212	11.4	-	-	-	S2
	$Cs_2AgInCl_6$: 1.5%Mn	330	16	-	-	-	S3
	$Cs_2AgIn_{0.833}Bi_{0.176}Cl_6$	260	39	-	3119	85	S4
Co-doping	$Cs_2(Ag/Na)InCl_6$: 1.0%Cu^+	240	62.6	(0.374,0.380)	4060	86	S5
	$Cs_2AgInCl_6$: Bi-Sm	-	13.04	(0.535,0.440)	2000	82	S6
	$Cs_2Ag_{0.7}Na_{0.3}InCl_6$: Bi	-	87.2	(0.38,0.44)	4347	87.8	S7
	$Cs_2Ag_{0.7}Na_{0.3}In_{0.9}Bi_{0.1}Cl_6$	245	32.7	(0.44,0.41)	2953	88.7	S8
This Work	**$Cs_2AgInCl_6$: 0.13Sn^{2+}**	**363**	**29**	**(0.370,0.367)**	**4210**	**97**	**-**

Table S4 summarized the properties of some other doping works on single element doping and two elements co-doping in $Cs_2AgInCl_6$, including material properties (PLQY and Stokes shift) and WLED properties (CIE, CCT, Ra). The Stokes shift and PLQY of $Cs_2AgInCl_6$: 0.13Sn^{2+} is much larger than most of the other samples. The specifications of the WLED device are more optimal than all the other works. It can be found that the overall performance, no matter material and the WLED device, $Cs_2AgInCl_6$: 0.13Sn^{2+} is relatively excellent than many other works. These results positioned the findings within the broader field and highlight the specific advantages of Sn^{2+} doping.

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