Discovery of the Crystal Phase Transition on Lead-free Cesium Manganese Bromine Perovskite Nanocrystal by Solvent Concentration

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Abstract

We have been demonstrated the crystal phase transition for lead-free cesium manganese bromine perovskite nanocrystal synthesized by the modified hot-injection method due to change the concentration of solvent (trioctylphosphine; TOP). The compositions to be synthesized were determined by the amount of TOP solvent, and the structure phase of nanocrystal was changed from hexagonal CsMnBr_3 to tetragonal Cs_3MnBr_5 as the amount of TOP solvent increased. The emission peaks of CsMnBr_3 and Cs_3MnBr_5 nanocrystals were observed at 650 nm (red) and 520 nm (green), respectively. After a durability test at 85 °C and 85% humidity for 24 h, the lead-free perovskite CsMnBr_3 nanocrystal powder maintained its initial emission intensity, and the metal halide Cs_3MnBr_5 nanocrystal powder exhibited an increase in red emission due to the post-synthesis of CsMnBr_3 nanocrystals.

Introduction

Lead halide perovskites, which have the general formula APbX_3 (where $\text{A} = \text{CH}_3\text{NH}_3^+$ (MA), $\text{HC}(\text{NH}_2)_2^+$ (FA), or Cs^+ ; $\text{X} = \text{Cl}$, Br or I), has been studied since the middle of the 20th century [1–5]. Among these perovskites, inorganic cesium lead halide perovskite ($\text{Cs}_n\text{PbX}_{2+n}$, $\text{X} = \text{Cl}$, Br , I , or a mixture thereof) nanocrystals have attracted significant attention as an optical material for display and lamp applications (e.g. color converter material), as an alternative to quantum dot materials. Within the past decade, there have been rapid advances in the synthesis of cesium lead halide perovskite nanocrystals for use in solar cells, light-emitting diodes (LEDs), lasers, and photodetectors because of the excellent optoelectronic performance of these perovskite nanocrystals [6–13]. They have interesting optical, excitonic, and charge-transport properties, including an outstanding photoluminescence quantum yield (PLQY) and tunable optical bandgap.

Despite these advantages, however, the presence of Pb, a toxic element, in perovskite nanocrystals raises critical concerns with regard to commercialization. This is because the heavy metal Pb can affect human health and the environment [14, 15]. The US EPA has set the maximum allowable content of Pb in air and water as 0.15 $\mu\text{g/L}$ and 15 $\mu\text{g/L}$, respectively. The European Union regulates the use of heavy and toxic materials (including Pb) in electronic devices, and the use of lead-based technology is expected to decline in the future [16, 17] Therefore, the development of a lead-free cesium halide perovskite that retains the outstanding properties of cesium lead halide nanocrystals is important, and several studies have been conducted recently in this regard.

Metallic elements that have an electronic structure similar to that of Pb and can thus form stable perovskite structures—such as Sn, Sb, Bi, Eu, and Yb—have been considered as alternatives for Pb. Various lead-free halide perovskite nanocrystals, including those containing the aforementioned metal elements, have recently been developed and have achieved optoelectronic performance comparable to that of Pb-based counterparts [17–19]. These encouraging results obtained via exploration of lead-free

perovskite nanocrystals indicate a major imminent breakthrough in the fabrication of new optoelectronic devices.

In this study, to obtain lead-free inorganic halide perovskite nanocrystals, we focused on replacing Pb with the transition metal Mn. Mn has an ionic radius (0.083 nm for 6 coordination) similar to that of Pb (0.119 nm for 6 coordination), as well as a low toxicity, and has therefore attracted attention as a substitute for the B site in halide perovskites. Cesium manganese bromide perovskite nanocrystals, such as the red-emitting CsMnBr_3 and green-emitting Cs_3MnBr_5 , have been reported to exhibit excellent optical properties [20–23]. In this paper, we synthesized red-emitting CsMnBr_3 and Cs_3MnBr_5 perovskite nanocrystals using the modified hot-injection method and investigated the optical properties of these perovskite nanocrystals. Furthermore, we investigated the phase-tunable synthesis from Cs_3MnBr_5 to CsMnBr_3 with controlling the amount of solvent.

Results And Discussion

Figure 1 shows the XRD patterns of the cesium manganese bromide perovskite nanocrystals with the amount of TOP solvent as well as the standard XRD patterns of the CsMnBr_3 and Cs_3MnBr_5 from JCPDS card No. 26–0387 and No. 27–0117, respectively. The crystal structures of CsMnBr_3 and Cs_3MnBr_5 are shown in Fig. 2. The crystal structure of CsMnBr_3 consists of linear chains of distorted face-sharing $[\text{MnBr}_6]$ octahedron with a D_{3d} symmetry parallel to the c-axis, that are bridged by Cs ions. Interestingly, the Mn – Mn distance is very short (~ 0.32982 nm) along the c-axis, leading to strongly coupled optical transitions. The XRD pattern of the sample prepared with 10 mL TOP solvent was indexed to the standard hexagonal CsMnBr_3 structure (JCPDS No. 26–0387); this sample contains the $P6_3/mmc$ (#194) space group and has lattice parameters $a = b = 0.785878$ nm and $c = 0.659641$ nm. In the crystal structure of Cs_3MnBr_5 , the Mn^{2+} ions are coordinated by four Br^- ions to form a $[\text{MnBr}_4]$ regular tetrahedron geometry with D_{2d} symmetry. The Mn^{2+} site layers are separated by Cs^+ site layers in the direction of the c-axis, and the adjacent $[\text{MnBr}_4]$ tetrahedrons maintain a distance of $0.780593(6)$ nm. The XRD pattern of the sample prepared with 20 mL TOP solvent corresponds to a single-phase tetragonal Cs_3MnBr_5 structure (JCPDS No. 27–0117); this sample has the $I4/mcm$ (#140) space group and lattice constants $a = b = 0.992839$ nm and $c = 1.561187$ nm. The nanocrystal samples prepared with 12.5 and 17.5 mL TOP solvent exhibit a mixed phase with hexagonal CsMnBr_3 and tetragonal Cs_3MnBr_5 phases, and the phase transition of nanocrystal phase from CsMnBr_3 to Cs_3MnBr_5 was observed as the amount of TOP solvent increased.

The morphology of the synthesized nanocrystals with the amount of TOP solvent was analyzed using high-resolution TEM, as shown in Fig. 3. The TEM images of lead-free perovskite CsMnBr_3 nanocrystals present a dispersed hexagonal morphology with an average size of ~ 20 nm. The interplanar spacing relative to the (021) crystalline planes of the CsMnBr_3 nanocrystals is about 0.3 nm. In contrast, the TEM image of Cs_3MnBr_5 nanocrystals shows a dispersed tetragonal morphology with an average size of ~ 30

nm. The interplanar spacing relative to the (213) crystalline planes of the Cs_3MnBr_5 nanocrystals is about 0.33 nm. The nanocrystals prepared with 12.5 and 17.5 mL TOP solvent coexist with the CsMnBr_3 and Cs_3MnBr_5 nanocrystals; the compositional change between the CsMnBr_3 and Cs_3MnBr_5 nanocrystals is determined by the amount of TOP solvent.

Figure 4 presents the PL spectra of the obtained nanocrystals with the amount of TOP solvent. The inset images show the emission of the nanocrystals under irradiation with a 365 nm UV lamp; their color changes from red to green as the amount of TOP solvent increases from 10 to 20 mL. The emission spectrum of the lead-free perovskite CsMnBr_3 nanocrystals exhibits a broad red emission peak centered at 650 nm with a full-width-at-half-maximum (FWHM) of 95 nm. The red PL emission which assigned $^4\text{T}_1 \rightarrow ^6\text{A}_1$ transition in $[\text{MnBr}_6]^{4-}$ octahedrons of the CsMnBr_3 nanocrystals is considered to be due to the relaxation from the lowest excited state to the ground state of Mn^{2+} ions. This is consistent with reports of red emission from Mn^{2+} in the MnBr_6 octahedron [24, 25]. On the other hand, the emission spectrum of the Cs_3MnBr_5 nanocrystals shows green emission at 520 nm with an FWHM of 50 nm. The strong green emission is ascribed to the metal-centered d–d transition of the Mn^{2+} ion in the d^5 configuration with a $[\text{MnBr}_4]$ tetrahedral coordination geometry [26]. Interestingly, the PL spectra of the Cs–Mn–Br nanocrystals can be controlled by simply changing the amount of TOP solvent, as depicted in Fig. 4. With an increase of the amount of TOP solvent, the relative emission of red (CsMnBr_3) and green (Cs_3MnBr_5) shifts toward green emission, implying that our study can achieve tunable the color between green and red by simply controlling the amount of TOP solvent.

To evaluate the thermal and chemical stability of the CsMnBr_3 and Cs_3MnBr_5 nanocrystals, a durability test was performed under high-temperature and high-humidity conditions of 85°C and 85%, respectively, for 24 h. The PL behaviors of the CsMnBr_3 and Cs_3MnBr_5 nanocrystals after the durability test are shown in Fig. 5 (a). The lead-free perovskite CsMnBr_3 nanocrystal powder exhibits extremely high durability and maintains its initial PL intensity. In comparison, the PL intensity of the metal halide Cs_3MnBr_5 nanocrystal powder does not decrease but rather increases in the red emission (CsMnBr_3) region. It is considered that the materials that remained unreacted during the preparation of the nanocrystals reacted to form more CsMnBr_3 nanocrystals due to the high temperature during the durability test. Both nanocrystals exhibited no change in the PL peak wavelength and FWHM values after the durability test. The structures of CsMnBr_3 and Cs_3MnBr_5 are considered to have remained intact even after the durability test because no difference was observed between the XRD patterns before and after the test. The XRD patterns of the CsMnBr_3 and Cs_3MnBr_5 nanocrystals before and after the durability test are presented in Fig. 5 (b). Both samples exhibited identical XRD patterns before and after the test, indicating that the CsMnBr_3 and Cs_3MnBr_5 structures were not degraded during the durability test.

Conclusions

We discovered the crystal phase transition of lead-free cesium manganese bromine perovskite nanocrystal from hexagonal CsMnBr_3 to tetragonal Cs_3MnBr_5 due to change the concentration of TOP solvent for the first time. The CsMnBr_3 nanocrystals had a hexagonal structure and exhibited a dispersed hexagonal morphology with an average size of ~ 20 nm and an interplanar spacing of 0.3 nm. The Cs_3MnBr_5 nanocrystals had a tetragonal structure and exhibiting a dispersed tetragonal morphology with an average size of ~ 30 nm and an interplanar spacing of 0.33 nm. The compositional change between the CsMnBr_3 and Cs_3MnBr_5 nanocrystals was determined by the amount of TOP solvent, the nanocrystal phase is changed from CsMnBr_3 to Cs_3MnBr_5 as the amount of TOP increases. The emission peaks of the CsMnBr_3 and Cs_3MnBr_5 nanocrystals were observed to be at 650 nm (FWHM = 95 nm) and 520 nm (FWHM = 50 nm), respectively. With an increase in the amount of TOP solvent, the relative emission of red (CsMnBr_3) and green (Cs_3MnBr_5) shifted toward green emission. To examine the stability of the lead-free cesium manganese bromine perovskite nanocrystals, durability tests were performed. The CsMnBr_3 and Cs_3MnBr_5 nanocrystal powders fabricated from the nanocrystal solutions were subjected to high-temperature and high-humidity testing at 85°C and 85% humidity for 24 h. After the durability test, no change was observed in the PL intensity of the lead-free perovskite CsMnBr_3 nanocrystal however, an increase in red emission was observed for the metal halide Cs_3MnBr_5 nanocrystal. Our study demonstrates that phase-tunable synthesis between lead-free perovskite CsMnBr_3 and metal halide Cs_3MnBr_5 nanocrystals can be easily achieved by controlling the amount of TOP solvent; it's material represents a potential next-generation luminescence material for mini LED devices and applications in optoelectronic devices.

Method

Materials Cesium carbonate (Cs_2CO_3 , purity; 99.995%), manganese(II) bromide (MnBr_2 , purity; 98%), 1-octadecene (ODE, technical grade; 90%), trioctylphosphine (TOP, technical grade; 90%), oleic acid (OA, technical grade; 90%), and oleylamine (OLA, technical grade; 90%) were purchased from Aldrich.

Synthesis of CsMnBr_3 and Cs_3MnBr_5 nanocrystal Cs-oleate was prepared by mixing 0.13 g Cs_2CO_3 , 0.55 mL OA, 0.4 mL OLA, and 12 mL ODE in a 30 mL glass vial for 1 h at 170°C for dissolution. The solution containing MnBr_2 was prepared by mixing 0.5369 g MnBr_2 and 5–20 mL TOP in a 30 mL glass vial at 170°C for 1 h; then, Cs-oleate was quickly injected into the solution containing MnBr_2 . The CsMnBr_3 or Cs_3MnBr_5 nanocrystal solutions reacted at 170°C for 1 min and were cooled in an ice-water bath to suppress the crystal growth of the nanocrystals. The obtained $\text{CsMnBr}_3/\text{Cs}_3\text{MnBr}_5$ nanocrystal solution was separated via centrifugation at 4000 rpm for 5 min.

Characterizations The crystal structure of the CsMnBr_3 and Cs_3MnBr_5 nanocrystal was identified using X-ray powder diffraction (XRD; Rigaku SmartLab) analysis, and the microstructure and morphology of the nanocrystals was characterized using transmission electron microscopy (TEM; JEOL). The photoluminescence (PL) spectrum was recorded at room temperature using a fluorescence

spectrophotometer (PSI, DARSA PRO-3400), and the emission spectrum was obtained at an excitation wavelength of 365 nm. The lead-free cesium manganese bromine perovskite nanocrystal powder was prepared using the nanocrystal solution; a durability test was performed at 85°C and 85% humidity for 24 h.

Declarations

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Author Contributions

T. W. Kang, J. Hwang, B. S. Bae and S. W. Kim, contributed to the design experiments, interpreted the data and prepared the paper. E. J. Choi and Y. J. Park contributed to the experiments. All authors discussed the results and reviewed the manuscript.

Additional Information

The authors declare no competing financial interest.

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Figures

Figure 1

XRD patterns of the lead-free cesium manganese bromine perovskite nanocrystals by modified hot-injection method with the amount of TOP solvent.

Figure 2

Schematic of (a) CsMnBr_3 crystal structure with (b) the ab plane illustrating the octahedral coordination of Mn^{2+} , and (c) Cs_3MnBr_5 crystal structure with (d) the ab plane illustrating the tetrahedral coordination of Mn^{2+} .

Figure 3

Low- and high-resolution TEM images of the synthesized nanocrystals prepared using different amount of TOP solvent: (a) CsMnBr₃ (10 mL), (b) Cs₃MnBr₅ (20 mL).

Figure 4

PL spectra of CsMnBr₃ and Cs₃MnBr₅ nanocrystals with the amount of TOP solvent.

Figure 5

(a) PL spectra of the high-temperature and high-humidity testing of lead-free perovskite CsMnBr_3 (red) and metal halide Cs_3MnBr_5 (green) nanocrystals at 85 °C and 85% humidity for 24 h, and (b) XRD patterns of the CsMnBr_3 and Cs_3MnBr_5 nanocrystals before and after the durability test.