

Enhancing Photoluminescence and Stability of Mn-Doped $\text{Cs}_2\text{InCl}_5 \cdot \text{H}_2\text{O}$ Microcrystals with Introduced Bi^{3+} Ion

Liang Jing, Qingmei Cen, Qi Pang,* and Jin Zhong Zhang



Cite This: *J. Phys. Chem. C* 2023, 127, 2448–2455



Read Online

ACCESS |



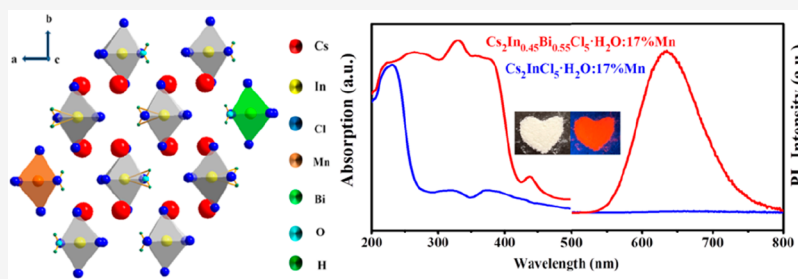
Metrics & More



Article Recommendations



Supporting Information



ABSTRACT: In this work, lead-free zero-dimensional (0D) all-inorganic perovskite Mn^{2+} -doped $\text{Cs}_2\text{InCl}_5 \cdot \text{H}_2\text{O}$ microcrystals (MCs) with introduced Bi^{3+} ion were synthesized by supersaturation recrystallization at room temperature. The electronic bandgap of the MCs is tuned from ~ 5.1 to ~ 3.1 eV, and the electronic absorption is enhanced in the 200–400 nm region by Bi^{3+} incorporation. Upon excitation at 365 nm, the MCs with introduced Bi^{3+} exhibit strong red emission peaking at 640 nm, which is attributed to the Mn^{2+} transition (${}^4\text{T}_{1\text{g}} \rightarrow {}^6\text{A}_{1\text{g}}$). Simultaneous Mn^{2+} and Bi^{3+} incorporation into $\text{Cs}_2\text{InCl}_5 \cdot \text{H}_2\text{O}$ shows 60 times enhancement of the 640 nm emission band compared to Mn^{2+} alone. This PL enhancement is attributed to the energy transfer (ET) from the $[\text{BiCl}_6]^{3-}$ octahedron, which acts as a UV light absorber and exciton donor, to $[\text{MnCl}_6]^{4-}$. In addition, a yellow-light-emitting diode (LED) device based on the $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5 \cdot \text{H}_2\text{O}:17\%\text{Mn}$ MCs was fabricated and evaluated, showing high color saturation at a drive current of 420 mA and good stability. This study demonstrates a new method for achieving efficient red emission by incorporating ns^2 metal ions and Mn ions in 0D lead-free metal halides.

INTRODUCTION

All-inorganic lead halide perovskites have attracted substantial attention due to their unique properties and potential applications.^{1–5} However, their toxicity (with Pb) and instability under ambient conditions limit their applications and have generated strong interest in developing nontoxic and stable alternatives.^{6–9} Low-dimensional lead-free luminescent metal halides with a unique soft lattice have aroused reviving interest due to their outstanding optical properties including a large absorption coefficient, high photoluminescence quantum yield (PLQY), broad emission band, and large Stokes shift.^{10–16} These advantages make them ideal candidates as a new class of luminescent materials and as an alternative to lead halide perovskites. Among these, zero-dimensional (0D) In-based metal halides, such as A_3InX_6 ($\text{A} = \text{Cs}$ and Rb),^{17,18} have become the focus of attention owing to their spatially and electronically decoupled 0D structure that favors strongly localized excitonic states.^{19–24} Specifically, through the control of the A cation and the octahedral unit, highly efficient and largely Stokes-shifted visible luminescence, stemming from self-trapped exciton (STE) states, was achieved in $5s^2$ metal Sb^{3+} - or Te^{4+} -doped 0D In-based halide crystals. For example, in 2020, Xia et al. discovered a novel all-inorganic lead-free $\text{Cs}_2\text{InCl}_5 \cdot \text{H}_2\text{O}$ single crystal (SC), and a broadband yellow

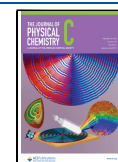
emission with a high PLQY of 95.5% by doping Sb^{3+} has been achieved.²² Kuang et al. reported an all-inorganic Te^{4+} -doped $\text{Cs}_2\text{InCl}_5 \cdot \text{H}_2\text{O}$ SC with bright orange emission, which shows the significant potential of these materials for application in wearable and portable thermometry devices.²⁵ In 2022, Chen et al. systematically investigated 0D Sb^{3+} -doped Cs_3InCl_6 luminescent NCs from the controlled synthesis and fundamental photophysics to the phase transformation.²⁶ In addition, Han et al. reported that $(\text{Rb}_x\text{Cs}_{1-x})_3\text{InCl}_6$ shows green emission with a microsecond long lifetime.¹⁷

Manganese (Mn^{2+}) is widely used as a suitable dopant in doping technology. The Mn^{2+} octahedron usually exhibits orange emission due to the ${}^4\text{T}_{1\text{g}} \rightarrow {}^6\text{A}_{1\text{g}}$ transition and magnetic properties and is insensitive to the physical and electronic structure of the host.^{27–30} For example, it has been demonstrated that Mn^{2+} -doped lead-based, copper-based,

Received: November 30, 2022

Revised: January 18, 2023

Published: January 27, 2023



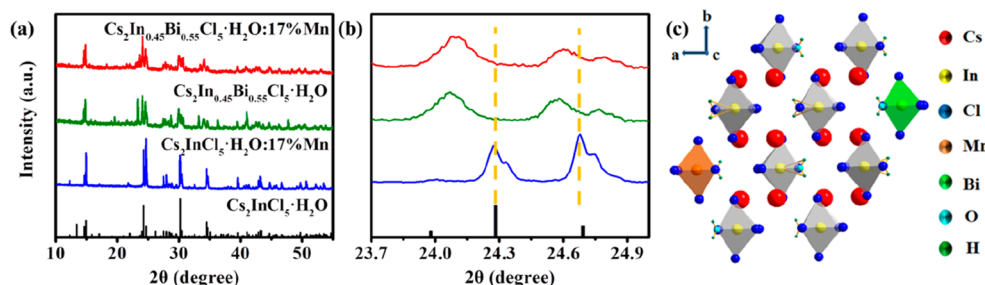


Figure 1. (a) XRD patterns of pristine Cs₂InCl₅·H₂O, Cs₂InCl₅·H₂O:17%Mn, Cs₂In_{0.45}Bi_{0.55}Cl₅·H₂O, and Cs₂In_{0.45}Bi_{0.55}Cl₅·H₂O:17%Mn. (b) Magnification of the XRD patterns in the 23.7–25.0° range. (c) Illustration of the crystal structure of Mn²⁺-doped and Bi³⁺-alloyed Cs₂InCl₅·H₂O.

bismuth-based, antimony-based, and other metal halide perovskites exhibit outstanding photoelectric properties.^{31–36} Despite these encouraging results, Mn²⁺ doping in 0D In-based halide crystals is still largely unexplored. Therefore, it is worthwhile to explore and significantly incorporate Mn²⁺ into the 0D In-based halide to improve the photoelectric performance. Furthermore, most 0D In-based halides are synthesized by using complex procedures at high reaction temperatures, and their excitation energies are too high (<350 nm), both of which are issues that must be addressed.

In this work, a series of novel Mn-doped Cs₂InCl₅·H₂O microcrystals (MCs) with introduced Bi³⁺ ions were prepared using room-temperature supersaturation recrystallization. The crystal structures of pristine and Mn²⁺/Bi³⁺-incorporated Cs₂InCl₅·H₂O MCs was determined by X-ray diffraction (XRD) while the morphology was characterized by scanning electron microscopy (SEM). X-ray photoelectron spectroscopy (XPS) was used to characterize the electronic structures. Their optical properties and dynamic properties were studied using temperature-dependent steady-state and time-resolved PL spectroscopy. The Mn²⁺-doped MCs with introduced Bi³⁺ ion exhibit a strong PL band peaked at 640 nm assigned to the 3d⁵ Mn²⁺ transition (⁴T_{1g} → ⁶A_{1g}) upon excitation with 365 nm light. The introduction of Bi³⁺ significantly enhances the Mn²⁺ emission. Furthermore, the Mn²⁺-doped and Bi³⁺-alloyed Cs₂InCl₅·H₂O MCs show good stability and demonstrate good potential for LED application.

METHODS

Chemicals. Cesium chloride (CsCl, 99.9%, Aladdin), indium(III) chloride (InCl₃, 99%, Aladdin), bismuth(III) chloride (BiCl₃, 99.9%, Aladdin), manganese chloride tetrahydrate (MnCl₂·4H₂O, 99.99%, Aladdin), hydrochloric acid (HCl, 36.0%–38.0%, KESHI), and isopropyl alcohol (IPA, 99.7%, GHTECH) were used as purchased without any further purification.

Synthesis. The Cs₂InCl₅·H₂O metal halides were easily synthesized by the vigorous stirring of InCl₃ (0.4 mmol) precursor in hydrochloric acid at room temperature. Then CsCl (0.8 mmol) was added to the reaction mixture, which immediately led to the precipitation of microcrystals. The reaction was continued for another 3.0 h to make sure that it is complete. The precipitates were washed with isopropanol and centrifuged at 8000 rpm two times. The powders were then dried at 50 °C for 2.0 h and then stored in a glass vial under ambient conditions for further characterization.

The synthesis procedure of the Cs₂InCl₅·H₂O:Mn method is very much similar to that for the Cs₂InCl₅·H₂O discussed above, except for adding appropriate amounts of MnCl₂·4H₂O

to the reaction mixture in hydrochloric acid. The optimum value of MnCl₂·4H₂O was found to be 0.08 mmol (the molar feed ratio of Mn/(Mn + In) is 17%), for which the best PL properties were obtained. Therefore, we finalized this composition when synthesizing different amounts of Bi alloyed Cs₂InCl₅·H₂O: Mn, and the samples were noted as Cs₂In_{1–x}Bi_xCl₅·H₂O:17%Mn. The different amounts of BiCl₃ (fed at *x* = 0, 0.20, 0.40, and 0.55) were 0, 0.08, 0.16, and 0.22 mmol, respectively. The synthesis method of Cs₂In_{1–x}Bi_xCl₅·H₂O is the same as that of Cs₂In_{1–x}Bi_xCl₅·H₂O:17%Mn. Similarly, Pb²⁺- or Sb³⁺-alloyed Cs₂InCl₅·H₂O:17%Mn were obtained.

Characterization. X-ray diffraction (XRD) measurements of the perovskite powders were performed on a SMAR-TLAB3KW powder diffractometer using a Cu Kα radiation source with operating voltage parameters of 40 kV and 30 mA. The UV–vis diffuse reflectance spectra of the solid powder were measured with a Techcomp UV2600 variable slit UV–vis spectrophotometer. Spectral characterizations were obtained with a FLS1000 fluorescence spectrometer from Edinburgh Instruments. In addition to temperature-dependent PL, PL and PLE were measured at room temperature using xenon (Xe900) as the excitation source. Time-resolved PL (TRPL) is measured with an excitation source microsecond lamp. PLQY is an Edinburgh Instruments integrating sphere using a FLS-1000 fluorescence spectrometer and PMT-900 detector to record absolute PLQY measurements. Electron paramagnetic resonance (EPR) spectra were acquired at room temperature in the X-band of a Bruker-A300-10/12 spectrometer. The morphology and size of the sample powders were characterized by scanning electron microscopy (SEM). The elemental composition and distribution of the material were observed by energy-dispersive X-ray spectroscopy (EDS) coupled with an SEM. X-ray photoelectron spectroscopy (XPS) was performed using a Thermal Fisher ESCALAB 250XI spectrometer.

RESULTS AND DISCUSSION

Pristine Cs₂InCl₅·H₂O and Cs₂InCl₅·H₂O:17%Mn MCs were synthesized via a mild one-step solution method in hydrochloric acid at room temperature. We introduced different amounts of BiCl₃ to the precursor solution of In³⁺ and Mn²⁺ ions with the molar ratio of Bi to (In + Bi) set to 0, 0.20, 0.40, and 0.55. A schematic illustration of the formation of the Cs₂In_{1–x}Bi_xCl₅·H₂O:17%Mn is shown in Figure S1a. The XRD patterns of the pristine Cs₂InCl₅·H₂O, Cs₂InCl₅·H₂O:17%Mn, Cs₂In_{0.45}Bi_{0.55}Cl₅·H₂O, and Cs₂In_{0.45}Bi_{0.55}Cl₅·H₂O:17%Mn are shown in Figure 1a. All samples possess orthorhombic phase structures of Cs₂InCl₅·H₂O, indicating the appropriate Mn²⁺

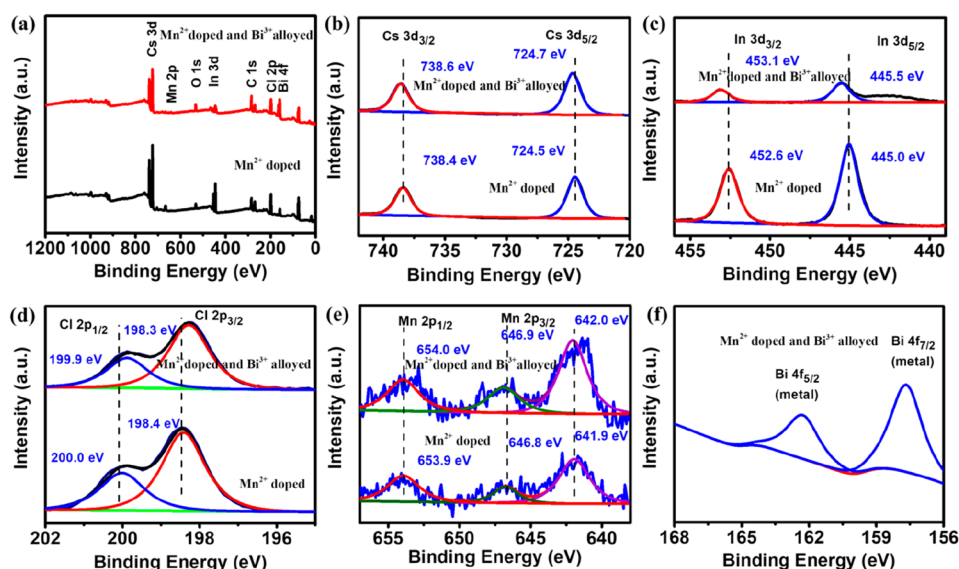


Figure 2. (a) XPS survey spectra and high-resolution XPS spectra of (b) Cs 3d, (c) In 3d, (d) Cl 2p, (e) Mn 2p, and (f) Bi 4f of Mn^{2+} -doped and Bi^{3+} -alloyed $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}$ MCs.

doping or Bi^{3+} alloying does not change the crystalline phase. A set of characteristic peaks in the 2θ region of 23.7° – 25° can be assigned to the (002) and (221) crystal planes (Figure 1b). There is no significant shift in the angles of $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}$ and $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ as In^{3+} and Mn^{2+} have a comparable ionic radius. The diffraction peaks of $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}$ shift to lower angles compared to that of $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}$ owing to the larger ions radius of Bi^{3+} than In^{3+} , causing lattice expansion. Similarly, the diffraction peaks of Bi^{3+} alloyed $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ shift to a lower angle. However, with more Bi^{3+} incorporated (fed at $y = 0.60$), a one-dimensional (1D) $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ orthorhombic phase is formed. Extra impurities can be observed at 33.6° , 41.5° , and 48.4° which are assigned to the diffraction of $\text{Cs}_3\text{Bi}_2\text{Cl}_9$, as shown in Figure S1b. Therefore, we determined Bi^{3+} fed at $y = 0.55$ as the optimal alloying amount for the following discussion. The pure $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}$ phase was confirmed by XRD analysis with the space group $Pnma$ (Figure 1c). In this structure, each In^{3+} ion is coordinated with five Cl^- ions and one O^{2-} ion from the coordinating water, forming a structural unit of $[\text{InCl}_5\text{H}_2\text{O}]^{2-}$ octahedron. The $[\text{InCl}_5\text{H}_2\text{O}]^{2-}$ octahedrons are isolated from each other and separated by two Cs^+ cations to form a 0D structure.

Figure S2a,b shows the SEM images of the $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ and $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$. The SEM images of both samples show microsize particles. The EDS spectra were measured to determine the elemental composition of $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$. In Figure S2c–h, elements of Cs, In, Cl, Mn, and Bi are found in the EDS spectrum, indicating both Mn^{2+} and Bi^{3+} are successfully doped or alloyed.

The actual doping content of Mn^{2+} and Bi^{3+} in different amounts of Bi^{3+} alloyed samples was determined by ICP-OES, and the results are shown in Table S1. With the increase of Bi^{3+} content, ICP results showed that the Bi^{3+} content also increased, while the Mn^{2+} content remained almost constant. In the $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ sample, the actual alloying level of In^{3+} was estimated to be 52.09%, while the actual amounts of Mn^{2+} and Bi^{3+} were 10.45% and 37.45%. Therefore, it can be seen that Mn^{2+} is slightly doped while Bi^{3+}

is alloyed to $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}$. The results are consistent with the indium-based phase shown by XRD. In the following, we use the feed molar ratio for discussion.

To determine the elemental composition and electronic properties of $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$, XPS was conducted to investigate the surface chemical environment of $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ and $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ (Figure 2a–f). As shown in Figure 2a, both samples exhibit characteristic peaks correlated to Cs, In, Mn, Cl, C, and O elements and add Bi in the Bi alloying samples. In Figure 2b, after Bi^{3+} alloyed, two Cs 3d peaks at 738.4 and 724.5 eV corresponding to Cs $3d_{3/2}$ and Cs $3d_{5/2}$ both move 0.2 eV toward higher binding energy achieving 738.6 and 724.7 eV. As shown in Figure 2c, the In^{3+} 3d spectra of $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}$ have two characteristic peaks: In $3d_{3/2}$ and $3d_{5/2}$ at 452.6 and 445.0 eV, respectively. With the Bi^{3+} alloyed, the binding energies of In $3d_{3/2}$ and $3d_{5/2}$ move to a higher energy with 0.5 eV, resulting in a reduction in the overlap of the electron cloud. The Mn $2p_{1/2}$ and Mn $2p_{3/2}$ peaks also have a weak shift of 0.1 eV to a higher binding energy at 653.9 and 641.9 eV. The peaks of Cs 3d, Mn 2p, and In^{3+} 3d all move toward higher binding energy corresponding to the unalloyed sample due to Bi^{3+} incorporating, in which the lattice expands when Bi^{3+} with a larger ionic radius replaces In^{3+} ions and results in electron density reducing around these ions. Meanwhile, the electronegativity of Bi is larger than those of Mn, Cs, and In, which leads to Cs, In, and Mn moving to high binding energies. In Figure 2d, Cl^- is shifted 0.1 eV to lower binding energy due to Cl^- having the largest electronegativity. As shown in Figure 2f, two peaks appear at 162.2 and 157.6 eV, further indicating that Bi^{3+} was successfully incorporated.

Electron paramagnetic resonance (EPR) experiments were conducted to investigate the magnetic property of Mn^{2+} -doped $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}$. Figure 3 shows the X-band electron paramagnetic resonance (EPR) spectra of Bi^{3+} -alloyed and unalloyed samples at room temperature. Both of the graphs show the 6-fold hyperfine split structure caused by the spin ($S = 5/2$) and nuclear spin ($I = 5/2$) of the unpaired $3d^5$ electron of the Mn^{2+} ion, which provides direct experimental access to the alignment ordering of the Mn^{2+} spins and to the presence

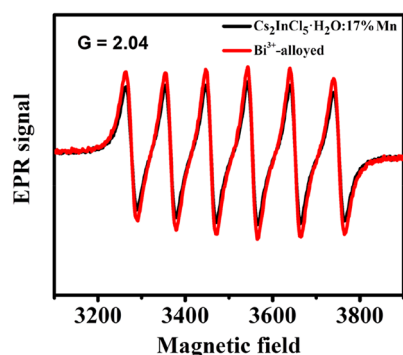


Figure 3. X-band EPR spectra of $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ and Bi^{3+} -alloyed $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ MCs.

of magnetic coupling effects that are indicative of interdopant interactions and confirms that Mn^{2+} ions are successfully doped and the Bi^{3+} alloying had little effect on the Mn^{2+} ion. The external test obtained $G = 2.04$, which was similar to a previous report.³⁷

The influence of Mn doping on the optical properties and band structures of the Bi^{3+} -alloyed $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}$ was studied using UV–vis absorption and PL spectroscopy. As shown in Figure 4a, the pristine $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}$ and $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ show an abrupt absorption edge at 250 nm. This is similar to the reported absorption spectra of 0D $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}$ NCs, and the very weak absorption at 350 nm is ascribed to the parity transition of In^{3+} .²⁵ While, through Bi^{3+} alloying, a higher absorption is located at 250–400 nm with two absorption humps at about 330 and 376 nm, which are assigned to the transitions of octahedral $[\text{BiX}_6]^{3-}$ from the $6s^2-6s^1p^1$.^{38–40} The absorption edge of $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}$ red-

shifts from ~ 260 to ~ 420 nm, which indicates that the bandgap would be reduced by Bi^{3+} alloying. Two distinct absorption peaks at 438 and 535 nm in $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ are assigned to the characteristic absorption peaks of the Mn^{2+} transition from ${}^6\text{A}_{1g}$ to ${}^4\text{T}_{1g}$. Therefore, the enhanced UV light harvesting for $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ compared with $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ is contributed to the introduced $[\text{BiX}_6]^{3-}$ octahedrons. To determine the nature of the bandgap (E_g), we then analyzed the Tauc plot of the diffuse reflectance spectrum of $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ and $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ (Figure 4b). By setting the exponential factor to 2, all directly allowed transition characteristics of $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ and $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ can be well fitted. The fitting results show that the electronic bandgap can be dramatically tuned from ~ 5.1 to ~ 3.1 eV by Bi^{3+} alloying, indicating that the Bi^{3+} alloying allowed us to tune the absorption band edge of $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}$.

The PL spectra of the pristine $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}$, $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$, $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}$, and $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ are shown in Figure 4c. The pristine sample and $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ show a weak PL when excited at 250 nm. However, they were nonluminous upon excitation at 365 nm. The $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}$ also shows no PL excited at 365 nm. Interestingly, upon alloying Bi^{3+} into $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$, the sample exhibits strong red emission centered at ~ 640 nm with a PLQY of 1.82% and full width at half-maximum (FWHM) of ~ 80 nm, which is ascribed to the parity and spin-forbidden ${}^4\text{T}_{1g}(\text{G}) \rightarrow {}^6\text{A}_{1g}(\text{S})$ transition of octahedral coordinated Mn^{2+} ions rather than the broadband STEs emission. Therefore, it is reasonable to assume that in the system of $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}$ MCs cobound by ns^2 metal ions and Mn^{2+} , the luminescence of STE is inhibited due to the

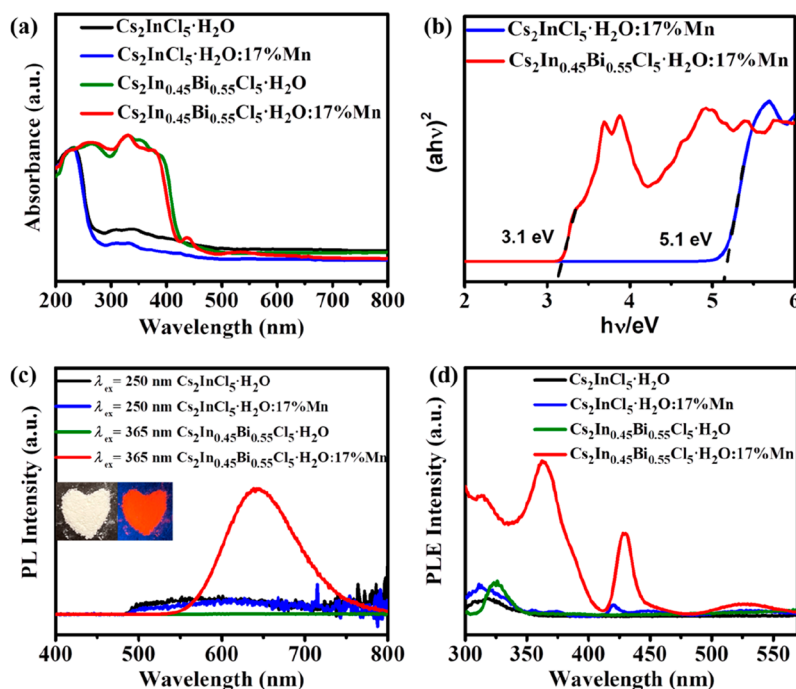


Figure 4. (a) UV–vis absorption spectra of the $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ and $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ MCs, (b) related Tauc plot, (c) PL (excitation at 365 nm; inset: a photograph of the $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ under natural light (left) and UV light (right) a 365 nm UV lamp), and (d) PLE (monitored at 640 nm, the intensity of the original sample, Mn^{2+} -doped or Bi^{3+} -alloyed are magnified by 5 times) spectra of the $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}$, $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$, $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}$, and $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ MCs.

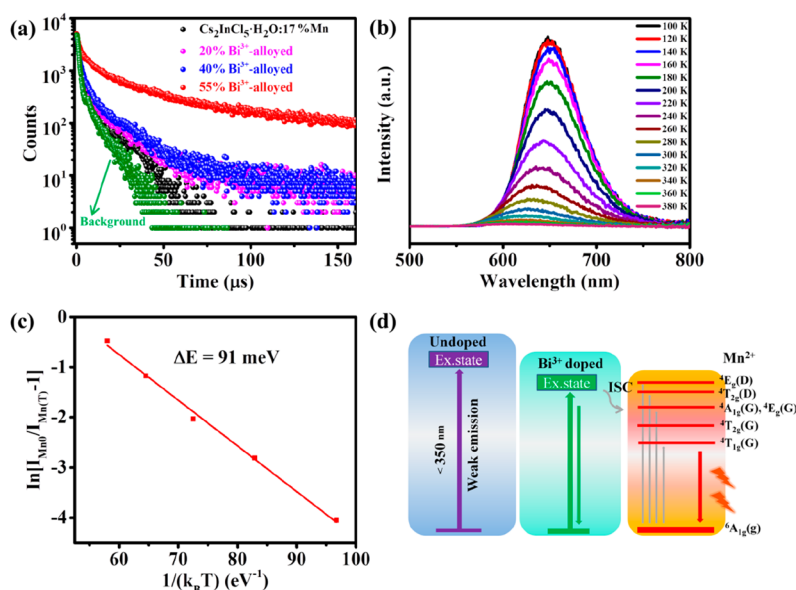


Figure 5. (a) Time-resolved PL decay profiles of different amounts Bi³⁺-incorporated Cs₂InCl₅·H₂O:17%Mn MCs (upon excitation at 365 nm). (b) Temperature-dependent PL spectra of Cs₂In_{0.45}Bi_{0.55}Cl₅·H₂O:17%Mn MCs. (c) Fitting results of the integrated PL intensity as a function of temperature for Cs₂In_{0.45}Bi_{0.55}Cl₅·H₂O:17%Mn MCs. Thermal quenching of PL was fitted using the relation $I(A) = I_0/[1 + A \exp(-E_a/k_B T)]$, where E_a is the thermal activation energy for PL quench, I_0 is the integrated PL intensity at 0 K, and k_B is the Boltzmann constant. (d) Energy levels and fluorescent mechanism, where ISC represents intersystem crossing.

presence of Mn²⁺, which has also been reported previously.^{41–43} The Bi³⁺ alloying enhances the PL intensity by 60 times compared to that of Cs₂InCl₅·H₂O:17%Mn. The PL enhancement can be attributed to energy transfer (ET) from Bi³⁺ activators to Mn²⁺. We also studied other samples with different Bi/(In + Bi) molar feed ratios; as shown in Figure S3a,b, the PL intensity increases and absorption bands red-shift as the Bi content increases, with the highest PLQY for the Cs₂In_{0.45}Bi_{0.55}Cl₅·H₂O:17%Mn sample of 1.82%, which is 92 times compared to the unalloyed Cs₂InCl₅·H₂O:17%Mn (Table S2). However, the PLQY of Cs₂In_{0.45}Bi_{0.55}Cl₅·H₂O:17%Mn is still low, and we speculate that there are two main reasons why PLQY is so low. One is the samples prepared by room-temperature supersaturation recrystallization have many defects, resulting in trap-assisted nonradiative recombination. The other is that Cs₂InCl₅·H₂O is a 0D structure with soft lattices which slows the ET from Bi³⁺ activators to Mn²⁺ centers. This result is similar to previous reports.^{35,44} The samples with different doping amounts of Mn²⁺ were further explored. The PL intensity increases with the increase of Mn²⁺ (Figure S3c). However, more Mn²⁺ will lead to Mn²⁺ self-quenching, which will reduce PL intensity. A molar feed ratio of 17% of Mn-doped Cs₂In_{0.45}Bi_{0.55}Cl₅·H₂O shows the highest PL intensity. As a control experiment, we also use Pb²⁺ or Sb³⁺ ions to replace Bi³⁺ to alloyed Cs₂InCl₅·H₂O:Mn. From Figure S4a, Pb²⁺ or Sb³⁺ ion alloying also shows a higher absorption at 200–400 nm, and the absorption edge red-shifts approximately 200 nm compared to the unalloyed sample. However, the Mn²⁺ characteristic absorption peak appears only in the case of Bi³⁺ alloying. In Figure S4b, the Pb²⁺-alloyed sample shows no PL, and the PL intensity of the Sb³⁺-alloyed sample is lower than that of Bi³⁺ alloying.

To better establish that the introduction of Bi³⁺ improves the absorption of light, the PLE spectra of the powder samples were measured as shown in Figure 4d. The pristine Cs₂InCl₅·H₂O and single Mn²⁺-doped or Bi³⁺-alloyed samples display a

relatively low-intensity response to the weak absorption. However, the PLE intensity is significantly enhanced by the co-alloying of Bi³⁺ and In³⁺. The maximum excitation peak at about 365 nm is the typical excitation band arising from the Bi³⁺ absorption (the spin-orbital-allowed ¹S₀–³P₁),⁴⁵ and the peaks at 430 nm are assigned to the ⁶A_{1g} → ⁴T_{1g} transition of Mn²⁺. The excitation-wavelength-dependent PL and emission-wavelength-dependent PLE spectra were measured. As shown in Figure S5a,b, no significant shift is found in PL spectra when the excitation wavelength increases from 320 to 400 nm. The independence of PL excitation spectra of emission wavelength also confirms that the broad red emission originates from the relaxation of the same excited state.⁴⁶

To help determine the mechanism of Mn²⁺-induced emission, TRPL was measured to understand the effect of Bi³⁺ ion alloying on optical properties and exciton dynamics (Figure 5a). The TRPL decay curves of the Bi³⁺-alloyed sample emission can be fitted by double-exponential decay

$$I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \quad (1)$$

where A_1 and A_2 are amplitudes and τ_1 and τ_2 represent fast and slow decay components, respectively. The average lifetime is calculated using $\tau_{\text{avg}} = (A_1 \tau_1^2 + A_2 \tau_2^2)/(A_1 \tau_1 + A_2 \tau_2)$. The lifetime distribution statistics are shown in Table S3. The fitting results show two components: (i) the fast component is assigned to trap-assisted nonradiative recombination, and (ii) the slow component is attributed to the ⁴T_{1g} → ⁶A_{1g} radiation recombination of Mn²⁺. The fast PL decay times increased from 1.5 μs for single Mn²⁺-doped MCs to 2.2 μs for Cs₂In_{0.45}Bi_{0.55}Cl₅·H₂O:17%Mn MCs. The slow decay times increased from 15.8 μs for single Mn²⁺-doped MCs to 25.2 μs for Cs₂In_{0.45}Bi_{0.55}Cl₅·H₂O:17%Mn MCs. With rising Bi³⁺ concentration, the average lifetime of Mn²⁺ increased from 6.0 μs for single Mn²⁺-doped MCs to 21.0 μs for Cs₂In_{0.45}Bi_{0.55}Cl₅·H₂O:17%Mn MCs and has a variation tendency similar to its emission intensity. The prolonged

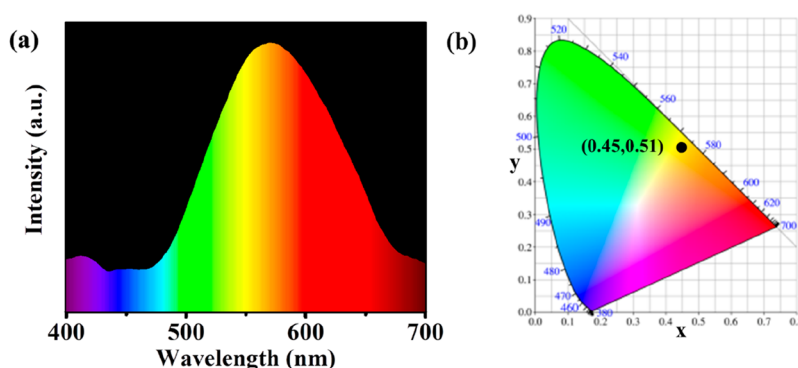


Figure 6. (a) PL spectrum of the fabricated LED device (using a 365 nm near-UV chip) based on $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ powder under driving currents of 420 mA. (b) Chromaticity coordinates (black dot) in the CIE 1931 system.

Mn^{2+} lifetime could be assigned to the ET from the $[\text{BiCl}_6]^{3-}$ unit, which acts as UV light absorber and exciton donor, to $[\text{MnCl}_6]^{4-}$ and results in the enhanced concentration of electrons in the excited state, improving the ${}^4\text{T}_{1g}-{}^6\text{A}_{1g}$ transition process in Mn^{2+} .^{38,47–51}

To further reveal the mechanism behind the observed PL, the temperature-dependent PL spectra of $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ were measured, as shown in Figure 5b. From 100 to 360 K, the PL peak intensity decreases with increasing temperature, indicating that $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}$ is sensitive to temperature. The emission peaks show a blue-shift trend with increasing temperature, which is due to the increase of the bandgap of ${}^4\text{T}_{1g}-{}^6\text{A}_{1g}$ caused by the lattice expansion with the increasing temperature. Moreover, the thermal activation energy (E_a) required for transferring excitons to Mn^{2+} can be estimated through the following equation^{38,46}

$$I(A) = I_0/[1 + A \exp(-E_a/k_B T)] \quad (2)$$

where $I_{\text{Mn}}(T)$ and I_0 are the integrated PL intensity at T and 0 K, respectively, and k_B is the Boltzmann constant. As shown in Figure 5c, the E_a was calculated to be 91 meV for $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$, which is much lower than the E_a of exciton-to- Mn^{2+} transfer in Mn^{2+} -doped CsPbCl_3 nanocrystal (~ 314 meV), indicating that $[\text{BiX}_6]^{3-}$ transferred to Mn^{2+} via ISC process is readily spontaneous.

Based on the above analysis, the major photophysical processes involved in the Bi^{3+} -alloyed $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ MCs are explained below and illustrated in Figure 5d. The pristine $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}$ and $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ show very weak PL at a different excitation wavelength due to the parity transition of In^{3+} .²⁵ Upon Bi^{3+} alloying, the $[\text{BiCl}_6]^{3-}$ octahedron is formed and serves as an excellent light absorber to produce photoexcitons, which can be immediately transferred to the $[\text{MnCl}_6]^{4-}$ octahedron via intersystem crossing (ISC). The accepted excitons can effectively increase the exciton density in ${}^4\text{T}_{1g}$, promoting the transition process of ${}^4\text{T}_{1g} \rightarrow {}^6\text{A}_{1g}$ of Mn^{2+} and resulting in the PL intensity enhancement, similar to a previous report.³⁸

The coupling effect between electrons and phonons can usually be obtained by fitting the relationship between FWHM and temperature by eq 3:⁵²

$$\text{FWHM} = 2.36\sqrt{S}\hbar\omega\sqrt{\coth\left(\frac{\hbar\omega}{2kT}\right)} \quad (3)$$

The Huang–Rhys factor (S) and phonon frequency ($\hbar\omega_{\text{phonon}}$) are calculated to be 22.68 and 23.57 meV, respectively.

Compared with other luminescent materials, the Huang–Rhys factor of Bi^{3+} -alloyed $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ is relatively high, indicating strong electron–phonon coupling of Bi^{3+} in $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ MCs.

The relative PL intensity was conducted as a function of exposure time in the water. As shown in Figure S6a, the relative PL intensity of $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ MCs remains at 61.5% after 1 h in the water. As shown in Figure S6b, the XRD patterns of $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ MCs which were stored in air for 80 days were conducted, and there were no obvious impurities or phase transitions compared to the freshly prepared sample. The results show that the $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ powder MC sample has stability against water and moisture.

The prepared phosphor powders were studied as color conversion materials to fabricate LEDs. The $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ red emitting powder was mixed with curable resin and coated on a commercially available 365 nm GaN LED chip. Figure 6a displays the PL spectra of the LED device under a current of 420 mA. The chromaticity coordinate in the CIE 1931 system is drawn in Figure 6b. The LED device exhibits bright yellow emission with coordinates of (0.46, 0.52), corresponding to a color-rendering index of 56. In addition, the correlated color temperature (CCT) is 3508 K, in line with the national lighting standards, and the LED device exhibits up to 88.5% color purity. The emission from the device is considerably blue-shifted. We speculate that the reason for the considerable blue-shift is caused by the high temperature generated by the large amount of Joule heat generated during device testing under 420 mA driven current, which led to the increase of the bandgap of ${}^4\text{T}_{1g}-{}^6\text{A}_{1g}$ caused by the lattice expansion with the increasing temperature.⁵³ Figure S7 shows the PL spectra ($\lambda_{\text{ex}} = 365$ nm) of the fabricated device at drive currents by raising the drive current from 300 to 420 mA. It can be observed that the PL band shape exhibits no distinct change. From 320 to 420 mA, the intensity of the emission grows steadily and linearly, showing that the built LED operates effectively at larger driving currents. These results indicate that inorganic lead-free 0D perovskites have certain development potential in solid-state lighting.

CONCLUSION

In summary, a lead-free all-inorganic heterometallic luminescent perovskite $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ was prepared by a facile precipitation method at room temperature in hydrochloric acid. With Bi^{3+} alloying, the absorption band edge

shifts to longer wavelengths, and a 60-fold enhancement is achieved in PL intensity for $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ compared to the $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$. The PL intensity enhancement was attributed to the formation of a $[\text{BiCl}_6]^{3-}$ octahedron upon Bi^{3+} alloying and the synergistic effect in the $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$, where the $[\text{BiCl}_6]^{3-}$ unit acts as UV light absorber and exciton donor, which can be subsequently transferred to the $[\text{MnCl}_6]^{4-}$ unit via ISC and promote the transition process of ${}^4\text{T}_{1g} \rightarrow {}^6\text{A}_{1g}$ of Mn^{2+} . In addition, the as-prepared $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ was studied as a color conversion material with a commercial 365 nm GaN LED chip for yellow light emission. This work provides deep insights into the excited-state dynamics of Bi^{3+} and Mn^{2+} in $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}$, thus laying a foundation for the future design of efficient red-emitting lead-free perovskite-derivative metal halides via ns^2 metal and Mn^{2+} ion alloying and doping.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.2c08308>.

Schematic preparation process, XRD patterns, PL, absorbance and PLQY of $\text{Cs}_2\text{In}_{1-x}\text{Bi}_x\text{Cl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$, SEM images, stability, ICP-OES, the parameter for TRPL profiles of $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ and $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$, PL and absorbance of Pb^{2+} , Sb^{3+} , Bi^{3+} -alloyed $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$, excitation wavelength-dependent PL spectra and emission wavelength-dependent PLE spectra of $\text{Cs}_2\text{In}_{0.45}\text{Bi}_{0.55}\text{Cl}_5\cdot\text{H}_2\text{O}:17\%\text{Mn}$ (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Qi Pang – School of Chemistry and Chemical Engineering/
Guangxi Key Laboratory of Electrochemical Energy
Materials, Guangxi University, Nanning 530004 Guangxi,
People's Republic of China; orcid.org/0000-0002-5190-1250; Email: pqigx@163.com

Authors

Liang Jing – School of Chemistry and Chemical Engineering/
Guangxi Key Laboratory of Electrochemical Energy
Materials, Guangxi University, Nanning 530004 Guangxi,
People's Republic of China

Qingmei Cen – School of Chemistry and Chemical
Engineering/Guangxi Key Laboratory of Electrochemical
Energy Materials, Guangxi University, Nanning 530004
Guangxi, People's Republic of China

Jin Zhong Zhang – Department of Chemistry and
Biochemistry, University of California, Santa Cruz, Santa
Cruz, California 95064, United States; orcid.org/0000-0003-3437-912X

Complete contact information is available at:
<https://pubs.acs.org/doi/10.1021/acs.jpcc.2c08308>

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant 21965003). J.Z.Z. acknowledges the US NSF (CHE-1904547) for financial support.

■ REFERENCES

- (1) Shamsi, J.; Urban, A. S.; Imran, M.; De Trizio, L.; Manna, L. Metal Halide Perovskite Nanocrystals: Synthesis, Post-Synthesis Modifications, and Their Optical Properties. *Chem. Rev.* **2019**, *119*, 3296–3348.
- (2) Wang, Y.; Jia, C.; Fan, Z.; Lin, Z.; Lee, S. J.; Atallah, T. L.; Caram, J. R.; Huang, Y.; Duan, X. Large-Area Synthesis and Patterning of All-Inorganic Lead Halide Perovskite Thin Films and Heterostructures. *Nano Lett.* **2021**, *21*, 1454–1460.
- (3) Dutta, A.; Vyas, M. K.; Bhowmik, K.; Ota, J.; Hait, S. K.; Chandrasekaran, K.; Saxena, D.; Ramakumar, S. S. V. Phase Sensitivity of All-Inorganic Lead Halide Perovskite Nanocrystals. *Mater. Lett.* **2022**, *4*, 2106–2124.
- (4) Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX_3 , X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett.* **2015**, *15*, 3692–3696.
- (5) Swift, M. W.; Lyons, J. L. First-Principles Survey of Acceptor Dopants for P-Type Cesium Lead Bromide. *J. Phys. Chem. C* **2022**, *126*, 12294–12300.
- (6) Román-Vázquez, M.; Vidyasagar, C. C.; Muñoz-Flores, B. M.; Jiménez-Pérez, V. M. Recent Advances on Synthesis and Applications of Lead- and Tin-Free Perovskites. *J. Alloys Compd.* **2020**, *835*, 155112.
- (7) Lyu, M.; Yun, J. H.; Chen, P.; Hao, M.; Wang, L. Addressing Toxicity of Lead: Progress and Applications of Low-Toxic Metal Halide Perovskites and Their Derivatives. *Adv. Energy Mater.* **2017**, *7*, 1602512.
- (8) Li, W.; Liu, Q.; Zhang, Y.; Li, C.; He, Z.; Choy, W. C. H.; Low, P. J.; Sonar, P.; Kyaw, A. K. Biodegradable Materials and Green Processing for Green Electronics. *Adv. Mater.* **2020**, *32*, 2001591.
- (9) He, S.; Fang, S.; Han, T.; Lang, T.; Cai, M.; You, H.; Peng, L.; Cao, S.; Liu, B.; Qiang, Q.; et al. Spectral Red-Shift of $\text{Cs}_4\text{Mn}(\text{Bi}_{1-x}\text{In}_x)_2\text{Cl}_{12}$ Layered Double Perovskite by Adjusting the Microstructure of the $[\text{MnCl}_6]^{4-}$ Octahedron. *J. Phys. Chem. C* **2021**, *125*, 16938–16945.
- (10) Shi, H.; Han, D.; Chen, S.; Du, M.-H. Impact of Metal ns^2 Lone Pair on Luminescence Quantum Efficiency in Low-Dimensional Halide Perovskites. *Phys. Rev. Mater.* **2019**, *3*, No. 034604.
- (11) McCall, K. M.; Morad, V.; Benin, B. M.; Kovalenko, M. V. Efficient Lone-Pair-Driven Luminescence: Structure-Property Relationships in Emissive $5s^2$ Metal Halides. *Mater. Lett.* **2020**, *2*, 1218–1232.
- (12) Arfin, H.; Kshirsagar, A. S.; Kaur, J.; Mondal, B.; Xia, Z.; Chakraborty, S.; Nag, A. ns^2 Electron (Bi^{3+} and Sb^{3+}) Doping in Lead-Free Metal Halide Perovskite Derivatives. *Chem. Mater.* **2020**, *32*, 10255–10267.
- (13) Zhou, G.; Su, B.; Huang, J.; Zhang, Q.; Xia, Z. Broad-Band Emission in Metal Halide Perovskites: Mechanism, Materials, and Applications. *Mater. Sci. Eng. R Rep.* **2020**, *141*, 100548.
- (14) Tan, Z.; Li, J.; Zhang, C.; Li, Z.; Hu, Q.; Xiao, Z.; Kamiya, T.; Hosono, H.; Niu, G.; Lifshitz, E.; Cheng, Y.; Tang, J. Highly Efficient Blue-Emitting Bi-Doped Cs_2SnCl_6 Perovskite Variant: Photoluminescence Induced by Impurity Doping. *Adv. Funct. Mater.* **2018**, *28*, 18011.
- (15) Zhou, B.; Liu, Z.; Fang, S.; Zhong, H.; Tian, B.; Wang, Y.; Li, H.; Hu, H.; Shi, Y. Efficient White Photoluminescence from Self-Trapped Excitons in $\text{Sb}^{3+}/\text{Bi}^{3+}$ -Codoped $\text{Cs}_2\text{NaInCl}_6$ Double Perovskites with Tunable Dual-Emission. *ACS Energy Lett.* **2021**, *6*, 3343–3351.
- (16) Wang, C.; Mao, X.; Wang, Z.; Xu, X.; Guo, W.; Zhang, R. Synthesis and Exciton Dynamics of a One-Dimensional Organic Copper Halide Perovskite. *J. Phys. Chem. C* **2022**, *126*, 4959–4964.
- (17) Han, P.; Zhou, W.; Zheng, D.; Zhang, X.; Li, C.; Kong, Q.; Yang, S.; Lu, R.; Han, K. Lead-Free All-Inorganic Indium Chloride Perovskite Variant Nanocrystals for Efficient Luminescence. *Adv. Opt. Mater.* **2022**, *10*, 2101344.

- (18) Han, P.; Luo, C.; Yang, S.; Yang, Y.; Deng, W.; Han, K. All-Inorganic Lead-Free 0D Perovskites by a Doping Strategy to Achieve a PLQY Boost from < 2% to 90. *Angew. Chem., Int. Ed.* **2020**, *59*, 12709–12713.
- (19) Majher, J. D.; Gray, M. B.; Liu, T.; Holzapfel, N. P.; Woodward, P. M. Rb_3InCl_6 : A Monoclinic Double Perovskite Derivative with Bright Sb^{3+} -Activated Photoluminescence. *Inorg. Chem.* **2020**, *59*, 14478–14485.
- (20) Shao, H.; Wu, X.; Zhu, J.; Xu, W.; Xu, L.; Dong, B.; Hu, J.; Dong, B.; Bai, X.; Cui, H.; et al. Mn^{2+} Ions Doped Lead-Free Zero-Dimensional K_3SbCl_6 Perovskite Nanocrystals Towards White Light Emitting Diodes. *Chem. Eng. J.* **2021**, *413*, 127415.
- (21) Li, M.; Xia, Z. Recent Progress of Zero-Dimensional Luminescent Metal Halides. *Chem. Soc. Rev.* **2021**, *50*, 2626–2662.
- (22) Jing, Y.; Liu, Y.; Jiang, X.; Molokeev, M. S.; Lin, Z.; Xia, Z. Sb^{3+} Dopant and Halogen Substitution Triggered Highly Efficient and Tunable Emission in Lead-Free Metal Halide Single Crystals. *Chem. Mater.* **2020**, *32*, 5327–5334.
- (23) Liu, X.; Xu, X.; Li, B.; Liang, Y.; Li, Q.; Jiang, H.; Xu, D. Antimony-Doping Induced Highly Efficient Warm-White Emission in Indium-Based Zero-Dimensional Perovskites. *CCS* **2020**, *2*, 216–224.
- (24) Zhu, D.; Zaffalon, M. L.; Zito, J.; Cova, F.; Meinardi, F.; De Trizio, L.; Infante, L.; Brovelli, S.; Manna, L. Sb-Doped Metal Halide Nanocrystals: A 0D Versus 3D Comparison. *ACS Energy Lett.* **2021**, *6*, 2283–2292.
- (25) Wei, J.; Luo, J.; Liao, J.; Ou, W.; Kuang, D. Te^{4+} -Doped $\text{Cs}_2\text{InCl}_5 \cdot \text{H}_2\text{O}$ Single Crystals for Remote Optical Thermometry. *Sci. China Mater.* **2022**, *65*, 764–772.
- (26) Gong, Z.; Zheng, W.; Huang, P.; Cheng, X.; Zhang, W.; Zhang, M.; Han, S.; Chen, X. Highly Efficient Sb^{3+} Emitters in 0D Cesium Indium Chloride Nanocrystals with Switchable Photoluminescence through Water-Triggered Structural Transformation. *Nano Today* **2022**, *44*, 101460.
- (27) Rajamanickam, N.; Chowdhury, T. H.; Isogami, S.; Islam, A. Magnetic Properties in $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite Thin Films by Mn Doping. *J. Phys. Chem. C* **2021**, *125*, 20104–20112.
- (28) Mir, W. J.; Jagadeeswararao, M.; Das, S.; Nag, A. Colloidal Mn-Doped Cesium Lead Halide Perovskite Nanoplatelets. *ACS Energy Lett.* **2017**, *2*, 537–543.
- (29) Zhou, S.; Zhu, Y.; Zhong, J.; Tian, F.; Huang, H.; Chen, J.; Chen, D. Chlorine-Additive-Promoted Incorporation of Mn^{2+} Dopants into CsPbCl_3 Perovskite Nanocrystals. *NANOSCALE* **2019**, *11*, 12465–12470.
- (30) Forde, A.; Thomas, S. A.; Petersen, R. J.; Brown, S. L.; Kilin, D. S.; Hobbie, E. K. Size-Dependent Doping Synergy and Dual-Color Emission in $\text{CsPb}_{1-x}\text{Mn}_x\text{Cl}_3$ Nanocrystals. *J. Phys. Chem. C* **2021**, *125*, 18849–18856.
- (31) Guria, A. K.; Dutta, S. K.; Adhikari, S. D.; Pradhan, N. Doping Mn^{2+} in Lead Halide Perovskite Nanocrystals: Successes and Challenges. *ACS Energy Lett.* **2017**, *2*, 1014–1021.
- (32) Das Adhikari, S.; Guria, A. K.; Pradhan, N. Insights of Doping and the Photoluminescence Properties of Mn-Doped Perovskite Nanocrystals. *J. Phys. Chem. Lett.* **2019**, *10*, 2250–2257.
- (33) Du, P.; Cai, P.; Li, W.; Luo, L.; Hou, Y.; Liu, Z. Ratiometric Optical Thermometer Based on the Use of Manganese(II)-Doped $\text{Cs}_3\text{Cu}_2\text{I}_5$ Thermochromic and Fluorescent Halides. *Microchimica Acta* **2019**, *186*, 730.
- (34) Li, X.; Chen, J.; Yang, D.; Chen, X.; Geng, D.; Jiang, L.; Wu, Y.; Meng, C.; Zeng, H. Mn^{2+} Induced Significant Improvement and Robust Stability of Radioluminescence in $\text{Cs}_3\text{Cu}_2\text{I}_5$ for High-Performance Nuclear Battery. *Nat. Commun.* **2021**, *12*, 3879.
- (35) Yan, J.; Zhang, S.; Wei, Q.; Cao, S.; Zhao, J.; Zou, B.; Zeng, R. Stoichiometry-Controlled Phase Engineering of Cesium Bismuth Halides and Reversible Structure Switch. *Adv. Opt. Mater.* **2022**, *10*, 2101406.
- (36) Wang, X.; Ali, N.; Bi, G.; Wang, Y.; Shen, Q.; Rahimi-Iman, A.; Wu, H. Lead-Free Antimony Halide Perovskite with Heterovalent Mn^{2+} Doping. *Inorg. Chem.* **2020**, *59*, 15289–15294.
- (37) De Siena, M. C.; Sommer, D. E.; Creutz, S. E.; Dunham, S. T.; Gamelin, D. R. Spinodal Decomposition During Anion Exchange in Colloidal Mn^{2+} -Doped CsPbX_3 ($X = \text{Cl}, \text{Br}$) Perovskite Nanocrystals. *Chem. Mater.* **2019**, *31*, 7711–7722.
- (38) Wei, J.; Liao, J.; Wang, X.; Zhou, L.; Jiang, Y.; Kuang, D. All-Inorganic Lead-Free Heterometallic $\text{Cs}_4\text{MnBi}_2\text{Cl}_{12}$ Perovskite Single Crystal with Highly Efficient Orange Emission. *Matter* **2020**, *3*, 892–903.
- (39) Sun, Y.; Fernández-Carrión, A. J.; Liu, Y.; Yin, C.; Ming, X.; Liu, B.-M.; Wang, J.; Fu, H.; Kuang, X.; Xing, X. Bismuth-Based Halide Double Perovskite $\text{Cs}_2\text{LiBiCl}_6$: Crystal Structure, Luminescence, and Stability. *Chem. Mater.* **2021**, *33*, 5905–5916.
- (40) Li, H. H.; Wang, C. F.; Wu, Y. X.; Jiang, F.; Shi, C.; Ye, H. Y.; Zhang, Y. Halogen Substitution Regulates the Phase Transition Temperature and Band Gap of Semiconductor Compounds. *ChemComm* **2020**, *56*, 1697–1700.
- (41) K, N. N.; Nag, A. Synthesis and Luminescence of Mn-Doped $\text{Cs}_2\text{AgInCl}_6$ Double Perovskites. *Chem. Commun.* **2018**, *54*, 5205–5208.
- (42) Locardi, F.; Cirignano, M.; Baranov, D.; Dang, Z.; Prato, M.; Drago, F.; Ferretti, M.; Pinchetti, V.; Fanciulli, M.; Brovelli, S.; et al. Colloidal Synthesis of Double Perovskite $\text{Cs}_2\text{AgInCl}_6$ and Mn-Doped $\text{Cs}_2\text{AgInCl}_6$ Nanocrystals. *J. Am. Chem. Soc.* **2018**, *140*, 12989–12995.
- (43) Wu, W.; Cong, W. Y.; Guan, C.; Sun, H.; Yin, R.; Yu, G.; Lu, Y. B. Investigation of the Mn Dopant-Enhanced Photoluminescence Performance of Lead-Free $\text{Cs}_2\text{AgInCl}_6$ Double Perovskite Crystals. *Phys. Chem. Chem.* **2020**, *22*, 1815–1819.
- (44) Liu, M.; Ali-Loytty, H.; Hiltunen, A.; Sarlin, E.; Qudsi, S.; Smatt, J. H.; Valden, M.; Vivo, P. Manganese Doping Promotes the Synthesis of Bismuth-Based Perovskite Nanocrystals While Tuning Their Band Structures. *Small* **2021**, *17*, e2100101.
- (45) Zhang, W.; Zheng, W.; Li, L.; Huang, P.; Gong, Z.; Zhou, Z.; Sun, J.; Yu, Y.; Chen, X. Dual-Band-Tunable White-Light Emission from $\text{Bi}^{3+}/\text{Te}^{4+}$ Emitters in Perovskite-Derivative Cs_2SnCl_6 Microcrystals. *Angew. Chem., Int. Ed.* **2022**, *61*, 202116085.
- (46) Meng, Q.; Zhou, L.; Pang, Q.; He, X.; Wei, T.; Zhang, J. Z. Enhanced Photoluminescence of All-Inorganic Manganese Halide Perovskite-Analogue Nanocrystals by Lead Ion Incorporation. *J. Phys. Chem. Lett.* **2021**, *12*, 10204–10211.
- (47) Zhou, W.; Fan, J.; Luo, J.; Wu, J.; Zhang, R.; Zhang, J.; Pang, Q.; Zhou, L.; Zhang, T.; Zhang, X. Novel High-Saturated Red-Emitting Phosphor $\text{Sr}_9(\text{Mg}_{0.5}\text{Mn}_{0.5})\text{K}(\text{PO}_4)_7: \text{Eu}^{2+}$ with Great Quantum Efficiency Enhancement by La^{3+} Codoping for White Led Application. *Mater. Today Chem.* **2023**, *27*, 101263.
- (48) Zhang, X.; Luo, J.; Sun, Z.; Zhou, W.; Wu, Z. C.; Zhang, J. Ultrahigh-Energy-Transfer Efficiency and Efficient Mn^{2+} Red Emission Realized by Structural Confinement in $\text{Ca}_9\text{LiMn}(\text{PO}_4)_7: \text{Eu}^{2+}, \text{Tb}^{3+}$ Phosphor. *Inorg. Chem.* **2020**, *59*, 15050–15060.
- (49) Hu, Y.; Yan, X.; Zhou, L.; Chen, P.; Pang, Q.; Chen, Y. Improved Energy Transfer in Mn-Doped $\text{Cs}_3\text{Cu}_2\text{I}_5$ Microcrystals Induced by Localized Lattice Distortion. *J. Phys. Chem. Lett.* **2022**, *13*, 10786–10792.
- (50) Wai, R. B.; Ramesh, N.; Aiello, C. D.; Raybin, J. G.; Zeltmann, S. E.; Bischak, C. G.; Barnard, E.; Aloni, S.; Ogletree, D. F.; Minor, A. M.; et al. Resolving Enhanced Mn^{2+} Luminescence near the Surface of CsPbCl_3 with Time-Resolved Cathodoluminescence Imaging. *J. Phys. Chem. Lett.* **2020**, *11*, 2624–2629.
- (51) Zhong, C. Y.; Li, L.; Chen, Q.; Jiang, K. Z.; Li, F. t.; Liu, Z. Q.; Chen, Y. Enhanced Exciton-to- Mn^{2+} Energy Transfer in 3D/0D Cesium-Lead-Chloride Composite Perovskites. *Adv. Opt. Mater.* **2022**, 2202321.
- (52) Wu, D.; Liu, L.; Liang, H.; Duan, H.; Nie, W.; Wang, J.; Peng, J.; Ye, X. $\text{LiBaF}_6: \text{Cr}^{3+}$ ($B = \text{Ca}, \text{Sr}$) fluoride phosphors with ultra-broad near-infrared emission for NIR pc-LEDs. *CERAM INT* **2022**, *48*, 387–396.
- (53) Zhang, K.; Zhu, N.; Zhang, M.; Wang, L.; Xing, J. Opportunities and Challenges in Perovskite Led Commercialization. *J. Mater. Chem. C* **2021**, *9*, 3795–3799.