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# Sn<sup>2+</sup> doping-induced large extra vibrational energy of an excited state for efficient blue emission in Cs<sub>2</sub>SnCl<sub>6</sub>:Bi<sup>†</sup>

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Luminescent metal halides doped with ns<sup>2</sup>-metal ions, such as 6s<sup>2</sup>-metal Bi<sup>3+</sup>, show excellent optoelectronic properties. However, the origin of the high photoluminescence quantum yield (PLQY) of Cs<sub>2</sub>SnCl<sub>6</sub>:Bi remains controversial and unclear. In this study, a series of Cs<sub>2</sub>SnCl<sub>6</sub>:Bi were synthesized by adopting different tin precursors of SnCl<sub>2</sub>/SnCl<sub>4</sub>. The samples from SnCl<sub>2</sub> exhibited much higher PLQY than those from SnCl<sub>4</sub>, and the doping concentrations of Bi<sup>3+</sup> had little effect on the high PLQY. When H<sub>3</sub>PO<sub>2</sub> is added to the precursor of SnCl<sub>4</sub> to reduce Sn<sup>4+</sup> to Sn<sup>2+</sup>, the prepared Cs<sub>2</sub>SnCl<sub>6</sub>:Bi shows bright emission light and high PLQY. The high PLQY of Cs<sub>2</sub>SnCl<sub>6</sub>:Bi is attributed to the co-doping of Bi<sup>3+</sup> and Sn<sup>2+</sup>. [SnCl<sub>4</sub>]<sup>2-</sup> and two V<sub>Cl</sub> induce a large extra vibrational energy of the heavy localized excitons from [BiCl<sub>5</sub>]<sup>2-</sup> to enhance the efficiency of radiative recombination for high PLQY. This work deepens the understanding of the luminescence mechanism of Cs<sub>2</sub>SnCl<sub>6</sub>:Bi and supplies significant references for developing more perovskite materials with outstanding luminescence.

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## Introduction

Luminescent metal halides have attracted the attention of many researchers. Due to their superior optical properties, such as tunable emissions, high photoluminescence quantum yield (PLQY) and long diffraction length, Pb-based halides show promising perspective in LEDs, solar cells, photodetectors and X-ray imaging.<sup>1–11</sup> However, the toxicity of the heavy metal Pb limits the development of practical applications.<sup>12,13</sup> Accumulated Pb in human body can cause numerous brain-related symptoms, such as intellectual disability. Lead-free metal halides as substitutions have become a research tendency in recent years. Tin (Sn), which also has the characteristics of ns<sup>2</sup> electrons and octahedral coordination, is a potential replacement for Pb. CsSnX<sub>3</sub> exhibits tunable emission light through changing the ratio of halogens, which is similar to the properties of CsPbX<sub>3</sub>.<sup>14–16</sup> However, CsSnX<sub>3</sub> is unstable in air conditions, in which Sn<sup>2+</sup> is easily oxidized to Sn<sup>4+</sup>, causing severe decomposition. Therefore, nontoxic and stable perovskite alternatives must be urgently developed.

Recently, many lead-free metal halides have been explored, such as Cs<sub>2</sub>NaInCl<sub>6</sub>, Cs<sub>2</sub>AgInCl<sub>6</sub>, Cs<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>, Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> and Cs<sub>2</sub>ZrCl<sub>6</sub>, owing to their excellent optoelectronic properties and stable structures.<sup>17–23</sup> Among them, Cs<sub>2</sub>SnCl<sub>6</sub> with its stable tetravalent cation is considered as a promising candidate for photoelectric applications.<sup>24,25</sup> The Cs<sub>2</sub>SnCl<sub>6</sub> crystal is derived from the three-dimensional CsSnCl<sub>3</sub> perovskite, which periodically removes half of the Sn atoms at the center of each [SnCl<sub>6</sub>]<sup>2-</sup> octahedron, forming a vacant-ordered double perovskite structure (space group *Fm* $\bar{3}$ *m*). The [SnCl<sub>6</sub>]<sup>2-</sup> octahedral structure is isolated by a Cs<sup>+</sup> cation. Pure Cs<sub>2</sub>SnCl<sub>6</sub> exhibits poor photoluminescence property, but it is an excellent host material. Cs<sub>2</sub>SnCl<sub>6</sub> is a zero-dimensional structure, and it can localize the excitons for the luminescent centers to achieve high effective emissions. Through doping with a luminescent center, such as Bi<sup>3+</sup>, Sb<sup>3+</sup> and Te<sup>4+</sup>, Cs<sub>2</sub>SnCl<sub>6</sub> can exhibit excellent luminescence with tunable emission wavelength.<sup>26–29</sup> Sb<sup>3+</sup>-doped Cs<sub>2</sub>SnCl<sub>6</sub> has been reported to emit orange light with a photoluminescence quantum yield (PLQY) of 37%, and Bi<sup>3+</sup> doping resulted in blue light emission with a PLQY of 79%.<sup>30–32</sup> The Bi<sup>3+</sup>/Te<sup>4+</sup> co-doped perovskite derivative Cs<sub>2</sub>SnCl<sub>6</sub> shows highly efficient and dual-band-tunable white-light emission owing to the strong electron-phonon coupling and efficient energy transfer.<sup>33–35</sup>

Interestingly, when Cs<sub>2</sub>SnCl<sub>6</sub>:Bi is synthesized by adopting SnCl<sub>2</sub> as a precursor of the Sn source, Cs<sub>2</sub>SnCl<sub>6</sub>:Bi can get a high PLQY of ~78%. However, if using SnCl<sub>4</sub> as a precursor to synthesize Cs<sub>2</sub>SnCl<sub>6</sub>:Bi, the PLQY of the prepared Cs<sub>2</sub>SnCl<sub>6</sub>:Bi is

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below 30%. The underlying reason for this phenomenon remains unclear. Motivated by this, we synthesized a series of  $\text{Bi}^{3+}$ -doped  $\text{Cs}_2\text{SnCl}_6$  samples using  $\text{SnCl}_2$  or  $\text{SnCl}_4$  as the precursor under different conditions. Through comparing the photophysical properties of the  $\text{Cs}_2\text{SnCl}_6$  samples with different  $\text{Bi}^{3+}$  doping content, we find that the samples from  $\text{SnCl}_2$  have much higher PLQY values than those from  $\text{SnCl}_4$ , and the doping content of  $\text{Bi}^{3+}$  has little effect on the high PLQY. When some reductive  $\text{H}_3\text{PO}_2$  is added in the precursor solution with  $\text{SnCl}_4$ , the prepared  $\text{Cs}_2\text{SnCl}_6\text{:Bi}$  shows brighter emission light and higher PLQY than the sample without  $\text{H}_3\text{PO}_2$ .  $\text{H}_3\text{PO}_2$  provides a reducing environment and reduces  $\text{Sn}^{4+}$  to  $\text{Sn}^{2+}$  during the reaction, and XPS spectra proved the existence of  $\text{Sn}^{2+}$  in  $\text{Cs}_2\text{SnCl}_6\text{:Bi}$  synthesized with  $\text{H}_3\text{PO}_2$ .  $[\text{SnCl}_4]^{2-}$  and two  $\text{V}_{\text{Cl}}$  induce the local lattice distortion, which can cause heavy localized excitons of  $[\text{BiCl}_5]^{2-}$ . The localized excitons make for a large extra vibrational energy to reduce the non-radiative transition and enhance the efficiency of radiative recombination. This work deepens the understanding of the luminescence mechanism of  $\text{Cs}_2\text{SnCl}_6\text{:Bi}$ , but also introduces novel ideas and approaches to develop more perovskite materials with outstanding luminescent properties.

## Results and discussion

As shown in the experimental processes in Fig. 1a,  $\text{SnCl}_2$  or  $\text{SnCl}_4$ ,  $\text{CsCl}$  and  $\text{BiCl}_3$  were added to the autoclave containing hydrochloric acid. The autoclave was heated in the oven at  $180^\circ\text{C}$  for 10 hours to obtain  $\text{Cs}_2\text{SnCl}_6\text{:Bi}$  single crystals. As shown in Fig. 1b, the single crystals show regular hexagonal shape, and the size is about several to tens of micrometers,

indicating good crystallinity. EDS mapping images show that Cs, Sn, Cl, and Bi are evenly distributed in Fig. 1d, meaning Bi was successfully doped into the lattice of  $\text{Cs}_2\text{SnCl}_6$ . Through changing the doping content of Bi and the Sn source from  $\text{SnCl}_2$  or  $\text{SnCl}_4$ , a series of  $\text{Cs}_2\text{SnCl}_6$  samples were prepared. The actual doping amount of Bi was tested by inductively coupled plasma optical emission spectrometry (ICP-OES), and the element contents were given in Table 1. The samples are named as  $\text{Sn}^{x+}\text{:yBi}$  ( $\text{Sn}^{x+}$  represents that the sample is synthesized by  $\text{SnCl}_2$  or  $\text{SnCl}_4$  in the raw materials;  $y$  represents the actual doping concentration of  $\text{Bi}^{3+}$  replacing the site of  $\text{Sn}^{4+}$ ). As shown in Fig. 1c, all of the samples are confirmed to be pure  $\text{Cs}_2\text{SnCl}_6$  with space group (PDF #70-2413). The position of the diffraction peak gradually shifted to a low angle as the concentration of doped  $\text{Bi}^{3+}$  increased, which indicates that  $\text{Bi}^{3+}$  was doped into the lattice of the  $\text{Cs}_2\text{SnCl}_6$  crystal. Rietveld refinement of the samples of  $\text{Sn}^{2+}\text{:0.08% Bi}$  and  $\text{Sn}^{4+}\text{:0.04% Bi}$  were performed to acquire information on the crystal structure, as shown in Fig. S1 (ESI<sup>†</sup>).  $\text{Sn}^{2+}\text{:0.08% Bi}$  and  $\text{Sn}^{4+}\text{:0.04% Bi}$  are in the  $Fm\bar{3}m$  space group. The lattice parameters of  $\text{Sn}^{2+}\text{:0.08% Bi}$  are  $a = b = c = 10.388 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ , as the lattice parameters of  $\text{Sn}^{2+}\text{:0.08% Bi}$  are  $a = b = c = 10.386 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ . Because the radius of the  $\text{Bi}^{3+}$  ion ( $1.03 \text{ \AA}$  for coordination number (CN) = 6) is larger than that of the  $\text{Sn}^{4+}$  ion ( $0.69 \text{ \AA}$  for CN = 6),  $\text{Sn}^{2+}\text{:0.08% Bi}$  has larger lattice parameters than  $\text{Sn}^{4+}\text{:0.04% Bi}$ . Therefore, these results further verified that the single phase was successfully obtained and the crystal structure was unchanged with the introduction of  $\text{Bi}^{3+}$  ions. Although the feeding amount of  $\text{BiCl}_3$  was from 1% to 8%, the actual doping contents of  $\text{Bi}^{3+}$  for all samples are at a very low level, less than 2%. In Table 1, all

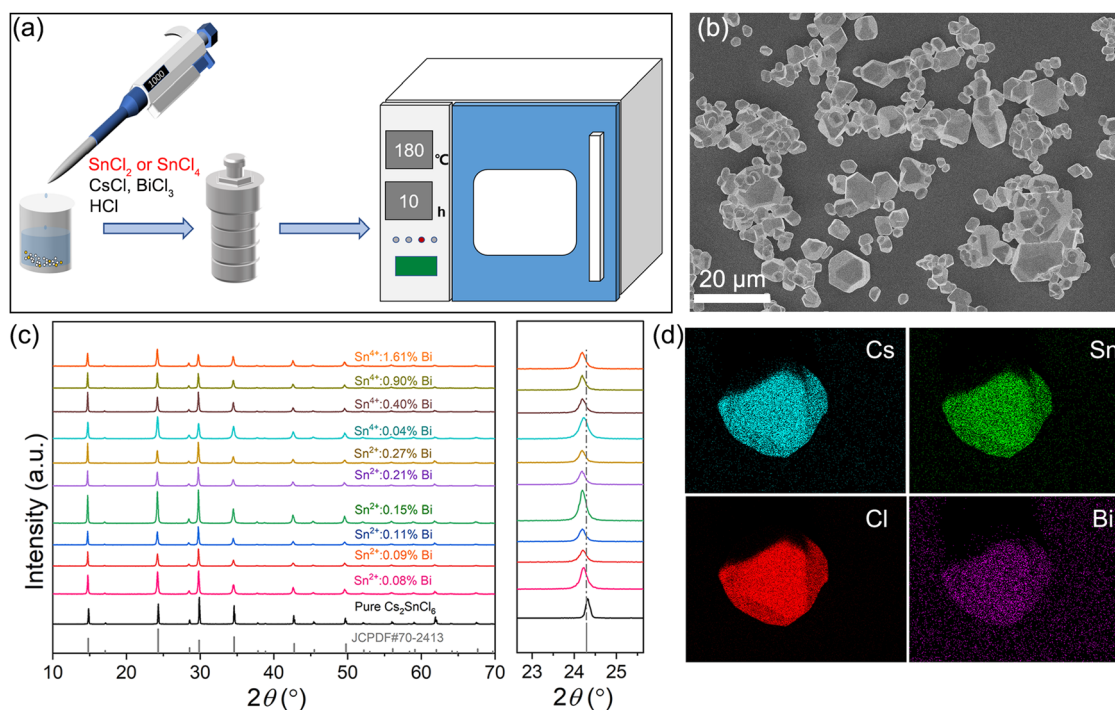


Fig. 1 (a) Schematic diagram of the synthesis process. (b) SEM image of the  $\text{Cs}_2\text{SnCl}_6\text{:Bi}$  particles. (c) XRD patterns of  $\text{Cs}_2\text{SnCl}_6\text{:Bi}$  with varied doping content and different tin precursors. (d) EDS mapping for showing the distribution of individual elements Cs, Sn, Cl and Bi.

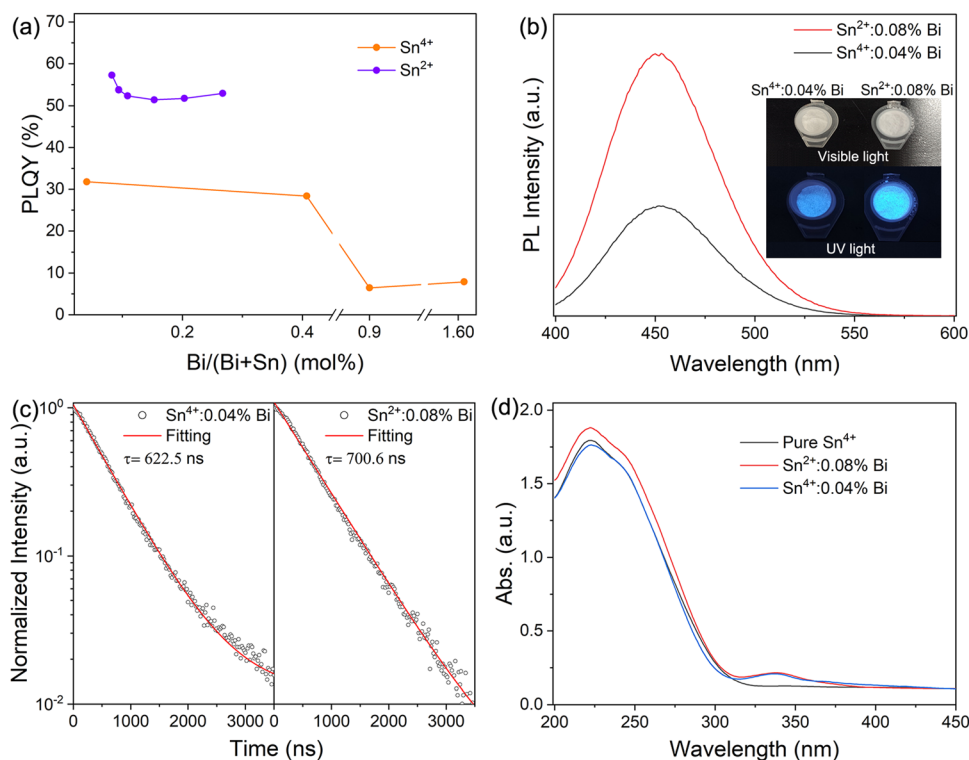


**Table 1** Doping content of Bi and PLQY for the samples synthesized by the precursor of SnCl<sub>2</sub> or SnCl<sub>4</sub>

Sn precursor	SnCl <sub>4</sub>				SnCl <sub>2</sub>					
Feeding Bi (%)	0.99	2.91	4.76	7.41	0.99	2.91	4.76	7.41	9.09	13.04
Incorporated Bi (%)	0.04	0.41	0.90	1.61	0.08	0.09	0.11	0.15	0.20	0.27
PLQY (%)	31.8	28.39	6.46	7.9	57.29	53.79	52.39	51.44	51.78	52.98

samples synthesized by SnCl<sub>2</sub> exhibit a higher PLQY than those by SnCl<sub>4</sub>, as shown in Fig. 2a (the values of PLQY were calculated according to the PL spectra in Fig. S2, ESI†). PLQY of the samples synthesized by the SnCl<sub>2</sub> precursor solution were above 50%, and did not change with the increase of the Bi<sup>3+</sup> doping contents. Conversely, the PLQY of the samples synthesized by the SnCl<sub>4</sub> precursor was varied with Bi<sup>3+</sup> doping concentration, and could not reach 50%. Thus, the kind of tin halides precursor was the major factor for the high PLQY, and the Bi<sup>3+</sup> doping content was a minor factor and had little effect on the high PLQY. In Fig. 2b and Fig. S3 (ESI†), all of the samples of Cs<sub>2</sub>SnCl<sub>6</sub>:Bi have a broad emission peak at 452 nm, and the optimal excitation wavelength of all samples is 349 nm. Moreover, when the mixture precursors of SnCl<sub>2</sub> and SnCl<sub>4</sub> were used, the PLQY of the prepared samples was enhanced from 12.53 to 49.38% with the increase of the SnCl<sub>2</sub> proportion in the precursor, as shown in Fig. S4 (ESI†). In order to research the reason for the different PLQY, we chose two samples of Sn<sup>2+</sup>:0.08%Bi and Sn<sup>4+</sup>:0.04%Bi, which have almost the same amount of

doping Bi, for photophysical performance testing and analysis. In Fig. 2b, comparing the PL spectra of Sn<sup>2+</sup>:0.08%Bi and Sn<sup>4+</sup>:0.04%Bi, the shape and center position of the emission peak are the same, whereas the intensity is different. The inset photograph shows that Sn<sup>2+</sup>:0.08%Bi emits brighter blue light under UV light (365 nm) than Sn<sup>4+</sup>:0.04%Bi. The PL decay curves of Sn<sup>2+</sup>:0.08%Bi and Sn<sup>4+</sup>:0.04%Bi are well fitted by a single exponential, and the lifetime values of Sn<sup>2+</sup>:0.08%Bi and Sn<sup>4+</sup>:0.04%Bi are close at 622.6 and 700.6 ns respectively (Fig. 2c). The PL spectra and lifetime values indicated that the blue emission comes from the same radiation transition. In Fig. 2d, comparing the absorption spectra of pure Cs<sub>2</sub>SnCl<sub>6</sub>, Sn<sup>2+</sup>:0.08%Bi and Sn<sup>4+</sup>:0.04%Bi, the absorption edge at 315 nm is from the host Cs<sub>2</sub>SnCl<sub>6</sub>, but Sn<sup>2+</sup>:0.08%Bi and Sn<sup>4+</sup>:0.04%Bi have a small absorption peak at 340 nm, which is attributed to the absorption of doping Bi ions. Thus, according to the above results, it can be concluded that the improvement of the radiative transition efficiency is the main reason for the improvement of PLQY in Sn<sup>2+</sup>:0.08%Bi.<sup>30</sup> We speculate that (1) using SnCl<sub>2</sub> as the



**Fig. 2** (a) PLQY for the samples with different doping contents of Bi<sup>3+</sup> using SnCl<sub>2</sub> or SnCl<sub>4</sub> as the precursor. (b) PL intensities of Sn<sup>2+</sup>:0.08%Bi and Sn<sup>4+</sup>:0.04%Bi, which have almost the same amount of doping Bi<sup>3+</sup>; the inset of (b) is the photograph of these two samples under visible light and UV light. (c) Time-resolved PL and respective fitting curves of Sn<sup>2+</sup>:0.08%Bi and Sn<sup>4+</sup>:0.04%Bi. (d) UV-Vis absorption spectra of Sn<sup>2+</sup>:0.08%Bi, Sn<sup>4+</sup>:0.04%Bi and Pure Sn<sup>4+</sup>.



raw material to synthesize  $\text{Cs}_2\text{SnCl}_6$  may introduce some  $\text{Sn}^{2+}$  into the lattice because both  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$  ions have octahedral coordination; (2)  $\text{Sn}^{2+}$  does not transfer energy to Bi, but only improves the radiative transition efficiency of  $\text{Bi}^{3+}$  due to the lattice distortion.

To further confirm the effect of  $\text{Sn}^{2+}$  in the precursor, we added a little  $\text{H}_3\text{PO}_2$  solution into the precursor solution with  $\text{SnCl}_4$  to reduce some  $\text{Sn}^{4+}$  to  $\text{Sn}^{2+}$ . The prepared  $\text{Cs}_2\text{SnCl}_6\text{:Bi}$  samples with/without  $\text{H}_3\text{PO}_2$  were named as  $\text{Sn}^{4+}\text{:Bi@H}_3\text{PO}_2$  and  $\text{Sn}^{4+}\text{:Bi}$ . As shown in Fig. 3a, the addition of  $\text{H}_3\text{PO}_2$  does not change the XRD patterns.  $\text{Sn}^{4+}\text{:Bi@H}_3\text{PO}_2$  and  $\text{Sn}^{4+}\text{:Bi}$  are the pure  $\text{Cs}_2\text{SnCl}_6$  phase without impure phases. In Fig. 3b, the normalized PLE spectra can well coincide, meaning that  $\text{H}_3\text{PO}_2$  did not change the transition level. In Fig. 3c, the PL intensity of  $\text{Sn}^{4+}\text{:Bi@H}_3\text{PO}_2$  is higher than that of  $\text{Sn}^{4+}\text{:Bi}$ . In the inset image, the  $\text{Sn}^{4+}\text{:Bi@H}_3\text{PO}_2$  powder shows brighter blue light under UV light. Meanwhile, the lifetime values are 730.4 and 744 ns for  $\text{Sn}^{4+}\text{:Bi@H}_3\text{PO}_2$  and  $\text{Sn}^{4+}\text{:Bi}$ , respectively. The PLQY of  $\text{Sn}^{4+}\text{:Bi@H}_3\text{PO}_2$  is up to 35.4%, which is more than twice that of  $\text{Sn}^{4+}\text{:Bi}$  (13.7%). These results of PL, PLE and lifetime are consistent with those of  $\text{Sn}^{4+}\text{:yBi}$  and  $\text{Sn}^{2+}\text{:yBi}$ .  $\text{H}_3\text{PO}_2$  is supposed to reduce some  $\text{Sn}^{4+}$  to  $\text{Sn}^{2+}$  in the precursor solution, and  $\text{Sn}^{2+}$  is then doped into the  $\text{Sn}^{4+}$  lattice of  $\text{Cs}_2\text{SnCl}_6$  together with Bi during the process of hydrothermal synthesis, resulting in a large increase of PLQY. Therefore, the  $\text{Sn}^{2+}\text{:yBi}$  samples using  $\text{SnCl}_2$  as the precursor are  $\text{Sn}^{2+}$  and Bi co-doped  $\text{Cs}_2\text{SnCl}_6$ .

To verify the presence of divalent tin ions in the prepared  $\text{Cs}_2\text{SnCl}_6\text{:Bi}$ , we performed XPS tests. Since  $\text{Sn}^{2+}$  on the surface

of particles is easily oxidized to the tetravalent form in under air conditions, to ensure the reliability of the XPS data, we cut the single crystal in an inert atmosphere and tested the fresh cross-section. In the inert atmosphere,  $\text{Sn}^{2+}$  on the fresh cross-section is not oxidized and can be accurately detected. The full-scan XPS spectra in Fig. S5 (ESI<sup>†</sup>) show that all elements were detected at the cross-section. In Fig. 4a and b, the Sn 3d spectra of  $\text{Sn}^{4+}\text{:Bi@H}_3\text{PO}_2$  shows the obvious peaks of  $\text{Sn}^{2+}$  at binding energies of 493.65 and 485.25 eV, while that of  $\text{Sn}^{4+}\text{:Bi}$  do not exhibit any peaks for  $\text{Sn}^{2+}$ . This result proves that the samples prepared by using  $\text{SnCl}_2$  or  $\text{SnCl}_4$  and  $\text{H}_3\text{PO}_2$  is Bi and  $\text{Sn}^{2+}$  co-doped  $\text{Cs}_2\text{SnCl}_6$ , and the improved PLQY may come from the distortion of the local structure caused by the divalent tin. The crystal diagram of the co-doped structure is shown in Fig. 5a. The  $\text{Cs}_2\text{SnCl}_6$  crystal is a vacant-ordered double perovskite (space group  $Fm\bar{3}m$ ).  $[\text{SnCl}_6]^{2-}$  octahedral is isolated by the  $\text{Cs}^+$  cation. When  $\text{SnCl}_2$  is used as a precursor and co-doped with Bi,  $\text{Sn}^{2+}$  partially replaces  $\text{Sn}^{4+}$  to form a 4-coordinated octahedral structure  $[\text{SnCl}_4]^{2-}$  with two Cl vacancies; Bi replaces  $\text{Sn}^{4+}$  to form a 5-coordinated octahedral structure with a Cl vacancy. Bi belongs to the isolated luminescence center, which serves to localize the excitons and enhance radiative recombination.<sup>30</sup> The spatial distortion of the  $[\text{BiCl}_5]^{2-}$  polyhedron will cause the change of luminescence properties, while the spatial distortion is affected by its surrounding environment. The incorporated  $\text{Sn}^{2+}$  in the state of  $[\text{SnCl}_4]^{2-}$  and two  $\text{V}_{\text{Cl}}$  can provide a large space to cause the local lattice distortion. When some  $[\text{SnCl}_4]^{2-}$  are adjacent with  $[\text{BiCl}_5]^{2-}$ , the heavy distortion of  $[\text{BiCl}_5]^{2-}$  occurs. This distortion

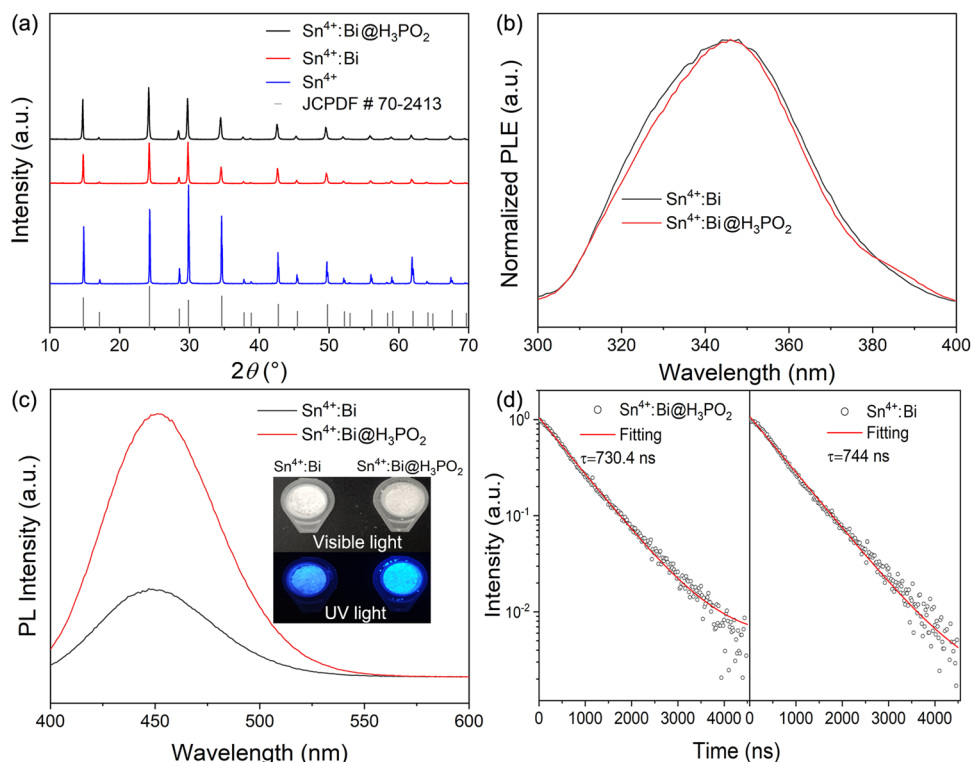


Fig. 3 (a) XRD patterns of  $\text{Sn}^{4+}\text{:Bi@H}_3\text{PO}_2$ ,  $\text{Sn}^{4+}\text{:Bi}$  and pure  $\text{Sn}^{4+}$ . (b) PLE, (c) PL spectra of  $\text{Sn}^{4+}\text{:Bi@H}_3\text{PO}_2$  and  $\text{Sn}^{4+}\text{:Bi}$ ; the inset of (c) is the photograph of  $\text{Sn}^{4+}\text{:Bi@H}_3\text{PO}_2$  and  $\text{Sn}^{4+}\text{:Bi}$  powders under visible light and UV light. (d) Time-resolved PL and respective fitting curves of  $\text{Sn}^{4+}\text{:Bi@H}_3\text{PO}_2$  and  $\text{Sn}^{4+}\text{:Bi}$ .



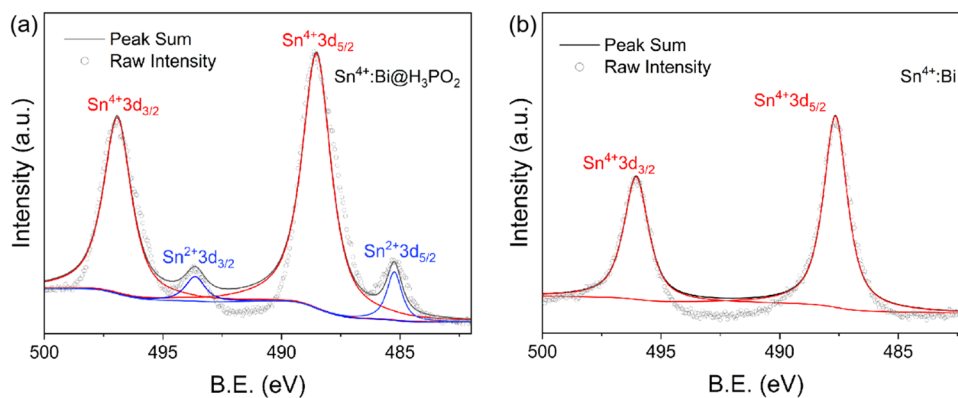


Fig. 4 High-resolution XPS spectra of Sn 3d for (a)  $\text{Sn}^{4+}:\text{Bi}@\text{H}_3\text{PO}_2$  and (b)  $\text{Sn}^{4+}:\text{Bi}$ .

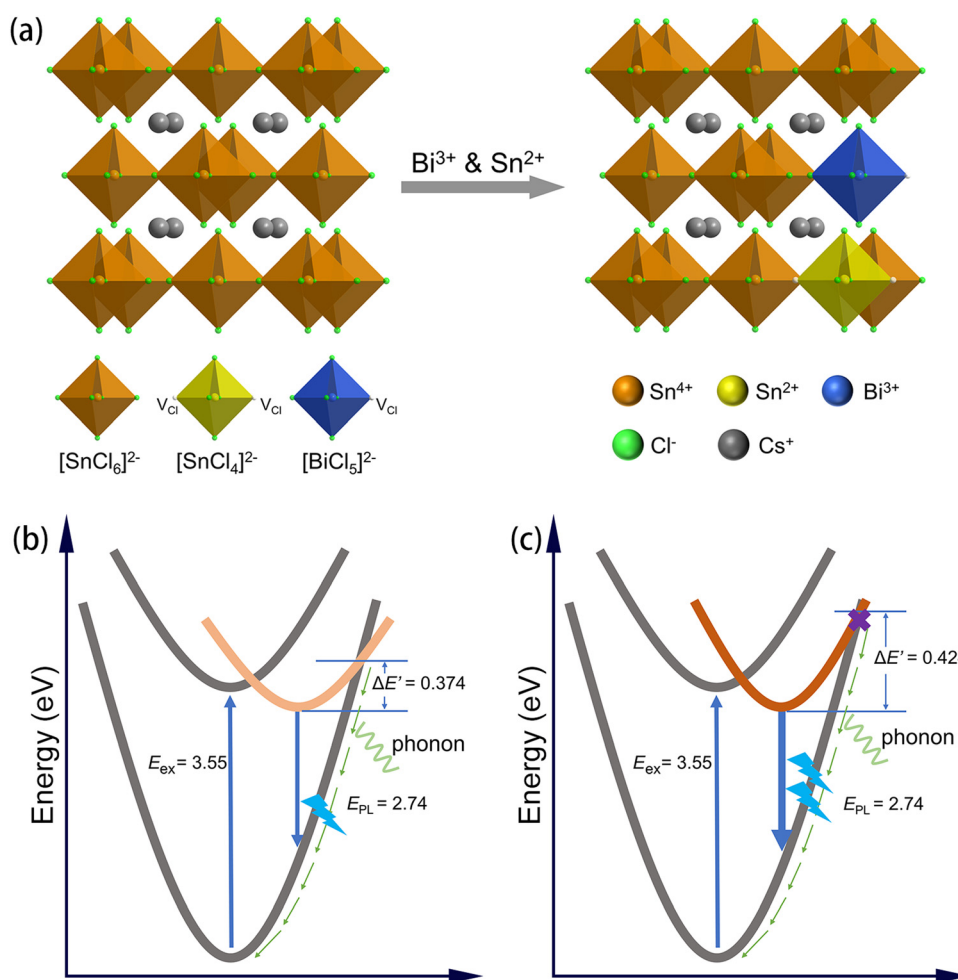


Fig. 5 (a) Schematic diagram of the crystal structure of  $\text{Bi}^{3+}$  and  $\text{Sn}^{2+}$ -doped  $\text{Cs}_2\text{SnCl}_6$ . Schematic of the energy level structure for (b)  $\text{Sn}^{4+}:\text{Bi}$  and (c)  $\text{Sn}^{4+}:\text{Bi}@\text{H}_3\text{PO}_2$ .

induces more localized excitons by the Jahn-Teller effect,<sup>30</sup> which can cause a large additional vibrational energy to prohibit the non-radiative transitions and enhance the efficiency of radiative recombination. To prove this inference, the extra vibrational energy is the direct evidence. Fig. S6 (ESI<sup>†</sup>) shows the change

in the temperature-dependent PL intensity. Above 125 °C,  $\text{Sn}^{4+}:\text{Bi}@\text{H}_3\text{PO}_2$  still emitted light, whereas  $\text{Sn}^{4+}:\text{Bi}$  no longer emitted light. The emission intensity of  $\text{Sn}^{4+}:\text{Bi}@\text{H}_3\text{PO}_2$  decreased more slowly than that of  $\text{Sn}^{4+}:\text{Bi}$  with the increase of temperature. According to eqn (1),



$$I = I_0 / (1 + e^{-\Delta E' / k_B T}) \quad (1)$$

where  $I$  is the PL intensity,  $\Delta E'$  is the extra vibrational energy required to produce a non-radiative transition, and  $k_B$  is the Boltzmann constant.<sup>36</sup> It can be determined that  $\text{Sn}^{4+}:\text{Bi}@H_3\text{PO}_2$  should have a higher  $\Delta E'$  than  $\text{Sn}^{4+}:\text{Bi}$ . In order to obtain the value of the extra vibrational energy, the PL spectra of the samples  $\text{Sn}^{2+}:0.08\% \text{Bi}$  and  $\text{Sn}^{4+}:0.04\% \text{Bi}$  were measured at different temperatures. Through fitting the PL intensity as a function of temperature as shown in Fig. S7 (ESI<sup>†</sup>), the values of  $\Delta E'$  for the samples  $\text{Sn}^{2+}:0.08\% \text{Bi}$  and  $\text{Sn}^{4+}:0.04\% \text{Bi}$  are 424 and 374 meV, respectively.  $\text{Sn}^{2+}:0.08\%$  had a larger value of the extra vibrational energy than  $\text{Sn}^{4+}:0.04\% \text{Bi}$ , which means that the non-radiative transitions of  $\text{Sn}^{2+}:0.08\% \text{Bi}$  can be further prohibited to improve the efficiency of radiative transitions. As shown in Fig. 5b and c, the incorporated  $\text{Sn}^{2+}$  in the state of  $[\text{SnCl}_4]^{2-}$  and two  $\text{V}_{\text{Cl}}$  increased the energy value of  $\Delta E'$  of  $[\text{BiCl}_5]^{2-}$  due to the more localized excitons, which reduces the probability of a non-radiative transition, and increases the probability of a radiative transition. Thus,  $\text{Cs}_2\text{SnCl}_6:\text{Bi}^{3+}$  and  $\text{Sn}^{2+}$  can finally achieve a significant improvement of PLQY.

## Conclusion

In summary, a series of  $\text{Cs}_2\text{SnCl}_6:\text{Bi}$  with different precursors have been synthesized, and the photophysical properties were investigated. Comparing  $\text{Cs}_2\text{SnCl}_6:\text{Bi}$  synthesized by  $\text{SnCl}_4$ ,  $\text{Cs}_2\text{SnCl}_6:\text{Bi}$  from  $\text{SnCl}_2$  shows much higher PLQY, and the doping content of  $\text{Bi}^{3+}$  has little effect on the high PLQY. The reductive  $\text{H}_3\text{PO}_2$  in the precursor solution of  $\text{SnCl}_4$  makes the prepared  $\text{Cs}_2\text{SnCl}_6:\text{Bi}$  show brighter emission light and higher PLQY (35.4%) than the sample without  $\text{H}_3\text{PO}_2$  (PLQY of 13.7%). This is because  $\text{H}_3\text{PO}_2$  reduces  $\text{Sn}^{4+}$  to  $\text{Sn}^{2+}$  during the reaction, and the XPS spectra proved the existence of  $\text{Sn}^{2+}$  in the  $\text{Cs}_2\text{SnCl}_6:\text{Bi}$  sample synthesized with  $\text{H}_3\text{PO}_2$ . The sample is actually  $\text{Bi}^{3+}$  and  $\text{Sn}^{2+}$  co-doped  $\text{Cs}_2\text{SnCl}_6$ .  $[\text{SnCl}_4]^{2-}$  and two  $\text{V}_{\text{Cl}}$  induce the local lattice distortion, which can cause the heavy localized excitons of  $[\text{BiCl}_5]^{2-}$  to enhance the efficiency of radiative recombination. This work improves the deep understanding of the luminescence mechanism of  $\text{Cs}_2\text{SnCl}_6:\text{Bi}$ , and provides a new idea for developing efficient perovskite materials.

## Experimental section

**Materials and chemicals:** cesium chloride ( $\text{CsCl}$ , Macklin, 99.9%), bismuth chloride ( $\text{BiCl}_3$ , Macklin, 99.99%), tin chloride dihydrate ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , Aladdin, 99.99%), tin tetrachloride ( $\text{SnCl}_4$ , Energy Chemical, 99%), hypophosphorous acid ( $\text{H}_3\text{PO}_2$ , Aladdin, 50 wt% in water), and hydrochloric acid ( $\text{HCl}$ , Guangzhou Chemical Reagent Factory, 37 wt% in water) were the starting reagents. All of the chemicals were used without further purification, unless otherwise stated.

**Preparation of precursors:** 4 mL  $\text{SnCl}_4$  was dissolved in 17 mL  $\text{HCl}$  to prepare 2 M  $\text{SnCl}_4$  solution. A total of 12 mmol (3784.08 mg)  $\text{BiCl}_3$  was dissolved in 6 mL  $\text{HCl}$  to prepare 2 M  $\text{BiCl}_3$  solution.

**Synthesis of  $\text{Cs}_2\text{SnCl}_6:\text{Bi}$ :** an amount of 336.72 mg (2 mmol)  $\text{CsCl}$ , 225.65 mg (1 mmol)  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  or 0.5 mL (1 mmol)  $\text{SnCl}_4$  precursor, and 0–50  $\mu\text{L}$  (0–0.1 mmol)  $\text{BiCl}_3$  precursor were added in a polytetrafluoroethylene (PTFE) container with 15 mL of 37%  $\text{HCl}$ . The container was placed in a muffle furnace and kept at 180 °C for 10 h. Crystals were obtained by slowly cooling the solution down to room temperature over the course of 20 h. White crystals of  $\text{Cs}_2\text{SnCl}_6:\text{Bi}$  could be separated by immediate centrifugation, and were washed three times with ethanol.

**Synthesis of  $\text{Cs}_2\text{SnCl}_6:\text{Bi}@H_3\text{PO}_2$ :** an amount of 336.72 mg (2 mmol)  $\text{CsCl}$ , 500  $\mu\text{L}$  (1 mmol)  $\text{SnCl}_4$  precursor, 50  $\mu\text{L}$  (0.1 mmol)  $\text{BiCl}_3$  precursor and 0.05 mL  $\text{H}_3\text{PO}_2$  were added in a polytetrafluoroethylene (PTFE) container with 15 mL of 37%  $\text{HCl}$ . The container was placed in a muffle furnace and kept at 180 °C for 10 h. Crystals were obtained by slowly cooling the solution down to room temperature over the course of 20 h. White crystals of  $\text{Cs}_2\text{SnCl}_6:\text{Bi}@H_3\text{PO}_2$  could be separated by immediate centrifugation and were washed three times with ethanol.

**Measurement and characterization:** the phase determination of the obtained samples was carried out by powder X-ray diffraction (XRD) (D2, Bruker, using a  $\text{Cu K}\alpha$  rotating anode). Depth-profile XPS spectra were recorded on an AXIS Supra, using an X-ray beam focused to an area of 2 mm<sup>2</sup> on the sample, and with an etching at the rate of 1 nm for 35 s. The PL, PLE, PLQY spectra and decay curve collection were recorded on an Edinburgh Instruments FS5 spectrometer equipped with a Xenon lamp and an integrating sphere. Inductively coupled plasma optical emission spectrometry (ICP-OES) was performed by using an atomic emission spectrometer (Agilent 5110). UV-vis absorption spectra were collected with a UV-3600i Plus spectrometer.

## Conflicts of interest

There are no conflicts to declare.

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