Inter-Conversion between Different Compounds of Ternary Cs-Pb-Br System

Jing Li 1,2, Huijie Zhang 1, Song Wang 3, Debing Long 1, Mingkai Li 1, Duofa Wang 1,2,4,5,* and Tianjin Zhang 1,2,4,5,*

1 Department of Materials Science and Engineering, Hubei University, Wuhan 430062, China; lijing5781@hotmail.com (J.L.); huijie928@163.com (H.Z.); debinglong@foxmail.com (D.L.); mingkaiilee@hotmail.com (M.L.)
2 Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Hubei University, Wuhan 430062, China
3 Hubei Key Laboratory of Low Dimensional Optoelectronic Materials and Devices, Hubei University of Arts and Science, Xiangyang 441053, China; wangsong1984@126.com
4 Hubei Provincial Key Laboratory of Polymers, Hubei University, Wuhan 430062, China
5 Ministry of Education Key Laboratory of Green Preparation and Application for Materials, Hubei University, Wuhan 430062, China
* Correspondence: duofawang@hotmail.com (D.W.); zhangtj@hubu.edu.cn (T.Z.);
Tel.: +86-27-8866-1729 (D.W. & T.Z.)

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Abstract: The perovskite CsPbBr$_3$ attracts great attention due to its potential in optoelectronics. However, stability remains a major obstacle to achieving its effecting application. In this work, we prepared CsPbBr$_3$ solids through a simple reaction and investigated reversible conversion between CsPbBr$_3$, Cs$_4$PbBr$_6$, and CsPb$_2$Br$_5$. We found that CsPbBr$_3$ can be respectively converted to Cs$_4$PbBr$_6$ or CsPb$_2$Br$_5$ by reacting with CsBr or PbBr$_2$. Thermodynamic analysis demonstrated that the chemical reactions above were exothermic and occurred spontaneously. Moreover, the formed Cs$_4$PbBr$_6$ could be converted to CsPbBr$_3$ reversely, and then progressively converted to Cs-deficient CsPb$_2$Br$_5$ by extraction of CsBr with water. The CsPb$_2$Br$_5$ was converted to CsPbBr$_3$ reversely under thermal annealing at 400 °C. The thermodynamic processes of these conversions between the three compounds above were clarified. Our findings regarding the conversions not only provide a new method for controlled synthesis of the ternary Cs-Pb-Br materials but also clarify the underlying mechanism for the instability of perovskites CsPbBr$_3$.

Keywords: CsPbBr$_3$; Cs$_4$PbBr$_6$; CsPb$_2$Br$_5$; perovskite; conversion

1. Introduction

All-inorganic cesium lead halide perovskite CsPbX$_3$ (X = I, Br, Cl) nanocrystals (NCs) have attracted considerable attention owing to the outstanding photophysical properties, such as high photoluminescence quantum yields, narrow emission bandwidths, and tunable band gaps that covers the full visible range [1,2]. Since the pioneering work by the Kovalenko group in 2015, considerable progress in the preparation and application of CsPbBr$_3$ NCs has been achieved within a very short time period [1]. CsPbBr$_3$ NCs with a controllable morphology and composition have been fabricated by different methods, such as hot-injection [3], solvothermal synthesis [4], room-temperature precipitation [5], and chemical vapor deposition (CVD) [6]. Moreover, a variety of photoelectronic devices—such as photovoltaics [7], lasing [8], light-emitting diodes and photodetectors [9,10]—have been prepared from CsPbBr$_3$ NC. In addition to CsPbBr$_3$ NCs, other types of materials of the ternary Cs-Pb-Br system, such as Cs$_4$PbBr$_6$ and CsPb$_2$Br$_5$, have also been reported [11,12]. The compounds
CsPbBr$_3$, Cs$_4$PbBr$_6$, and CsPb$_2$Br$_5$ differ in the stacking of PbBr$_6$ octahedra in their crystal structures. In CsPbBr$_3$, the lead halide octahedra share all corners and are electronically coupled in three directions in space. However, in the Cs$_4$PbBr$_6$ lattice the octahedra do not share any corners [11]. One lead atom and eight bromine atoms make up a hendecahedron with edge sharing in CsPb$_2$Br$_5$ [12]. It is reasonable to suspect that the existence of multiple compounds of Cs-Pb-Br system is probably relevant to the unstable luminescent property of CsPbBr$_3$, which is the main obstacle on the progress of CsPbBr$_3$. The photoluminescence quantum yield (PLQY) of colloidal CsPbBr$_3$ NCs of ~90% decreases dramatically to below ~20% when they are in the solid phase (such as in a thin film). Different mechanisms have been proposed to explain the luminescence quenching, such as loss of the high quality of the NC by aggregation, removal of the surface passivation, and chemical decomposition of the materials [11,13]. Therefore, investigation on the inter-conversion between the Cs-Pb-Br compounds above is rather important.

Very recently, it has been reported that these ternary Cs-Pb-Br compounds can be inter-converted by physical and chemical treatments. Conversion of pre-synthesized CsPbBr$_3$ NC to Cs$_4$PbBr$_6$ NCs have been reported by the extraction of PbBr$_2$ through amine- and thiol-mediation method [14,15]. Furthermore, a reverse conversion from Cs$_4$PbBr$_6$ to CsPbBr$_3$ has been reported by the Manna group through extraction of CsBr with Prussian Blue [16]. However, all the conversions above were performed on Cs-Pb-Br NCs with ligands on their surface and they were realized with mediation by a ligand. Investigations on the inter-conversion between the bare compounds of the Cs-Pb-Br system without ligand mediation are rarely reported, which is essential to reveal instability mechanism of CsPbBr$_3$.

In this work, we prepared CsPbBr$_3$ particles without ligands through a simple low temperature method and realized reversible conversions between CsPbBr$_3$ and Cs$_4$PbBr$_6$, and between CsPbBr$_3$ and CsPb$_2$Br$_5$. We combined our experimental observations with calculations of the total energy of the three Cs-Pb-Br compounds, we found that conversions of CsPbBr$_3$ to Cs$_4$PbBr$_6$ and to CsPb$_2$Br$_5$ could take place spontaneously. However, the reverse conversions required external intervention.

2. Materials and Methods

2.1. Materials

Lead(II) bromide (PbBr$_2$, Aladdin, 99.999%), cesium bromide (CsBr, Aladdin, 99.999%), hydrobromic acid (HBr, ≥40.0%), and N,N-dimethylformamide (DMF, Aladdin, 99.9%), were used without any further purification.

2.2. Synthesis of CsPbBr$_3$

The synthesis of CsPbBr$_3$ was performed via a simple reaction and crystallization method. Briefly, 0.5 mmol of PbBr$_2$ and 0.5 mmol of CsBr were dissolved in 10 mL of DMF and stirred until completely dissolved. The mixture was then placed in an oven at 40 °C to evaporate the solvent and induce the reaction to produce CsPbBr$_3$ solids.

2.3. Experiments on the Inter-Conversion between the Compounds

2.3.1. Forward Conversion from CsPbBr$_3$ to Cs$_4$PbBr$_6$ or CsPb$_2$Br$_5$

Cesium bromide (CsBr, 3 mmol) was first dissolved in hydrobromic acid (HBr, 2 mL). Pre-synthesized CsPbBr$_3$ (1 mmol) was added to the solution and stirred to react with CsBr and produce Cs$_4$PbBr$_6$, which precipitated at the bottom of the mixture. The precipitate was collected by evaporating the HBr solvent. For the conversion to CsPb$_2$Br$_5$, lead(II) bromide (PbBr$_2$, 1 mmol) was first dissolved in hydrobromic acid (HBr, 2 mL). Then the CsPbBr$_3$ solid (1 mmol) was added to the solution with stirring to react with PbBr$_2$. The CsPb$_2$Br$_5$ was produced and precipitated at the bottom of the mixture. The precipitate was collected by evaporating the HBr solvent.
2.3.2. Reverse Conversion from Cs$_4$PbBr$_6$ or CsPb$_2$Br$_5$ to CsPbBr$_3$

A 0.25 mmol portion of Cs$_4$PbBr$_6$ was added to de-ionized water (1 mL) and stirred, to trigger the reverse conversion from Cs$_4$PbBr$_6$ to CsPbBr$_3$. The conversion of CsPb$_2$Br$_5$ to CsPbBr$_3$ was conducted by annealing the CsPb$_2$Br$_5$ solids for 4 h at 400 °C in air.

2.4. Materials Characterization

Crystal structures were measured with an X-ray diffractometer (Bruker D8 Advance, Karlsruhe, Baden-Wurttemberg, Germany) with Cu-Ka radiation ($\lambda = 1.5406$ Å). Scanning electron microscope (SEM) and energy dispersive spectrum (EDS) measurements were performed on a JSM7100F, Tokyo, Honshu, Japan. A transmission electron microscope (TEM) (FEI; Tecnai-G20 and 200 kV, Hillsboro, OR, USA) was used to characterize the microstructure of the CsPb$_3$, Cs$_4$PbBr$_6$ and CsPb$_2$Br$_5$. Absorption spectra were measured on a UV-Visible-NIR spectrophotometer (SHIMADZU UV-3600, Kyoto, Honshu, Japan).

2.5. First-Principle Calculations

First-principle calculations were performed on the basis of density functional theory (DFT) as implemented in the QUANTUM ESPRESSO (QE) code. The exchange and correlation terms were described using the general gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE). The energy cutoff for the plane wave basis set was 600 eV. The accuracy of the self-consistent field (SCF) energy convergence and the convergence accuracy of the internal stress of the crystal were less than $1.4 \times 10^{-5}$ eV/atom and 0.05 Gpa, respectively. For the different alloy configurations, Monkhorst-Pack grids were determined automatically for the Brillouin zone integration and the KPPRA parameter was set to be 1000.

3. Results and Discussion

3.1. Synthesis of CsPbBr$_3$ and Forward Conversion to Cs$_4$PbBr$_6$ and CsPb$_2$Br$_5$.

Synthesis of CsPbBr$_3$ (PDF#18-0364) was performed via a simple reaction and crystallization method without the use of any ligands. Full details are described in the experimental section. Characterization results of the prepared solids by XRD and absorption spectroscopy, shown in Figure 1a,b, demonstrated that the product was pure monoclinic CsPbBr$_3$.

The as-synthesized CsPbBr$_3$ solids were used to perform the forward conversion from CsPbBr$_3$ to Cs$_4$PbBr$_6$ and CsPb$_2$Br$_5$. First, CsBr was dissolved in HBr, and a certain amount of the CsPbBr$_3$ solid synthesized above (yellow) was added into the solution (CsPbBr$_3$/CsBr = 1:3, mole ratio) with stirring. This approach ensured that only H was introduced into the reaction system, containing Cs, Pb, and Br, which simplified the analysis on the reaction. After stirring for several hours, a white precipitate formed, which was revealed to be rhombohedral Cs$_4$PbBr$_6$ by XRD, as shown in Figure 1c. To reveal whether CsPbBr$_3$ remnants exist in the product since both CsPbBr$_3$ and Cs$_4$PbBr$_6$ exhibit diffraction peaks near 27°, the absorption spectrum of Cs$_4$PbBr$_6$ product was measured and is shown in Figure 1d. A typical absorption peak at 315 nm was observed, which is characteristic of Cs$_4$PbBr$_6$, and no absorption peaks corresponding to CsPbBr$_3$ appear [17]. This result further confirmed the conversion from CsPbBr$_3$ to Cs$_4$PbBr$_6$. As far as the additional small diffraction peak near 29° denoted by purple dot in Figure 1c is concerned, it corresponds to CsBr. Because the ratio of the reactants CsPbBr$_3$/CsBr was 1:3 and the only product was Cs$_4$PbBr$_6$, Equation (1) is proposed to describe the chemical reaction of the conversion. Except for operating as the solvent, the HBr also supplies abundance of Br$^+$ and promotes the chemical reaction according to Equation (1).

$$\text{CsPbBr}_3 + 3\text{CsBr} = \text{Cs}_4\text{PbBr}_6$$  \hspace{1cm} (1)
The conversion from CsPbBr$_3$ to CsPb$_2$Br$_5$ was realized by a similar reaction. First, PbBr$_2$ was dissolved in HBr and CsPbBr$_3$ solid was added into the solution (CsPbBr$_3$/PbBr$_2$ = 1:1, mole ratio). After several hours, white solids precipitated at the bottom of the mixture. XRD characterization, as shown in Figure 1e, of the precipitate revealed that it was pure tetragonal CsPb$_2$Br$_5$, indicating that the conversion from CsPbBr$_3$ to CsPb$_2$Br$_5$ occurred. To confirm the conversion, the absorption spectra of the reactant and product were measured. As shown in Figure 1f, the absorption edge moved to 380 nm, indicating that CsPbBr$_3$ was converted into CsPb$_2$Br$_5$. The conversion was believed to occur through Equation (2), as shown below, based on the fact that the ratio of the reactants CsPbBr$_3$/PbBr$_2$ was 1:1 and the only product formed was CsPb$_2$Br$_5$.

$$\text{CsPbBr}_3 + \text{PbBr}_2 = \text{CsPb}_2\text{Br}_5$$ (2)

![Figure 1](image-url)

**Figure 1.** The XRD pattern of (a) CsPbBr$_3$, (c) Cs$_4$PbBr$_6$ and (e) CsPb$_2$Br$_5$. The absorption spectra of (b) CsPbBr$_3$, (d) Cs$_4$PbBr$_6$, and (f) CsPb$_2$Br$_5$.

The morphology of each material was examined by scanning electron microscope (SEM) imaging, as shown in Figure S1. Energy dispersive spectroscopy (EDS) results, also shown in Figure S1, indicated that the molar ratios of Cs/Pb/Br were 1.18/1/2.89, 1/1.87/5.57, and 4.18/1/6.36 respectively, which agreed well with the stoichiometries of CsPbBr$_3$, CsPb$_2$Br$_5$, and Cs$_4$PbBr$_6$. The microstructure of each Cs-Pb-Br ternary compound was characterized by high resolution TEM (HRTEM), as shown in Figure 2. Well-resolved lattice fringes were observed in the HRTEM images. In Figure 2b, the separation between
the fringes was 0.588 nm, which corresponded to the (001) plane of CsPbBr$_3$. In the HRTEM images of CsPb$_2$Br$_5$ and Cs$_4$PbBr$_6$, the (110) and (220) planes were clearly observed, with lattice separations of 0.609 and 0.451 nm, respectively. These EDS and HRTEM results further confirmed that the conversions had occurred.

In the conversions above, we did not use high temperature, high pressure or a catalyst to trigger the reactions. Hence, the Equations (1) and (2) are thermodynamically controlled process and the driving force, described by the free energy should be negative. Therefore, we calculated the total energy ($E_t$) of the Equations (1) and (2) by first principles. The changes of the total energy ($\Delta E_t$) for Equations (1) and (2) were $-9508.07$ eV and $-15019.13$ eV, respectively, indicating that the chemical reactions were exothermic and could occur spontaneously. The total energy of each materials is shown in Table S1 in the supporting information. These results explain why this simple method can successfully realize the conversion of CsPbBr$_3$ into Cs$_4$PbBr$_6$ or CsPb$_2$Br$_5$.

### 3.2. Reverse Conversion by Water Extraction and Thermal Annealing

For the reverse conversion from Cs$_4$PbBr$_6$ to CsPbBr$_3$, we used the water extraction method proposed by the Sun group [18]. By mixing a Cs$_4$PbBr$_6$ quantum dot dispersion in nonpolar hexane with water, Sun et al. found that CsBr could be extracted from Cs$_4$PbBr$_6$ owing to the high solubility of CsBr in water. This effect led to a conversion from Cs$_4$PbBr$_6$ to CsPbBr$_3$.  

Figure 2. (a,c,e) TEM images; and (b,d,f) high-resolution lattice resolved TEM images of a representative CsPbBr$_3$, CsPb$_2$Br$_5$, and Cs$_4$PbBr$_6$, respectively.
Here, we found that water could also extract CsBr from Cs$_4$PbBr$_6$ solids without ligands on their surface. However, the reaction we observed was much more vigorous and quick. These differences between our observations and those of Sun et al. could be attributed to the absence of protective ligands on the surface of our NCs, unlike the Cs$_4$PbBr$_6$ quantum dot dispersion reported by Sun [18]. When the Cs$_4$PbBr$_6$ solids were added into deionized water, the color of the precipitate changed to yellow immediately, and returned to white again over a longer time, suggesting that chemical reactions occurred in two stages. The precipitate at different stages was removed from the deionized water and the composition was measured by XRD.

As shown in Figure 3a, most of the Cs$_4$PbBr$_6$ transformed to CsPbBr$_3$ within 1 min. However, CsPbBr$_3$ was not the final product. The conversion into CsPb$_2$Br$_5$ proceeded within 5 min, and the major product was CsPb$_2$Br$_5$ after 1 h. Therefore, we suggest that the water not only extracted CsBr from Cs$_4$PbBr$_6$, but also extracted CsBr from CsPbBr$_3$ to produce CsPb$_2$Br$_5$. The composition of the solution was also investigated to clarify the nature of the chemical transformation. To confirm the water extraction mechanism for the conversions, we evaporated the water and performed XRD measurements on the solid obtained, which was determined to be CsBr, as shown in the supporting information Figure S2. Therefore, we propose the following Equations for the chemical reactions occurring at each stage of the transformation as:

$$\text{Cs}_4\text{PbBr}_6 = \text{CsPbBr}_3 + 3\text{CsBr}, \quad (3)$$

$$2\text{CsPbBr}_3 = \text{CsPb}_2\text{Br}_5 + \text{CsBr} \quad (4)$$

Figure 3b shows the absorption spectrum measured from the precipitate samples removed from deionized water after different reaction times. A strong characteristic absorption edge at 560 nm appeared after 1 min and its intensity decreased at longer reaction times. This result indicates that the CsPbBr$_3$ was produced within 1 min and converted to CsPb$_2$Br$_5$ over longer reaction times. These findings are consistent with the XRD results.

![Figure 3](image.png)

**Figure 3.** (a) PXRD pattern of Cs$_4$PbBr$_6$ solids after water treatment for different time, the red diamonds represent CsPbBr$_3$, the black hearts represents CsPb$_2$Br$_5$, the black dots represents Cs$_4$PbBr$_6$; (b) Absorption spectra of PXRD pattern of Cs$_4$PbBr$_6$ solids after water treatment for different times.

To confirm the two-step transformation model suggested above, we added pure CsPbBr$_3$ into deionized water and investigated the conversion. We found that the transformation in Equation (4) occurred and a white precipitate was formed quickly. As shown in the XRD pattern obtained from the precipitate in Figure 4a, the diffraction peaks related to CsPbBr$_3$ became weak and strong diffraction peaks corresponding to CsPb$_2$Br$_5$ were observed after 1 min. Moreover, the intensity of CsPb$_2$Br$_5$ gradually increased as the reaction progressed. The absorption spectra in Figure 4b, show that the absorption peak at 560 nm from CsPbBr$_3$ became progressively weaker. We note that the absorption
CsPbBr₃ could be converted to CsPb₂Br₅ through extraction of CsBr by water. The conversion induced by water extraction is undoubtedly one of the reasons leading to the unstable luminescent property of CsPbBr₃. The water vapor in the air can extract CsBr from CsPbBr₃ and trigger the conversion into CsPb₂Br₅, which subsequently results in the degradation of luminescence.

The decomposition is depicted by the Equation:

\[
2\text{CsPbBr}_3 \rightarrow \text{CsPb}_2\text{Br}_5 + \text{PbBr}_2
\]

The absorption spectra in Figure 5b show that the absorption peak relevant to CsPbBr₃ was considerably enhanced, indicating the generation of CsPbBr₃, which is consistent with the XRD results shown in Figure 5a. As far as the mechanism of the Equation (5) is concerned, it is ascribed to the decomposition of CsPb₂Br₅ energetically driven by high temperature annealing.

In conclusion, we examined a reversible conversion between CsPbBr₃, Cs₄PbBr₆, and CsPb₂Br₅. The water vapor in the air can extract CsBr from CsPbBr₃ and trigger the conversion into CsPb₂Br₅, which subsequently results in the degradation of luminescence.

We realized a conversion from CsPb₂Br₅ to CsPbBr₃, using a previously reported annealing method [19]. We annealed the CsPb₂Br₅ solids at 400 °C in air for 4 h and monitored the associated XRD and absorption properties. Figure 5a shows XRD data of the CsPb₂Br₅ before and after annealing. The corresponding diffraction peaks before annealing were indexed to CsPb₂Br₅. After annealing, the main product corresponded to CsPbBr₃ and PbBr₂, and a small amount of CsPb₂Br₅ remained. The decomposition is depicted by the Equation:

\[
\text{CsPb}_2\text{Br}_5 \rightarrow \text{CsPbBr}_3 + \text{PbBr}_2
\]

Figure 4. (a) XRD patterns and (b) absorption spectra of CsPbBr₃ solids after water treatment for different times. Red diamonds represent CsPbBr₃ and black hearts denote the diffraction peaks of CsPb₂Br₅.

Figure 5. (a) XRD pattern, and (b) absorption spectra of CsPb₃Br₅ particles after annealing at 400 °C temperature. In the XRD pattern, the red diamonds denotes the diffraction peak of CsPbBr₃, the black dots denotes the diffraction peak of PbBr₂ and black hearts denote the diffraction peaks of CsPb₂Br₅.
4. Conclusions

In conclusion, we examined a reversible conversion between CsPbBr$_3$, Cs$_4$PbBr$_6$, and CsPb$_2$Br$_5$. First, CsPbBr$_3$ solids were synthesized through a simple reaction of CsBr and PbBr$_2$ in HBr. Addition of the prepared CsPbBr$_3$ solids into the CsBr/PbBr$_2$ solution in HBr resulted in its conversion into Cs$_4$PbBr$_6$ and CsPb$_2$Br$_5$, through Equations (1) and (2), respectively. Thermodynamic analysis revealed that the transformations above were exothermic and occurred spontaneously. Moreover, we found that when added into the water Cs$_4$PbBr$_6$ converted to CsPbBr$_3$ first, and then to Cs-deficient CsPb$_2$Br$_5$. These results are attributed to the ionic nature of the Cs-Pb-Br system and the high solubility of CsBr in water, which led to extraction of CsBr by water. The CsPb$_2$Br$_5$ was converted to CsPbBr$_3$ through thermal annealing at 400 °C. Our results on the inter-conversion of the Cs-Pb-Br compounds sheds a light on understanding the mechanism and developing new solutions for the instability problem of the Cs-Pb-Br compounds. Moreover, it supplies important information on the controllable preparation of the Cs-Pb-Br materials.

Supplementary Materials: The following are available online at http://www.mdpi.com/1996-1944/11/5/717/s1, Figure S1: Scanning electron microscope (SEM) and Energy dispersive X-spectroscopy (EDS); Figure S2: The XRD pattern of CsBr (PDF#73-0391) obtained from the solvent of water by evaporation; Table S1: The total energy of each materials is calculated based on the optimized structure using DFT.

Author Contributions: J.L., H.Z., and S.W. performed the experiments; D.L. and M.L. performed the calculation; D.W. and T.Z. design this study and analyzed the data; all authors read and approved the final manuscript.

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