Materials Advances



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Cite this: *Mater. Adv.*, 2023, 4, 2365

Received 6th March 2023, Accepted 26th April 2023

DOI: 10.1039/d3ma00107e

rsc.li/materials-advances

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.^{1–11} However, the toxicity of the heavy metal Pb limits the development of practical applications.^{12,13} 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 ns² electrons and octahedral coordination, is a potential replacement for Pb. CsSnX₃ exhibits tunable emission light through changing the ratio of halogens, which is similar to the properties of CsPbX₃.¹⁴⁻¹⁶ However, CsSnX₃ is unstable in air conditions, in which Sn²⁺ is easily oxidized to Sn⁴⁺, causing severe decomposition. Therefore, nontoxic and stable perovskite alternatives must be urgently developed.

Sn²⁺ doping-induced large extra vibrational energy of an excited state for efficient blue emission in Cs₂SnCl₆:Bi⁺

Luminescent metal halides doped with ns^2 -metal ions, such as $6s^2$ -metal Bi^{3+} , show excellent optoelectronic properties. However, the origin of the high photoluminescence quantum yield (PLQY) of Cs_2SnCl_6 :Bi remains controversial and unclear. In this study, a series of Cs_2SnCl_6 :Bi were synthesized by adopting different tin precursors of $SnCl_2/SnCl_4$. The samples from $SnCl_2$ exhibited much higher PLQY than those from $SnCl_4$, and the doping concentrations of Bi^{3+} had little effect on the high PLQY. When H_3PO_2 is added to the precursor of $SnCl_4$ to reduce Sn^{4+} to Sn^{2+} , the prepared Cs_2SnCl_6 :Bi shows bright emission light and high PLQY. The high PLQY of Cs_2SnCl_6 :Bi is attributed to the co-doping of Bi^{3+} and Sn^{2+} . $[SnCl_4]^{2-}$ and two V_{Cl} induce a large extra vibrational energy of the heavy localized excitons from $[BiCl_5]^{2-}$ to enhance the efficiency of radiative recombination for high PLQY. This work deepens the understanding of the luminescence mechanism of Cs_2SnCl_6 :Bi and supplies significant references for developing more perovskite materials with outstanding luminescence.

Recently, many lead-free metal halides have been explored, such as Cs₂NaInCl₆, Cs₂AgInCl₆, Cs₃Bi₂I₉, Cs₃Cu₂I₅ and Cs₂ZrCl₆, owing to their excellent optoelectronic properties and stable structures.^{17–23} Among them, Cs₂SnCl₆ with its stable tetravalent cation is considered as a promising candidate for photoelectric applications.^{24,25} The Cs₂SnCl₆ crystal is derived from the threedimensional CsSnCl₃ perovskite, which periodically removes half of the Sn atoms at the center of each $[SnCl_6]^{2-}$ octahedron, forming a vacant-ordered double perovskite structure (space group $Fm\bar{3}m$). The $[SnCl_6]^{2-}$ octahedral structure is isolated by a Cs⁺ cation. Pure Cs₂SnCl₆ exhibits poor photoluminescence property, but it is an excellent host material. Cs₂SnCl₆ is a zerodimensional structure, and it can localize the excitons for the luminescent centers to achieve high effective emissions. Through doping with a luminescent center, such as Bi³⁺, Sb³⁺ and Te4+, Cs2SnCl6 can exhibit excellent luminescence with tunable emission wavelength.^{26–29} Sb³⁺-doped Cs₂SnCl₆ has been reported to emit orange light with a photoluminescence quantum yield (PLQY) of 37%, and Bi³⁺ doping resulted in blue light emission with a PLQY of 79%.³⁰⁻³² The Bi³⁺/Te⁴⁺ co-doped perovskite derivative Cs₂SnCl₆ shows highly efficient and dualband-tunable white-light emission owing to the strong electronphonon coupling and efficient energy transfer.33-35

Interestingly, when Cs_2SnCl_6 :Bi is synthesized by adopting $SnCl_2$ as a precursor of the Sn source, Cs_2SnCl_6 :Bi can get a high PLQY of ~78%. However, if using $SnCl_4$ as a precursor to synthesize Cs_2SnCl_6 :Bi, the PLQY of the prepared Cs_2SnCl_6 :Bi is

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[†] Electronic supplementary information (ESI) available. See DOI: https://doi.org/ 10.1039/d3ma00107e

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below 30%. The underlying reason for this phenomenon remains unclear. Motivated by this, we synthesized a series of Bi3+-doped Cs₂SnCl₆ samples using SnCl₂ or SnCl₄ as the precursor under different conditions. Through comparing the photophysical properties of the Cs₂SnCl₆ samples with different Bi³⁺ doping content, we find that the samples from SnCl₂ have much higher PLQY values than those from SnCl₄, and the doping content of Bi³⁺ has little effect on the high PLQY. When some reductive H_3PO_2 is added in the precursor solution with SnCl₄, the prepared Cs₂SnCl₆:Bi shows brighter emission light and higher PLQY than the sample without H₃PO₂. H₃PO₂ provides a reducing environment and reduces Sn⁴⁺ to Sn²⁺ during the reaction, and XPS spectra proved the existence of Sn²⁺ in Cs₂SnCl₆:Bi synthesized with H_3PO_2 . [SnCl₄]²⁻ and two V_{Cl} induce the local lattice distortion, which can cause heavy localized excitons of $[BiCl_5]^{2-}$. 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 Cs₂SnCl₆: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, $SnCl_2$ or $SnCl_4$, CsCl and $BiCl_3$ were added to the autoclave containing hydrochloric acid. The autoclave was heated in the oven at 180 °C for 10 hours to obtain Cs_2SnCl_6 :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 Cs₂SnCl₆. Through changing the doping content of Bi and the Sn source from SnCl₂ or SnCl₄, a series of Cs₂SnCl₆ 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 Sn^{x+} :yBi (Sn^{x+} represents that the sample is synthesized by SnCl₂ or SnCl₄ in the raw materials; y represents the actual doping concentration of Bi³⁺ replacing the site of Sn⁴⁺). As shown in Fig. 1c, all of the samples are confirmed to be pure Cs₂SnCl₆ with space group (PDF #70-2413). The position of the diffraction peak gradually shifted to a low angle as the concentration of doped Bi³⁺ increased, which indicates that Bi³⁺ was doped into the lattice of the Cs₂SnCl₆ crystal. Rietveld refinement of the samples of Sn²⁺:0.08% Bi and Sn⁴⁺:0.04% Bi were performed to acquire information on the crystal structure, as shown in Fig. S1 (ESI[†]). Sn²⁺:0.08% Bi and Sn⁴⁺:0.04% Bi are in the $Fm\bar{3}m$ space group. The lattice parameters of Sn²⁺:0.08% Bi are a = b = c = 10.388 Å, $\alpha = \beta = \gamma = 90^{\circ}$, as the lattice parameters of Sn²⁺:0.08% Bi are a = b = c = 10.386 Å, $\alpha = \beta = \gamma = 90^{\circ}$. Because the radius of the Bi³⁺ ion (1.03 Å for coordination number (CN) = 6) is larger than that of the Sn^{4+} ion (0.69 Å for CN = 6), Sn²⁺:0.08% Bi has larger lattice parameters that Sn⁴⁺: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 Bi³⁺ ions. Although the feeding amount of BiCl₃ was from 1% to 8%, the actual doping contents of 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 Cs_2SnCl_6 :Bi particles. (c) XRD patterns of Cs_2SnCl_6 :Bi with varied doping content and different tin precursors. (d) EDS mapping for showing the distribution of individual elements Cs, Sn, Cl and Bi.

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Table 1 Doping content of Bi and PLQY for the samples synthesized by the precursor of SnCl₂ or SnCl₄

Sn precursor	SnCl ₄				SnCl ₂					
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 SnCl₂ exhibit a higher PLQY than those by SnCl₄, 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 SnCl₂ precursor solution were above 50%, and did not change with the increase of the Bi³⁺ doping contents. Conversely, the PLQY of the samples synthesized by the SnCl₄ precursor was varied with Bi³⁺ doping concentration, and could not reach 50%. Thus, the kind of tin halides precursor was the major factor for the high PLQY, and the Bi³⁺ 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 Cs₂SnCl₆: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 SnCl₂ and SnCl₄ were used, the PLOY of the prepared samples was enhanced from 12.53 to 49.38% with the increase of the SnCl₂ 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 Sn²⁺:0.08%Bi and Sn⁴⁺: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 Sn²⁺:0.08%Bi and Sn⁴⁺: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 Sn²⁺:0.08%Bi emits brighter blue light under UV light (365 nm) than Sn⁴⁺:0.04%Bi. The PL decay curves of Sn²⁺:0.08%Bi and Sn⁴⁺:0.04%Bi are well fitted by a single exponential, and the lifetime values of Sn2+:0.08%Bi and Sn⁴⁺: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 Cs₂SnCl₆, Sn²⁺:0.08%Bi and Sn⁴⁺:0.04%Bi, the absorption edge at 315 nm is from the host Cs₂SnCl₆, but Sn²⁺:0.08%Bi and Sn⁴⁺: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 Sn²⁺:0.08%Bi.³⁰ We speculate that (1) using SnCl₂ as the



Fig. 2 (a) PLQY for the samples with different doping contents of Bi^{3+} using $SnCl_2$ or $SnCl_4$ as the precursor. (b) PL intensities of $Sn^{2+}:0.08\%Bi$ and $Sn^{4+}:0.04\%Bi$, which have almost the same amount of doping Bi^{3+} ; 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 $Sn^{2+}:0.08\%Bi$ and $Sn^{4+}:0.04\%Bi$. (d) UV-Vis absorption spectra of $Sn^{2+}:0.08\%Bi$, $Sn^{4+}:0.04\%Bi$ and Pure Sn^{4+} .

raw material to synthesize Cs_2SnCl_6 may introduce some Sn^{2+} into the lattice because both Sn^{2+} and Sn^{4+} ions have octahedral coordination; (2) Sn^{2+} does not transfer energy to Bi, but only improves the radiative transition efficiency of Bi^{3+} due to the lattice distortion.

To further confirm the effect of Sn^{2+} in the precursor, we added a little H₃PO₂ solution into the precursor solution with $SnCl_4$ to reduce some Sn^{4+} to Sn^{2+} . The prepared Cs_2SnCl_6 :Bi samples with/without H₃PO₂ were named as Sn⁴⁺:Bi@H₃PO₂ and Sn⁴⁺:Bi. As shown in Fig. 3a, the addition of H₃PO₂ does not change the XRD patterns. Sn⁴⁺:Bi@H₃PO₂ and Sn⁴⁺:Bi are the pure Cs₂SnCl₆ phase without impure phases. In Fig. 3b, the normalized PLE spectra can well coincide, meaning that H₃PO₂ did not change the transition level. In Fig. 3c, the PL intensity of Sn⁴⁺:Bi@H₃PO₂ is higher than that of Sn⁴⁺:Bi. In the inset image, the Sn⁴⁺:Bi@H₃PO₂ powder shows brighter blue light under UV light. Meanwhile, the lifetime values are 730.4 and 744 ns for Sn⁴⁺:Bi@H₃PO₂ and Sn⁴⁺:Bi, respectively. The PLQY of Sn⁴⁺:Bi@H₃PO₂ is up to 35.4%, which is more than twice that of Sn⁴⁺:Bi (13.7%). These results of PL, PLE and lifetime are consistent with those of Sn⁴⁺:yBi and Sn²⁺:yBi. H₃PO₂ is supposed to reduce some Sn⁴⁺ to Sn²⁺ in the precursor solution, and Sn²⁺ is then doped into the Sn⁴⁺ lattice of Cs₂SnCl₆ together with Bi during the process of hydrothermal synthesis, resulting in a large increase of PLQY. Therefore, the Sn²⁺:yBi samples using SnCl₂ as the precursor are Sn²⁺ and Bi co-doped Cs₂SnCl₆.

To verify the presence of divalent tin ions in the prepared Cs_2SnCl_6 :Bi, we performed XPS tests. Since 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 crosssection. In the inert atmosphere, Sn²⁺ on the fresh cross-section is not oxidized and can be accurately detected. The full-scan XPS spectra in Fig. S5 (ESI⁺) show that all elements were detected at the cross-section. In Fig. 4a and b, the Sn 3d spectra of Sn^{4+} :Bi@H₂PO₂ shows the obvious peaks of Sn^{2+} at binding energies of 493.65 and 485.25 eV, while that of Sn4+:Bi do not exhibit any peaks for Sn²⁺. This result proves that the samples prepared by using SnCl₂ or SnCl₄ and H₃PO₂ is Bi and Sn²⁺ codoped Cs₂SnCl₆, 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 Cs₂SnCl₆ crystal is a vacant-ordered double perovskite (space group $Fm\bar{3}m$). [SnCl₆]²⁻ octahedral is isolated by the Cs⁺ cation. When SnCl₂ is used as a precursor and co-doped with Bi, Sn²⁺ partially replaces Sn⁴⁺ to form a 4-coordinated octahedral structure [SnCl₄]²⁻ with two Cl vacancies; Bi replaces Sn⁴⁺ to form a 5coordinated octahedral structure with a Cl vacancy. Bi belongs to the isolated luminescence center, which serves to localize the excitons and enhance radiative recombination.³⁰ The spatial distortion of the [BiCl₅]²⁻ polyhedron will cause the change of luminescence properties, while the spatial distortion is affected by its surrounding environment. The incorporated Sn²⁺ in the state of $[SnCl_4]^{2-}$ and two V_{Cl} can provide a large space to cause the local lattice distortion. When some $[SnCl_4]^{2-}$ are adjacent with $[BiCl_5]^{2-}$, the heavy distortion of $[BiCl_5]^{2-}$ occurs. This distortion



Fig. 3 (a) XRD patterns of Sn^{4+} : Bi@H₃PO₂, Sn^{4+} : Bi and pure Sn^{4+} . (b) PLE, (c) PL spectra of Sn^{4+} : Bi@H₃PO₂ and Sn^{4+} : Bi; the inset of (c) is the photograph of Sn^{4+} : Bi@H₃PO₂ and Sn^{4+} : Bi







Fig. 5 (a) Schematic diagram of the crystal structure of Bi^{3+} and Sn^{2+} -doped Cs_2SnCl_6 . Schematic of the energy level structure for (b) Sn^{4+} :Bi and (c) Sn^{4+} :Bi@H₃PO₂.

induces more localized excitons by the Jahn-Teller effect,³⁰ 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⁺) shows the change in the temperature-dependent PL intensity. Above 125 $^{\circ}$ C, Sn⁴⁺: Bi@H₃PO₂ still emitted light, whereas Sn⁴⁺:Bi no longer emitted light. The emission intensity of Sn⁴⁺:Bi@H₃PO₂ decreased more slowly than that of Sn⁴⁺:Bi with the increase of temperature. According to eqn (1),

where I is the PL intensity, $\Delta E'$ is the extra vibrational energy required to produce a non-radiative transition, and $k_{\rm B}$ is the Boltzmann constant.³⁶ It can be determined that Sn⁴⁺:Bi@H₃PO₂ should have a higher $\Delta E'$ than Sn^{4+} :Bi. In order to obtain the value of the extra vibrational energy, the PL spectra of the samples Sn²⁺:0.08% Bi and Sn⁴⁺:0.04% Bi were measured at different temperatures. Through fitting the PL intensity as a function of temperature as shown in Fig. S7 (ESI⁺), the values of $\Delta E'$ for the samples Sn²⁺:0.08% Bi and Sn⁴⁺:0.04% Bi are 424 and 374 meV, respectively. Sn²⁺:0.08% had a larger value of the extra vibrational energy than Sn⁴⁺:0.04% Bi, which means that the non-radiative transitions of Sn²⁺:0.08% Bi can be further prohibited to improve the efficiency of radiative transitions. As shown in Fig. 5b and c, the incorporated Sn²⁺ in the state of $[SnCl_4]^{2-}$ and two V_{Cl} increased the energy value of $\Delta E'$ of $[BiCl_5]^{2-}$ due to the more localized excitons, which reduces the probability of a non-radiative transition, and increases the probability of a radiative transition. Thus, Cs₂SnCl₆:Bi³⁺ and Sn²⁺ can finally achieve a significant improvement of PLQY.

Conclusion

In summary, a series of Cs₂SnCl₆:Bi with different precursors have been synthesized, and the photophysical properties were investigated. Comparing Cs₂SnCl₆:Bi synthesized by SnCl₄, Cs₂SnCl₆:Bi from SnCl₂ shows much higher PLQY, and the doping content of Bi³⁺ has little effect on the high PLQY. The reductive H₃PO₂ in the precursor solution of SnCl₄ makes the prepared Cs₂SnCl₆:Bi show brighter emission light and higher PLQY (35.4%) than the sample without H₃PO₂ (PLQY of 13.7%). This is because H_3PO_2 reduces Sn^{4+} to Sn^{2+} during the reaction, and the XPS spectra proved the existence of Sn²⁺ in the Cs₂SnCl₆:Bi sample synthesized with H₃PO₂. The sample is actually Bi³⁺ and Sn²⁺ co-doped Cs₂SnCl₆. [SnCl₄]²⁻ and two V_{Cl} induce the local lattice distortion, which can cause the heavy localized excitons of [BiCl₅]²⁻ to enhance the efficiency of radiative recombination. This work improves the deep understanding of the luminescence mechanism of Cs₂SnCl₆:Bi, and provides a new idea for developing efficient perovskite materials.

Experimental section

Materials and chemicals: cesium chloride (CsCl, Macklin, 99.9%), bismuth chloride (BiCl₃, Macklin, 99.99%), tin chloride dihydrate (SnCl₂·2H₂O, Aladdin, 99.99%), tin tetrachloride (SnCl₄, Energy Chemical, 99%), hypophosphorous acid (H₃PO₂, Aladdin, 50 wt% in water), and hydrochloric acid (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 $SnCl_4$ was dissolved in 17 mL HCl to prepare 2 M $SnCl_4$ solution. A total of 12 mmol (3784.08 mg) BiCl₃ was dissolved in 6 mL HCl to prepare 2 M BiCl₃ solution. Synthesis of Cs₂SnCl₆:Bi: an amount of 336.72 mg (2 mmol) CsCl, 225.65 mg (1 mmol) SnCl₂·2H₂O or 0.5 mL (1 mmol) SnCl₄ precursor, and 0–50 μ L (0–0.1 mmol) BiCl₃ precursor were added in a polytetrafluoroethylene (PTFE) container with 15 mL of 37% 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 Cs₂SnCl₆:Bi could be separated by immediate centrifugation, and were washed three times with ethanol.

Synthesis of Cs₂SnCl₆:Bi@H₃PO₂: an amount of 336.72 mg (2 mmol) CsCl, 500 μ L (1 mmol) SnCl₄ precursor, 50 μ L (0.1 mmol) BiCl₃ precursor and 0.05 ml H₃PO₂ were added in a polytetrafluoroethylene (PTFE) container with 15 mL of 37% 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 Cs₂SnCl₆:Bi@H₃PO₂ 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 Cu K α rotating anode). Depth-profile XPS spectra were recorded on an AXIS Supra, using an X-ray beam focused to an area of 2 mm² 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 (Aglient 5110). UV-vis absorption spectra were collected with a UV-3600i Plus spectrometer.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grant No. 61874074), Science and Technology Project of Shenzhen JCYJ20220531100815034, Technology and Innovation Commission of Shenzhen (20200810164814001), Natural Science Foundation of Guangdong Province (General Program, Grant No. 2022A1515012055 and 2023A1515030014), and Shenzhen Fundamental Research Projects (Grant No. JCYJ20220531103411026).

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