Manganese-Doped, Lead-Free Double Perovskite Nanocrystals for Bright Orange-Red Emission

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ABSTRACT: Lead-free halide perovskite nanocrystals (NCs) have recently attracted attention due to their nontoxicity and stability as alternatives to lead-based perovskite NCs. Here, we report undoped and manganese-doped all-inorganic, lead-free double perovskite (DP) NCs: Cs₂NaInₓBi₁₋ₓCl₆ (0 < x < 1) and Cs₂NaInₓBi₁₋ₓCl₆:Mn (0 ≤ x ≤ 1) NCs. Undoped NCs exhibit blue emission. Through doping Mn²⁺ ions into Cs₂NaInₓBi₁₋ₓCl₆ NCs, we can avoid self-trapped exciton emission and realize bright orange-red emission of Mn²⁺ dopants with the highest photoluminescence quantum efficiency of 44.6%. The photoluminescence (PL) is tunable from yellow emission to orange-red emission corresponding to a red shift from 583 to 614 nm with increasing In content. Interestingly, the PL emission of Mn-doped NCs shows a red shift from the bulk size to the nanoscale. The Mn-doped NCs show good stability in air. In addition, we further prove the process of dark self-trapped state-assisted Mn²⁺ emission in DP NCs by ultrafast transient absorption techniques.

INTRODUCTION

All-inorganic, lead-free perovskite nanocrystals (NCs) have aroused great interest due to their simple synthesis process, nontoxicity, and high stability for optoelectronic applications, especially for double perovskites (DPs) NCs, which are characterized by a three-dimensional (3D) network similar to lead-based perovskite NCs and have the potential to be excellent light-emitting materials. Doping and alloying strategies can improve the photophysical properties and stability of DP NCs. Recently, the broadband, large red-shifted emission is the main focus of attention attributed to bright self-trapped exciton (STE) in DP NCs. However, other specific wave-band emission and dopants emission have been rarely studied in the visible region, in terms of dopants emission in DP NCs, which is often accompanied by bright STE emission, and for lead-based NCs, which is often accompanied by free exciton (FE) emission or bright STE emission. Thus, avoiding FE emission or bright STE emission can promote single, pure dopants emission. In addition, Mn-doped, Ag-based DP NCs have been reported, which facilitate dopants emission owing to the direct band gap structure, but those NCs have parity-forbidden transition and inhibit further improvement of photoluminescence (PL) properties. Moreover, there is a significant difference in the photophysical properties of DP NCs and DP bulk crystals. We have previously studied the size effect of alloying DPs for STE emission, but the size effect of doping DPs has not been investigated for dopants emission. These problems limit the application of these semiconductor materials as light emitters in the illumination field. It is a great challenge and significance to further enhance the light emission and clarify the exciton dynamics mechanism. To the best of our knowledge, there has been no report of a Mn-doped, direct bandgap of the allowed transition, Na-based DP colloidal NCs.

Here, we successfully synthesize undoped and Mn-doped lead-free direct bandgap Na-based mixed In/Bi DP NCs: Cs₂NaInₓBi₁₋ₓCl₆ (0 < x < 1) and Cs₂NaInₓBi₁₋ₓCl₆:Mn (0 ≤ x ≤ 1) NCs. Undoped NCs show blue-light emission. Through introducing Mn²⁺ ions into Cs₂NaInₓBi₁₋ₓCl₆ NCs, the PL properties are changed and improved to achieve bright orange-red emission with the best photoluminescence quantum efficiency (PLQE) of 44.6%. The PL are tunable from yellow emission to orange-red emission corresponding to a red shift from 583 to 614 nm with increasing In content. The Mn-doped NCs have an ultralong PL lifetime around 3–9 ms. Interestingly, the PL emission of Cs₂NaIn₀.₇₅Bi₀.₂₅Cl₆:Mn NCs shows a red shift from the bulk size to the nanoscale. We further prove the process of the dark STE state assisted Mn²⁺ PL in DP NCs by time-resolved PL (TR-PL) measurements.
and ultrafast transient absorption (TA) techniques. In addition, the Mn-doped NCs show better stability in air.

## RESULTS AND DISCUSSION

### Undoped Cs2NaIn0.75Bi0.25Cl6 DP NCs.

The Cs2NaIn0.75Bi0.25Cl6 (x = 0, 0.25, 0.5, 0.75, and 0.9) NCs are synthesized by variable temperature, one-pot hot injection. X-ray diffraction (XRD) patterns reveal that these NCs have face-centered cubic structures and Fm3m space group similar to Cs2NaBiCl6 (Figure 1a). Also, these NCs show high crystallinity and a single pure phase. These NCs exhibit a peak in Figure 1a, attributed to the ionic radius of In3+ (94 pm), which is smaller than that of Bi3+ (117 pm). To obtain the actual In/Bi ratio, inductively coupled plasma optical emission spectrometry (ICP-OES) was carried out (Table S1).

Compared to reported lead-free DP NCs, we find an interesting rule. Na-based DP NCs have no broad, large redshift PL emission in DP NCs. In addition, Na-based DP NCs have three advantages over reported Ag-based DP NCs,14 First, their morphology is more regular. Second, FE emission does not require reprocessing (surfactant passivation). Compared to reported lead-free DP NCs, we find an interesting rule. Na-based DP NCs have no broad, large redshift PL emission in DP NCs. In addition, Na-based DP NCs have three advantages over reported Ag-based DP NCs,14 First, their morphology is more regular. Second, FE emission does not require reprocessing (surfactant passivation).
monotonically shifted to high angles with increasing In content. The (220) peak, which shifts 0.8° from \( x = 0 \) to \( x = 1 \), coincides with the result of undoped NCs. We show that Mn\(^{2+}\) ions have been successfully doped into \( \text{Cs}_2\text{NaIn}_x\text{Bi}_{1-x}\text{Cl}_6 \) NCs by X-ray photoelectron spectroscopy (XPS) (Figure S3).

A transmission electron microscopy (TEM) image of \( \text{Cs}_2\text{NaIn}_{0.75}\text{Bi}_{0.25}\text{Cl}_6 \) NCs is shown in Figure 3b. The NCs are evenly distributed cubic-shaped having a mean size of 9.43 nm (Figure 3b,d). A high-resolution TEM (HRTEM) image of single NC shows a single phase and high crystallinity (Figure 3c). The high-angle annular dark-field (HAADF) and scanning transmission electron microscopy-energy dispersive X-ray spectroscopy (STEM-EDS) element mappings of \( \text{Cs}_2\text{NaIn}_{0.75}\text{Bi}_{0.25}\text{Cl}_6 \) NCs confirm visually that without phase separation and the homogeneous distribution of Cs, Na, In, Bi, Mn, and Cl in the single pure phase (Figure S4 and Table S2). The TEM images of \( x = 0, 0.25, 0.5, 0.75, \) and 1 Mn-

doped NCs also exhibit relatively even distribution and are mainly a cubic shape with mean sizes of 10.45 ± 0.5 nm (details in Figure S5). These results also indicate that the doping of the Mn\(^{2+}\) cation does not induce the formation of crystal defects. According to previous studies,\(^{21,22}\) doping Mn\(^{2+}\) ions can enhance the stability of perovskite NCs in air. The Na-based DP NCs are no exception, and Mn-doped NCs show better stability than undoped NCs in air (Figure S6).

The optical absorption spectra of Mn-doped \( \text{Cs}_2\text{NaIn}_x\text{Bi}_{1-x}\text{Cl}_6 \) (\( x = 0, 0.25, 0.5, 0.75, \) and 0.9) NCs are similar to the undoped NCs (Figure S7). It indicates that doping Mn\(^{2+}\) has little effect on the absorption of undoped NCs, consistent with absorption results of lead-based perovskites.\(^{19,23}\) As expected, Mn-doped NCs show bright pure Mn\(^{2+}\) PL, which are tunable from yellow emission to orange-red emission corresponding to from \( x = 0 \) to \( x = 0.9 \) (Figure S8a). However, \( \text{Cs}_2\text{NaInCl}_6\) NCs have very weak Mn\(^{2+}\) PL emission centered at 614 nm (Figure S8), due to the parity-forbidden transition of In-based DP.\(^{20}\) The highest PLQE of \( \text{Cs}_2\text{NaIn}_{0.9}\text{Bi}_{0.1}\text{Cl}_6 \) Mn NCs is up to 44.6%, much higher than the PLQE of Mn-doped \( \text{Cs}_2\text{AgInCl}_6 \) DP NCs.\(^{7}\) Excitingly, with increasing In content, the PL peak position of Mn-doped NCs exhibits a red shift from 583 to 614 nm (Figure S8b), contrary to the trend of absorption peak. TR-PL measurements are operated. The PL decay curves of Mn-doped NCs are shown in Figure S9, giving a long average lifetime of 3–9 ms, caused by the spin forbidden nature of the Mn\(^{2+}\) ions (\( ^{6}A_1 \rightarrow ^{6}A_1 \) transition).\(^{24,25}\) The PL lifetime of Mn-doped Na-based DP NCs is longer than that of Mn-doped, Ag-based DP and Pb-based perovskites NCs.\(^{7,21–23}\)

**Size Effect on PL Property.** As is known to all, semiconductor material decreases from the bulk size to the nanoscale, due to the quantum confinement effect,\(^{26,27}\) and the optical properties will be significantly different, which is generally manifested as the XRD diffraction peak becomes wider, and the absorption and PL peak become narrower and blue shift. For the reported \( \text{Cs}_2\text{AgInCl}_6 \) Mn NCs and bulk crystals,\(^{28}\) the optical properties are consistent with the above. To our surprise, the PL peak of Mn-doped Na-based DP NCs appears red shifted compared with the reported bulk crystals.\(^{29}\)

In order to facilitate the following research, we synthesize \( \text{Cs}_2\text{NaIn}_{0.75}\text{Bi}_{0.25}\text{Cl}_6 \) Mn bulk crystals for comparison and discussion. The XRD pattern of \( \text{Cs}_2\text{NaIn}_{0.75}\text{Bi}_{0.25}\text{Cl}_6 \) Mn NCs...
corresponds to that of bulk crystals, and the XRD diffraction peak of NCs is wider than that of bulk crystals (Figure S10). Both Cs$_2$NaIn$_{0.75}$Bi$_{0.25}$Cl$_6$:Mn NCs and bulk crystals show obvious exciton absorption peaks in Figure 5a. The central

position of the absorption peak has barely changed. The full width at half-maximum (fwhm) of the absorption peak of NCs (31.5 nm) is 17.4 nm narrower than that of bulk crystals (41.1 nm), so the absorption band edge is blue shifted. The PL spectra of Cs$_2$NaIn$_{0.75}$Bi$_{0.25}$Cl$_6$:Mn NCs and bulk crystals are also shown in Figure 5a. The fwhm of the PL peak of NCs (74.2 nm) is 10.5 nm narrower than that of bulk crystals (84.7 nm). Intriguingly, it is obvious that the position of the PL peak exhibits a red shift (~17 nm), contrary to Mn-doped or undoped Ag-based DP.\textsuperscript{5,7,11,28,30,31} This interesting phenomenon is rare in perovskite systems. The quantum confinement effect explains well the results of XRD and absorption, but it is obviously unreasonable to explain the PL properties of Mn-doped DP. Because Mn$^{2+}$ PL belongs to the sub-band transition ($d$--$d$ transition of Mn$^{2+}$). This phenomenon can be explained by contraction of the $T_1$ state of Mn$^{2+}$ (details in Supporting Information (SI)). The scheme is illustrated in Figure S11. In addition, the average PL lifetime (~8.7 ms) of NCs is longer than that of bulk crystals (~6 ms) (Figure 5b).

**Transient Absorption Measurement.** To further reveal the process of the dark STE state assisted Mn$^{2+}$ emission in DP NCs, the femtosecond TA technique was carried out. The pseudocolor TA plot of the Cs$_2$NaIn$_{0.75}$Bi$_{0.25}$Cl$_6$:Mn NCs is shown in Figure 6a. With 310 nm laser excitation, a broad positive photoinduced absorption (PIA) is observed across the probe region, which is direct evidence of the STEs.\textsuperscript{10,32,33} The same decay curves probed at different wavelengths (470, 505, 540, 580, and 630 nm) confirm that the PIA signal reflects the property of the same excited state in the inset of Figure 5b. The rise process of the PIA signal is clearly observed in Figure S12, but the rise time is too fast within the instrument response resolution (~100 fs). This result demonstrates that there is no potential barrier separating the FEs and STEs, and the dark STE state is beneficial to FE trapping. The PIA decay signal can be fitted by three components: an ultrafast lifetime of $\tau_1$: 1–3 ps, a middle lifetime of $\tau_2$: 100 ± 50 ps, and a slow lifetime of $\tau_3$: > 2 ns (Figure 6b).

For DP NCs, the smaller the size, the larger the specific surface area, the higher the surface activity, and a shorter crystallization time and larger temperature gradient of crystallization result in more permanent defects.\textsuperscript{34–36} Meanwhile, a doping strategy can reduce the defect state.\textsuperscript{10,21,37} To eliminate the influence of surface defects, the femtosecond TA of bulk Cs$_2$NaIn$_{0.75}$Bi$_{0.25}$Cl$_6$:Mn single crystal is characterized and analyzed (Figure S13a). As expected, the PIA signal of the bulk crystal is similar to that of NCs, but the middle-lifetime process disappears (Figure S13b). It is reasonable that the middle component of 100 ± 50 ps is attributed to surface defects trapping.\textsuperscript{9} The surface defects are clearly observed in the HRTEM image of single Cs$_2$NaIn$_{0.75}$Bi$_{0.25}$Cl$_6$:Mn NC (Figure S14). Energy transfer (ET) is an extremely fast picosecond process in semiconductor nanomaterials.\textsuperscript{38} The ultrafast component (1–3 ps) is assigned to the energy transfer from the dark STE state to the $T_1$ excited state of Mn$^{2+}$. The slow lifetime of >2 ns is assigned to the dark STEs, consistent with our previous study.\textsuperscript{10} The femtosecond TA of undoped Cs$_2$NaIn$_{0.75}$Bi$_{0.25}$Cl$_6$ NCs also has a positive PIA signal and a slow component of >2 ns (Figure S15). It proves that dark STE state is independent of Mn doping or undoping in Na-based mixed In/Bi DP NCs. Combined with the above, the overall exciton dynamics of Cs$_2$NaIn$_{0.75}$Bi$_{0.25}$Cl$_6$:Mn NCs is illustrated in Scheme 1.

**CONCLUSION**

In conclusion, we have successfully synthesized a series of undoped and Mn-doped all-inorganic, lead-free, direct bandgap...
Na-based mixed In/Bi PD NCs using variable temperature hot injection. Undoped NCs exhibit band edge blue-light emission with the highest PLQE of 38%. Through doping Mn\(^{2+}\) ions into Cs\(_2\)NaIn\(_{1-x}\)Bi\(_x\)Cl\(_6\) NCs, PL properties of Mn-doped NCs are changed and improved to achieve bright orange-red emission due to \(4T_1 \rightarrow A_1\) transition of Mn\(^{2+}\) dopants and have an ultralong PL lifetime around 3–9 ms. The PL are tunable from yellow emission to orange-red emission corresponding to a red shift from 583 to 614 nm with increasing In content. The best PLQE of Mn-doped NCs is 44.6%. Mn-doped NCs show better stability than undoped NCs to air exposure for more than two months. Therefore, it is promising as a new highly efficient orange-red-light emitting material for applications of LEDs. In addition, we find an interesting phenomenon is that the PL emission of Cs\(_2\)NaIn\(_{0.75}\)Bi\(_{0.25}\)Cl\(_6\) NCs shows a red shift from the bulk size to the nanoscale. We further prove the process of dark STE state assisted Mn\(^{2+}\) PL in DP NCs by the TR-PL measurements and ultrafast TA techniques. This work highlights the rational use of the advantages of excited states and the design of new high-performance semiconductor nanomaterials to introducing appropriate dopants, in order to obtain desired photophysical properties for photovoltaic devices.

**EXPERIMENTAL SECTION**

**Materials.** Cesium acetate (Cs(OAc), 99.99%, Aladdin), sodium acetate (Na(OAc), 99.99%, anhydrous, Aladdin), indium acetate (In(OAc))\(_3\), 99.99%, Alfa Aesar), bismuth acetate (Bi(OAc))\(_3\), 99.99%, Sigma-Aldrich), manganese acetate (Mn(OAc))\(_2\), 98%, anhydrous, Alfa Aesar), chlorotrimethylsilane (TMSCl, 99%, Sigma-Aldrich), 1-octadecene (90%, Alfa Aesar), oleylamine (OLA, Aladdin, 80%), oleic acid (OA, 90%, Alfa Aesar), toluene (99.5%, Sinopharm Chemical Reagent Co., Ltd., China), n-hexane (97%, Aladdin), cesium chloride (CsCl, 99%, Aladdin), sodium chloride (NaCl, 99.99%, Alfa Aesar), indium chloride (InCl\(_3\), 98%, Sigma-Aldrich), bismuth chloride (BiCl\(_3\), anhydrous, 99%, Alfa Aesar), manganese chloride (MnCl\(_2\), 99.99%, Alfa Aesar), and hydrochloric acid (analytical pure, Sinopharm Chemical Reagent Co., Ltd., China). All chemicals were used as received without further purification.

**Synthesis of Undoped and Mn-Doped Cs\(_2\)NaIn\(_{1-x}\)Bi\(_x\)Cl\(_6\) (x = 0, 0.25, 0.5, 0.75, 0.9, and 1) NCs through Variable Temperature Hot Injection.** The undoped Cs\(_2\)NaIn\(_{1-x}\)Bi\(_x\)Cl\(_6\) NCs were prepared by variable temperature hot injection. A total of 0.65 mmol Cs(OAc), 0.45 mmol Na(OAc), x mmol In(OAc)\(_3\) and (0.5 – x) mmol Bi(OAc))\(_3\) were added in a mixture of oleic acid (2.8 mL), oleylamine (0.7 mL), and octadecene (10 mL), which was warmed to 110 °C under a vacuum for 60 min. The reaction mixture was heated slowly to room temperature (RT) at a speed of 5 °C/h. Finally, the crystals were filtered and dried in a vacuum at 80 °C for 12 h.

**Optical Absorption Spectroscopy.** For colloidal NCs, steady-state optical absorption measurement was performed using a PerkinElmer Lambda 35 double-beam spectrometer equipped with an integrating sphere to exclude the signal due to light scattering. For single crystal powder, steady-state absorption spectra were recorded using a UV–vis (SHIMADZU UV2600) spectrometer. Optical diffuse reflectance measurements were performed by equipping with an integrating sphere at room temperature and BaSO\(_4\) as the 100% reflectance reference. The reflectance data were converted to absorption according to the Kubelka–Munk equation:

\[
F(R) = \frac{(1 - R)^2}{2R} = \frac{\alpha}{S}
\]

where \(R\) is the reflectance, \(\alpha\) and \(S\) are the absorption and scattering coefficients, respectively.

**PL Spectroscopy.** Steady-state PL spectra were recorded on a Horiba JobinYvon FluoroMax-4P spectrofluorometer. Time-resolved PL (TR-PL) measurements were carried out on an OB920 luminescence lifetime spectrometer (Edinburgh Instruments Ltd., UK) using time-correlated single photon counting (TCSPC) technology. The PLQE measurement was performed using an absolute PL quantum yield spectrometer (Hamamatsu C11347).

**Ultrafast Transient Absorption Spectroscopy.** TA experiments are operated by using a homemade femtosecond pump–probe setup. Laser pulses (800 nm, 50 fs pulse length, 1 kHz repetition rate) were generated by a Ti: sapphire femtosecond laser source (Hurricane, Spectra-Physics). An optical parametric amplifier was used to change the laser wavelength. For the probe, we use the supercontinuum generation from a thin CaF\(_2\) plate. The mutual polarization between pump and probe beams was set to the magic angle (54.7°) by placing a Berek compensator in the pump beam. The kinetics of the different scabs stayed the same showing no
sign of degradation. Excitation power and spot size measurements were used to determine the excitation fluence (pump wavelength: 310 nm; pump fluence: $6.2 \times 10^{14}$ photons/pulse/cm$^2$). During the measurement, millimeter-scale bulk crystal was placed on the quartz substrate; colloidal NCs were contained in a 1 mm cuvette.

- **ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscentsci.0c00056.

ICP-OES results; TEM images, TR-PL decay curves, XPS spectra; HAADF images, STEM-EDS results, air stability measurements, steady-state absorption spectra, PL spectra, XRD patterns, schematic illustration of size effect of Mn$^{2+}$ PL emission, PIA onsets, pseudocolor TA plots and PIA decay dynamics plots, HRTEM image (PDF)

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**Notes**
The authors declare no competing financial interest.

- **ACKNOWLEDGMENTS**

This work was supported by the National Key Research and Development Program of China (Grant 2017YFA0204800), the National Natural Science Foundation of China (Grant Nos. 21833009, 21533010, 21525315), DICP DMTO201601, DICP ZJBS201703, and the Science Challenging Program (JCKY201612AS01).

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