

Supporting information

Title: The Scaling of Ligand Concentration and Soret Effect Induced Phase Transition in CsPbBr₃ Perovskite Quantum Dots

*Jiagen Li¹, Menglei Hu², Zhaojin Wang², Yihua Lu¹, Kai Wang^{*2}, Xi Zhu^{*1}*

1. Shenzhen Institute of Artificial Intelligence and Robotics for Society (AIRS), The Chinese University of Hong Kong, Shenzhen, Guangdong, P.R. China. 518172
2. Department of Electrical and Electronic Engineering, Southern University of Science and Technology, Shenzhen, Guangdong, P.R. China 518055

Email: wangk@sustech.edu.cn, zhuxi@cuhk.edu.cn

Contents

S1. Experimental section

S2. Characterization of CsPbBr₃ and Cs₄PbBr₆ nanocrystal

S1. Experimental section

Materials and chemicals

Lead bromide (PbBr₂, Aladdin, 99%), cesium bromide (CsBr, Aladdin, 99%), oleic acid (OA, Aladdin, AR), oleylamine (OAm, Aladdin, 90%), dimethylformamide (DMF, Aladdin, ≥99.9%), P-xylene (C₈H₁₀, Aladdin, 98%) and ethyl acetate (C₂H₈O₂, Aladdin, 99%) were used as received without further purification.

Synthesis of CsPbBr₃ Nanocrystals

The synthesis process was carried out at room temperature. 0.4 mmol of PbBr₂ and 0.4 mmol CsBr were dissolved in 10 ml of DMF. Various amount of OA and OLA were added to achieve different ligand/Pb molar ratio (C_{lig}). After completely stirring, 0.2 ml of precursor was rapidly injected into 2 ml of P-xylene solution with continuing stirring. Green emission can be observed under ultraviolet light which indicated that CsPbBr₃ had been successfully formed.

Temperature gradient generation

The temperature gradient with length in solution was generated by a refrigeration module integrated under the reaction container. The refrigeration system was made up with a high power (100W) semiconductor cooling chip and two cooling fans. With continuous refrigerating, the temperature at bottom of reaction container kept at 255K. Around 25K temperature difference from room temperature (280K) was generated in 1mm thick solution.

S2. Characterization of CsPbBr₃ and Cs₄PbBr₆ nanocrystal

Table S1. Transition temperature, phase system, space group of CsPbBr₃ and Cs₄PbBr₆ nanocrystal.

Sample	Phase system	T (K)	Space Group
	Cubic	404	PM3M
CsPbBr ₃	Tetragonal	363	P4/MBM
	Orthorhombic		PMBN
Cs ₄ PbBr ₆	Hexagonal		R-3C

XRD: X-ray diffraction (XRD) patterns were recorded with film diffractometer (Rigaku SmartLab SE Multipurpose X-ray diffraction system) with Cu K- α wavelength of 1.54 Å.

TEM: High-resolution TEM (HR-TEM) was performed by TECNAI F30.

In-situ PL characterization and analysis: PL signal was collected through optical fiber to spectrometer (Ocean Optics USB 2000+) under 365nm UV LED excitation. A 400nm long-pass filter was applied to prevent high power excitation light. A customized high-throughput spectrum analyzer is used to extract the demand optical information from spectrum files generated by spectrometer software, shown in Figure S2(a). Center wavelength and intensity of peaks was firstly identification. Then multi-peak Lorentz fitting is applied based on SciPy¹. The emission wavelength and FWHM (Full width at half maximum) of the product are calculated from a Lorentz curve with maximum peak value. Additionally, bandgap of CsPbBr₃ QDs mapping from PL information was correlated by considering the size-dependent Stokes-shift, data from Kuno et al².

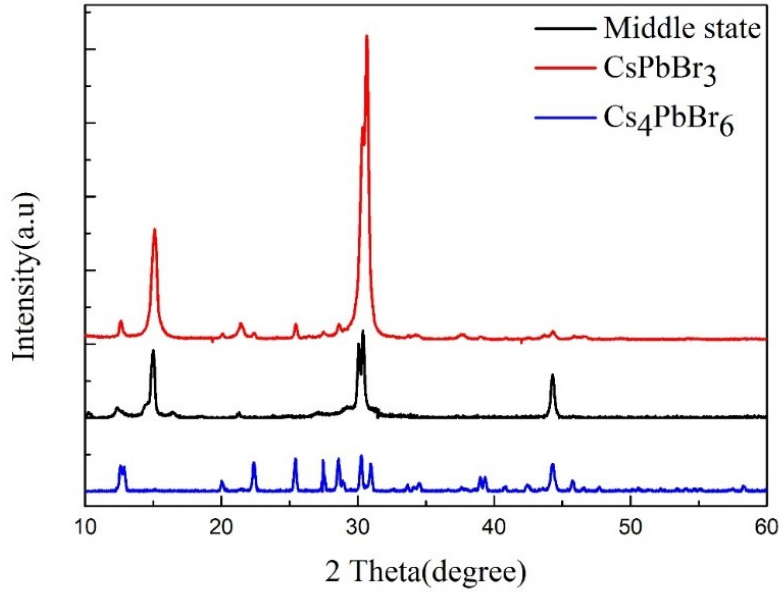


Figure S1. XRD pattern of the CsPbBr₃, Cs₄PbBr₆ and middle state.

Time-resolved PL characterization:

Table S2. Parameters of fitted Time-resolved PL of middle state and CsPbBr₃.

Sample	A ₁ (Counts)	A ₂ (Counts)	A ₃ (Counts)	τ ₁ (ns)	τ ₂ (ns)	τ ₃ (ns)	τ _a (ns)
Middle state	2.69(0%)	1111.2(0.23%)	478950(99.77%)	5.85	0.84	0.28	0.28
CsPbBr ₃	244.06(1.48%)	4334.10(26.42%)	11825(72.08%)	69.07	9.0	2.69	18.24

Time-resolved PL for our two samples is performed to discuss the lifetime of excitons. As Figure S6 showed, it is easy to distinguish that the instrument response function (IRF) has much larger dynamics than the decays of two samples. The decay curves show totally different trends that intensity decreasing speed of CsPbBr₃ is much slower than the middle state sample, which indicated they have different optical properties. To analyze the numerical details, PL decay curves were convoluted using multiple

exponential functions. After comparing the chi-square with 1, we find that curves were best fitted by tri-exponential function and their parameters were listed in Table 3, where

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + A_3 \exp(-t/\tau_3) \quad \text{Eq S1}$$

After estimate the PL decay for CsPbBr₃ we get three components of 69.07 ns(1.48%), 9.0 ns (26.42%) and 2.69 ns(72.08%), also presented in Table S3; the former originates from the power dependent process in the perovskite active layer and the latter is from free carrier recombination in the radiative channel and the last one is from auger effect.^{3,4} While the PL decay for CsPbBr₃/Cs₄PbBr₆ hybrid structure have three components 5.85 ns(0%), 0.8384ns (0.23%) and 0.27901ns(99.77%). The average lifetime was calculated, the weight mean of each sample were taken as following equation

$$\tau_{avg} = (A_1\tau_1 + A_2\tau_2 + A_3\tau_3)/(A_1 + A_2 + A_3) \quad \text{Eq S2}$$

So, the average lifetime of CsPbBr₃ (18.24 ns) is much larger than the middle state (0.28 ns), which indicate the emission ability of Cs₄PbBr₆ is more possible to be induced by the hybrid structure induced defects, which agree with recent report.⁵

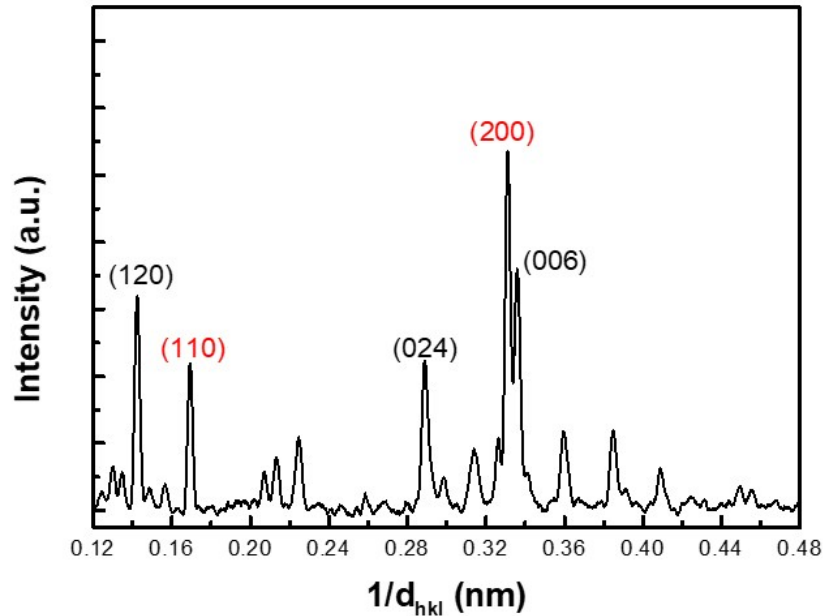


Figure S2. The XRD pattern of Cs₄Pb(Br₂I₄) hybrid with CsPb(Br₁I₂) nanocrystals. (110), (200) crystal plane (marked in red) of CsPb(Br₁I₂) and (120), (024), (006) plane (marked in black) which belong to

Cs₄Pb(Br₂I₄) nanocrystals were observed to prove the hybrid of two phases.

Supporting References

1. K. Yamada, S. Funabiki, H. Horimoto, T. Matsui, T. Okuda and S. Ichiba, *Chem. Lett.*, 1991, **20**, 801.
2. M. C. Brennan, J. E. Herr, T. S. Nguyen-Beck, J. Zinna, S. Draguta, S. Rouvimov, J. Parkhill and M. Kuno, *Journal of the American Chemical Society*, 2017, **139**, 12201-12208.
3. O. Gunawan, T. K. Todorov and D. B. Mitzi, *Applied Physics Letters*, 2010, **97**, 233506.
4. Q. Chen, H. Zhou, T.-B. Song, S. Luo, Z. Hong, H.-S. Duan, L. Dou, Y. Liu and Y. Yang, *Nano letters*, 2014, **14**, 4158-4163.
5. Q. A. Akkerman, S. Park, E. Radicchi, F. Nunzi, E. Mosconi, F. De Angelis, R. Brescia, P. Rastogi, M. Prato and L. Manna, *Nano letters*, 2017, **17**, 1924-1930.