Facile synthesis and characterization of CsPbBr$_3$ and CsPb$_2$Br$_5$ powders

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Abstract. All-inorganic caesium lead-halide perovskite CsPbBr$_3$ and CsPb$_2$Br$_5$ powders have emerged as attractive optoelectronic materials owing to their stabilities and highly efficient photoluminescence (PL). Herein we report a facile chemical route to prepare highly luminescent monoclinic CsPbBr$_3$ and tetragonal CsPb$_2$Br$_5$ powders at room temperature. The CsPbBr$_3$ powders exhibit regular crystal shape and demonstrate polyhedral geometry with an average particle size of 10 μm. The CsPb$_2$Br$_5$ powders show platelet morphologies and the lateral sizes of the particles are from 5 up to 200 μm. Both CsPbBr$_3$ and CsPb$_2$Br$_5$ powders present a narrow emission line-width and PL emission of 528 and 527 nm, respectively. A direct band gap of 2.35 eV and an indirect band gap of 3.01 eV are calculated for CsPbBr$_3$ and CsPb$_2$Br$_5$ powders, respectively. In addition, the monoclinic CsPbBr$_3$ can be transformed to tetragonal CsPb$_2$Br$_5$ in the presence of water. The large-scale synthesis of CsPbBr$_3$ and CsPb$_2$Br$_5$ will be advantageous in future applications of optoelectronic devices.

Keywords. CsPbBr$_3$; CsPb$_2$Br$_5$; powders; synthesis; characterization.

1. Introduction

Due to excellent charge transport properties [1] and broad chemical tenability [2], hybrid organic–inorganic lead halide-based perovskites have been broadly studied for potential applications in photovoltaic cells [3,4], light-emitting diodes (LEDs), lasers and photodetectors [5–10]. However, hybrid organic–inorganic perovskites are very sensitive to the environment, especially to water or moisture, which hinders large-scale practical and commercial applications [11,12]. Recently, the all-inorganic perovskites have been proposed as an alternative candidate for optoelectronics because of their higher chemical stability and unique electronic properties as compared with their hybrid organic–inorganic counterparts [13–15]. The general composition of all-inorganic perovskite is CsPbX$_3$ (X = Cl, Br and I), which has triggered a surge of investigations.

CsPbBr$_3$ and CsPb$_2$Br$_5$ are a kind of all-inorganic perovskites. Both of them have emerged as attractive semiconducting materials owing to their unique optoelectronic properties. Kulbak et al. [16] prepared solar cells using CsPbBr$_3$ as a light absorber material. The solar cells showed performances comparable to those from the organic material, especially in generating high open circuit voltages. Pan et al. [17] reported that CsPbBr$_3$ quantum dots (QDs) can produce high photoluminescence (PL) quantum yield with unprecedented operational stability in ambient conditions and high pump fluences. Song et al. [18] for the first time reported QD LEDs based on all-inorganic perovskite CsPbBr$_3$, showing a promising luminescence intensity of 946 cd m$^{-2}$. Zhang et al [19] prepared LEDs using all-inorganic CsPbBr$_3$–CsPb$_2$Br$_5$ composite as the emitting layer, displaying a maximum lumiance of 3853 cd m$^{-2}$, with current density of 8.98 cd A$^{-1}$ and external quantum efficiency of 2.21%. Tang et al [20] reported that CsPb$_2$Br$_5$ microplates exhibited large optical gain and lasing emission under both one- and two-photon excitation, as well as enhanced stability.

Arising from the high performance, the synthesis and properties of CsPbBr$_3$ and CsPb$_2$Br$_5$ attract much attention. Traditionally, caesium lead-halide perovskites nanopowders have been prepared by the reaction of PbBr$_2$ with metal–organic complex in organic solvent (for example, octadecene and oleylamine) at relatively high temperature [20–22]. However, the metal–organic complex decomposition is a complex, expensive and limited-scale synthesis method. The growing interest in caesium lead-halide perovskites motivates us to develop simple and cheap alternative methods for large-scale synthesis of CsPbBr$_3$ and CsPb$_2$Br$_5$ powders.

In this article, we report a facile precipitation route for synthesis of CsPbBr$_3$ and CsPb$_2$Br$_5$ powders in aqueous solution. The process is quite simple, so that the production rate is expected to be much higher than those of other methods. Detailed crystal structural characterization reveals that CsPbBr$_3$ and CsPb$_2$Br$_5$ powders crystallize in a monoclinic and tetragonal phase, respectively. Optical measurements show that both CsPbBr$_3$ and CsPb$_2$Br$_5$ display strong PL. These powders have potential applications in optoelectronics.
2. Experimental

2.1 Preparation of CsPbBr$_3$ and CsPb$_2$Br$_5$ powders

Lead(II) acetate trihydrate (Pb(CH$_3$COO)$_2$·3H$_2$O) (Macklin Chemical, China, purity: 99.5%), hydrobromic acid (HBr) (Macklin Chemical, China, 40% w/w) and caesium bromide (CsBr) (Macklin Chemical, China, purity: 99.5%) were selected as the starting materials.

First, lead(II) acetate trihydrate was fully dissolved in hydrobromic acid at room temperature to obtain solution I. Caesium bromide was fully dissolved in a blend solution of hydrobromic acid and deionized water at room temperature to obtain solution II. Later, solution II was added slowly into solution I with successive stirring. The mole ratio of Cs$^+$/Pb$^{2+}$ in mixed solution was adjusted to 1/1, 2/1 and 1/2. The obtained products were washed by diethyl ether three times, and were dried in vacuum for 12 h.

2.2 Characterization

The X-ray diffraction (XRD) measurements of the powders were performed with an X-ray diffractometer (Bruker D8 Davinci, Germany) with Cu K$_\alpha$ radiation (40 kV, 60 mA) in the range of 2$\theta$ = 10–50$^\circ$. The scan was performed at a scan rate of 5$^\circ$/min$^{-1}$ with the step size of 0.02$^\circ$. The morphologies of the powders were examined by field emission scanning electron microscopy (SEM, Hitachi S-4800, Tokyo, Japan). The PL spectra were measured using a 473 nm solid-state laser for excitation, detected using a grating spectrometer. UV–Vis absorption spectra were collected using a Hitachi-U2001 spectrophotometer in the reflectance mode.

3. Results and discussion

The phases of powders obtained with various mole ratios of Cs$^+$/Pb$^{2+}$ in the solution are studied. Figure 1 shows the XRD pattern of sample obtained with Cs$^+$/Pb$^{2+}$ mole ratio of 1/1. It is found that the diffraction peaks of monoclinic CsPbBr$_3$ (PDF#18-0364) and tetragonal CsPb$_2$Br$_5$ (PDF#25-0211) coexist in the sample. As the Cs$^+$/Pb$^{2+}$ mole ratio rises to 2/1, the diffraction peaks of tetragonal CsPb$_2$Br$_5$ disappear completely, and only diffraction peaks of monoclinic CsPbBr$_3$ can be observed, as shown in figure 2. The as-obtained monoclinic CsPbBr$_3$ powders show an orange colour. When the Cs$^+$/Pb$^{2+}$ mole ratio decreases to 1/2, the XRD pattern (figure 3) contains the sharp diffraction peaks of tetragonal CsPb$_2$Br$_5$, indicating that well-crystallized tetragonal CsPb$_2$Br$_5$ powder is prepared. The as-obtained tetragonal CsPb$_2$Br$_5$ powder shows a white colour.

Based on the results of the XRD analysis, it can be seen that the Cs$^+$/Pb$^{2+}$ mole ratio has an effect on the phase of final product in this synthesis process. Generally speaking, the reaction that occurs for the formation of CsPbBr$_3$ by CsBr and PbBr$_2$ is

$$\text{CsBr} + \text{PbBr}_2 \rightarrow \text{CsPbBr}_3 \quad (1)$$

According to this reaction, as the Cs$^+$/Pb$^{2+}$ mole ratio is 1/1, the product should be pure CsPbBr$_3$. However, the real product is a mixture of monoclinic CsPbBr$_3$ and tetragonal CsPb$_2$Br$_5$ (figure 1). Pure CsPbBr$_3$ powder can be prepared when the Cs$^+$/Pb$^{2+}$ mole ratio is 2/1 (figure 2). Intriguingly, when the Cs/Pb mole ratio is 1/2, pure CsPb$_2$Br$_5$ can be obtained, in accordance with the reaction

$$\text{CsBr} + 2\text{PbBr}_2 \rightarrow \text{CsPb}_2\text{Br}_5 \quad (2)$$

Here, it is believed that at the conditions of this synthesis, different Cs$^+$/Pb$^{2+}$ mole ratios lead to modification of the solution environment, resulting in a change in the
Figure 3. XRD pattern of powders obtained at a Cs\(^+\)/Pb\(^{2+}\) mole ratio of 1/2. Inset is photographs of as-obtained CsPb\(_2\)Br\(_5\) powders.

thermodynamically favoured phase of the caesium lead halide. Therefore, in this work, the Cs\(^+\)/Pb\(^{2+}\) mole ratio influences the phase of final product.

It is reported that caesium lead bromide belongs to the family of trihalides compounds, in which several successive phase transitions occur between room temperature and melting temperatures. CsPbBr\(_3\) crystallizes in monoclinic polymorph at room temperature and with rising temperature it transforms to tetragonal phase. Above 130\(^\circ\)C, CsPbBr\(_3\) crystallizes in cubic polymorph with the perovskite structure [23,24]. The existing methods for CsPbBr\(_3\) nanopowders are normally at the high synthesis temperature of 150 or 170\(^\circ\)C, producing a cubic perovskite phase [25,26]. In this work, the CsPbBr\(_3\) crystallizes in the monoclinic phase, which can be attributed to the room temperature synthesis.

The morphologies of the CsPbBr\(_3\) and CsPb\(_2\)Br\(_5\) powders synthesized are shown in figure 4. Both of the CsPbBr\(_3\) and CsPb\(_2\)Br\(_5\) powders are well separated. The CsPbBr\(_3\) powders have regular crystal shape and demonstrate polyhedral geometry. The average particle size of CsPbBr\(_3\) powders are 10 \(\mu\)m (figure 4a). The CsPb\(_2\)Br\(_5\) powders show platelet morphologies and the lateral sizes of the particles are from 5 up to 200 \(\mu\)m (figure 4b).

It is well known that the crystal growth behaviour is determined by the intrinsic symmetry of its crystal structure. Therefore, the different morphologies of CsPbBr\(_3\) and CsPb\(_2\)Br\(_5\) powders in this synthesis process result from their different intrinsic symmetries of the crystal structures. The monoclinic phase of CsPbBr\(_3\) presents a perovskite structure, in which the [Pb\(_2\)Br\(_5\)]\(^{4-}\) octahedron extends to three dimensions via sharing the vertex and Cs\(^+\) ions localize in the octahedral voids, as shown in figure 5a. Figure 5b shows the crystal structure of the tetragonal CsPb\(_2\)Br\(_5\). It is found that one layer of Cs\(^+\) ion is sandwiched between two layers of [Pb\(_2\)Br\(_5\)]\(^-\). The features of the tetragonal CsPb\(_2\)Br\(_5\) crystal structure are similar to that of layered double hydroxides, whose platelet morphology has been easily obtained by the facile precipitation method [27].

In order to study the chemical stability of CsPbBr\(_3\) in water, distilled water is added to the CsPbBr\(_3\) powders. Figure 6 shows the colour changes of CsPbBr\(_3\) powders soaked in water. It can be seen that the initial orange colour changes to white colour completely in 90 s, illustrating that CsPbBr\(_3\) is very sensitive to water and CsPbBr\(_3\) transforms to a new phase in the presence of water. To further investigate the phase transformation of CsPbBr\(_3\) in water, the crystal structures of obtained white product and material obtained by drying the clear supernatant (figure 6) are analysed. As shown in figures 7 and 8, the white product is characterized as tetragonal CsPb\(_2\)Br\(_5\) (PDF#25-0211), and the matter obtained by drying the clear supernatant is confirmed as cubic CsBr (PDF# 73-0391). According to the results of XRD analysis (figures 7 and 8), it is proposed that CsPbBr\(_3\) decomposes to CsPb\(_2\)Br\(_5\) and CsBr in the presence of water, which occurs as follows:

\[ 2\text{CsPbBr}_3 \rightarrow \text{CsPb}_2\text{Br}_5 + \text{CsBr} \] (3)
Figure 5. Perovskite crystal structure of (a) CsPbBr$_3$ and (b) perovskite-related crystal structure of CsPb$_2$Br$_5$.

Figure 6. Photograph of the colour changes of CsPbBr$_3$ powders soaked in water.

Figure 7. XRD pattern of the white product shown in figure 6.

Figure 8. XRD pattern of material obtained by drying the clear supernatant shown in figure 6.

In this reaction process, water can be acted as a catalyser, as reported in the decomposition of organic–inorganic hybrid perovskite CH$_3$NH$_3$PbI$_3$ [11,28]. The optical properties of the CsPbBr$_3$ and CsPb$_2$Br$_5$ powders are studied by measuring the UV–Vis absorption and PL spectra. Figure 9a shows the UV–Vis adsorption and PL
Figure 9. Absorption (right) and PL (left) spectra of (a) CsPbBr$_3$ powders, and (b) direct band gap Tauc plot of CsPbBr$_3$ from absorption spectrum. The PL under 473 nm excitation.

Figure 10. Absorption (right) and PL (left) spectra of (a) CsPb$_2$Br$_5$ powders, and (b) indirect band gap Tauc plot of CsPb$_2$Br$_5$ from absorption spectrum. The PL under 473 nm excitation.

emission spectra of CsPbBr$_3$ powders. The absorption onset for the CsPbBr$_3$ is found to be 521 nm. The PL emission spectrum of CsPbBr$_3$ exhibits a peak at 528 nm with a narrow full-width at half-maximum (FWHM) of 16 nm, which is similar to the optical features of CsPbBr$_3$ nanocrystals [29]. The direct band gap Tauc plot of CsPbBr$_3$ from absorption spectrum gives a direct gap of 2.35 eV, as shown in figure 9b. The optical absorption and PL emission spectra of CsPb$_2$Br$_5$ powders are shown in figure 10a, from which we can see a small Stokes shift, and the highly symmetric PL peak centres at 527 nm with a narrow FWHM of 12 nm, indicating its potential application for lasing. According to the absorption spectrum, an indirect band gap of 3.01 eV is calculated (figure 10b), which is in accordance with the reported results [30].

The PL property of microsized CsPbBr$_3$ powders obtained in this work is different from that of QDs. Pan et al [17] prepared CsPbBr$_3$ QDs with average sizes of 8.2, 9.2 and 10.6 nm; the PL positions of these samples are 496, 503 and 512 nm, respectively, implying that PL peak shifts to longer wavelength when the size of QDs is increased. These results are due to the quantum confinement. The typical PL peak of the CsPbBr$_3$ QDs in their work is 512 nm. Besides, Song et al [18] reported that the typical PL peak of the CsPbBr$_3$ QDs was located at 510 nm. In this work, the microsized CsPbBr$_3$ powders present a PL emission of 528 nm. These results demonstrate that the PL emission wavelength of microsized CsPbBr$_3$ powders is longer than that of CsPbBr$_3$ QDs. However, there is no obvious difference between PL properties of microsized and nanosized CsPb$_2$Br$_5$ powders. Ruan et al [31] reported that PL emission spectrum of CsPb$_2$Br$_5$ nanowires showed a peak at 525 nm. Meanwhile, the PL emission peak position of CsPb$_2$Br$_5$ nanosheets was at 529 nm. The microsized CsPb$_2$Br$_5$ powders obtained in our work have a PL emission peak at 527 nm. It can be concluded that the PL property of microsized CsPb$_2$Br$_5$ powders is similar to that of nanosized CsPb$_2$Br$_5$ particles.

4. Conclusions

A facile and scalable method for the synthesis of highly luminescent CsPbBr$_3$ and CsPb$_2$Br$_5$ powders is reported. The Cs$^+/\text{Pb}^{2+}$ mole ratio has a significant effect on the phase
of final product in the synthesis process. Both CsPbBr$_3$ and CsPb$_2$Br$_5$ powders present a narrow emission line-width and PL emission at 528 and 527 nm, respectively. These CsPbBr$_3$ and CsPb$_2$Br$_5$ powders have potential applications in opto-electronic devices.

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