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Chem. Mater., **Just Accepted Manuscript** • DOI: 10.1021/acs.chemmater.7b02415 • Publication Date (Web): 01 Aug 2017

Downloaded from <http://pubs.acs.org> on August 6, 2017

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Inside Perovskites: Quantum Luminescence from Bulk Cs₄PbBr₆ Single Crystals

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ABSTRACT: Zero-dimensional perovskite-related structures (oD-PRS) are a new frontier of perovskite-based materials. oD-PRS, commonly synthesized in powder form, manifest distinctive optical properties such as strong photoluminescence (PL), narrow emission linewidth, and high exciton binding energy. These properties make oD-PRS compelling for several types of optoelectronic applications, including phosphor screens and electroluminescent devices. However, it would not be possible to rationally design the chemistry and structure of these materials, without revealing the origins of their optical behaviour, which is contradictory to the well-studied APbX₃ perovskites. In this work, we synthesize single crystals of Cs₄PbBr₆ oD-PRS, and investigated the origins of their unique optical and electronic properties. The crystals exhibit a PL quantum yield higher than 40%, the highest reported for perovskite-based single crystals. Time-resolved and temperature dependent PL studies, supported by DFT calculations, and structural analysis, elucidate an emissive behaviour reminiscent of a quantum confined structure rather than a typical bulk perovskite material.

The emergence of metal halide perovskites have upended the conventional wisdom on solution-processed semiconductors, giving rise to low-temperature fabricated photovoltaics and optoelectronics with record photo-conversion efficiencies.¹⁻⁷ While ABX₃-type perovskites have been virtually the sole recipient of research efforts, recent discoveries point towards other, less-known members of the perovskite family.⁸⁻¹⁵ These materials exhibit remarkable optical properties, with a potential to be just as transformative as their more studied ABX₃ relatives. In particular, with advancements in materials processing, Cs₄PbBr₆ of so-called zero-dimensional perovskite-related semiconductors (oD-PRS) family was obtained, exhibiting appealing optoelectronic properties (strong and narrow photoluminescence) that are distinct from the ABX₃ class of perovskite.¹⁶⁻¹⁹ These new properties place Cs₄PbBr₆ in a promising position for applications like color converters

for light emitting diodes, electroluminescence devices, lasers, and photodetectors.²⁰⁻²⁶

From the classification point of view, oD-PRS's are a part of the perovskite family of compounds that possess a general formula of A_nBX_{2+n}. The value of *n* determines the perovskite's dimensionality in accordance to the connectivity of BX₆⁴⁻ octahedra: *n*=1 tri-dimensional (3D network of corner-shared octahedra), *n*=2 bi-dimensional (2D, octahedra planes), *n*=3 mono-dimensional (1D, octahedra chains), and *n*=4 zero-dimensional (oD, octahedra are not connected or isolated). Cs₄PbBr₆ oD-PRS is thus comprised of isolated PbBr₆⁴⁻ octahedra interspersed with Cs⁺ cations.^{9, 27}

However, besides the compelling properties, the origin of the photophysical behavior of Cs₄PbBr₆ still remains to be ascertained; particularly, the origin of the photoluminescence (PL). Moreover, the high PL quantum yield

(PLQY) in solid form represents one of the challenging aspects that contradicts the conventional expectation from typical perovskite materials. Only by unraveling these origins will it be possible to rationally design the chemistry and structure of the oD-PRS, in order to program their color, quantum yield, and exciton association (and dissociation).

We thus synthesized Cs_4PbBr_6 single crystals (to probe the materials behavior unencumbered by morphological defects) with the motivation to resolve the current bottleneck in the photophysical behavior and origins hindering the development and exploration of oD-PRS. The Cs_4PbBr_6 crystals display a bright green emission centered at 524 nm, an exciton binding energy of 159 ± 18 meV and a PLQY higher than 40%. Finally, from an in-depth study of time-resolved and temperature dependent PL combined with DFT calculations and structural analysis, we correlate the origin of the PL to the presence of intrinsic defects, such as from bromide vacancies, which endow oD-PRSs their unique quantum behaviour.

3D metal-halide perovskites recently showed retrograde solubility to readily form single crystals.²⁸⁻³⁰ This technique was also exploited to synthesize Cs_4PbBr_6 oD-PRS powder.¹⁶⁻¹⁹ However, one of the drawbacks of this technique is the formation of Cs_4PbBr_6 - CsPbBr_3 mixture phases during the crystallization process.¹⁶⁻¹⁹ To eliminate the CsPbBr_3 phase, which presents poor luminescent properties, several washing steps are required. On the other hand, we found that pure Cs_4PbBr_6 single crystals can be easily obtained through the well-established antisolvent vapor-assisted crystallization³¹⁻³³ (AVC) (Figure 1a). To obtain the crystals, 1 ml of precursor solution (0.25M lead bromide (PbBr_2), and 0.25M cesium bromide (CsBr) in dimethyl sulfoxide (DMSO)), is placed into the small crystallization flask, inserted in a closed container with 4 ml of diethyl-ether (DE) which plays the role of antisolvent. The low boiling point and high vapor pressure of DE enable its diffusion into the crystallization flask at room temperature, without any additional heating. After 48 hours, an immiscible interface between DE and DMSO is formed in the crystallization flask, resulting in the growth of several small crystals. The crystals are collected and washed with IPA/DMSO (3:1 v:v) mixed solvent (to remove the leftover solution) then dried and stored in a nitrogen atmosphere. The size of the crystals varies according to the crystallization time (i.e. more time spent for crystallization results in larger crystals): here, we collected 500- μm crystals after 48 hours of crystallization. The crystals exhibit a pale green color under ambient light, but when exposed to 365 nm UV irradiation, they luminesce bright green light (Figure 1b). Scanning Electron Microscopy (SEM) images confirmed the high quality of the crystals with smooth surfaces and well-defined rhomboid shape (Figure 1c).

To investigate the crystalline structure of Cs_4PbBr_6 and the quality of the crystals, we performed single crystal X-Ray Diffraction (SC-XRD). SC-XRD data confirmed that Cs_4PbBr_6 crystallizes in the trigonal space group $R\bar{3}c$ symmetry (Figure 1d and Supporting Information for details). The unit cell dimensions are $a=b=13.722$ Å, and $c=17.299$ Å

(more details can be found in the Supplementary Information, SI). The structure of Cs_4PbBr_6 consists of isolated octahedral PbBr_6^{4-} ions interspersed with Cs^+ cations. To validate the purity of our crystals, we compared the calculated XRD spectrum of the crystals with the experimental powder XRD spectrum of ground oD-PRS powder XRD spectrum (Figure 1e), and confirmed the single and pure phase of the crystals we grew.

To explore the optical properties of the Cs_4PbBr_6 single crystals, we collected the absorption and PL spectra (Figure 2a).^{34,35} The absorption spectrum resembles the spectrum of the oD-PRS powder (Figure S1), with an extrapolated absorption edge at 538 nm (2.30 eV).

The PL profile of Cs_4PbBr_6 exhibits a standard Gaussian peak centered at 524 nm with a FWHM of 24 nm. The PL peak partially overlaps with the absorption edge with a small Stokes shift of ~ 28 meV. The PLQY values of Cs_4PbBr_6 single crystals were measured with an integrating sphere under an excitation wavelength of 420 nm (see Figure S2). PLQY values between 40-42% were obtained from different crystals of differed sizes. To the best of our knowledge, these PLQY values are the highest reported to date for single crystals of halide perovskites.³⁶

To further decipher the PL properties of Cs_4PbBr_6 single crystals, we performed time-resolved PL experiments using

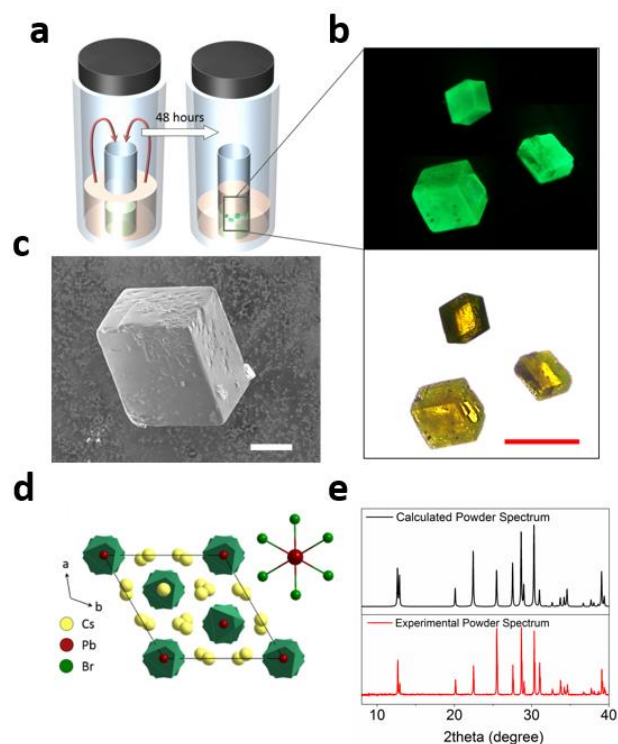


Figure 1. a) Schematic representation of the Cs_4PbBr_6 single crystal synthesis by AVC method. b) Fluorescent (top) and optical microscope picture of the single crystals (bottom). Red scale bar: 500 μm . c) SEM image of the single crystal. White scale bar: 50 μm . d) Crystal structure of Cs_4PbBr_6 obtained from SC-XRD. Green octahedral represent the isolated PbBr_6 characteristic of oD-PRS. e) XRD patterns of ground Cs_4PbBr_6 (red) and calculated single crystal of Cs_4PbBr_6 (black).

a Streak Camera with picosecond time resolution (Figure S3). According to the bi-exponential fitting of our data, we found that the average lifetime for the Cs₄PbBr₆ single crystal is 8.18 ns, which is in agreement with previous studies on oD-PRS powders.^{16, 17} This PL lifetime is closer to the lifetime of perovskite-quantum dots (QD) than usual perovskite single crystals.³⁷

To unravel the nature of the optical properties bared by our crystals, we combined density functional theory (DFT) and many-body calculations (Figure 2b). Based on the DFT electronic wavefunctions of the ground state, the optically allowed transitions were calculated by both the random phase approximation (RPA) and the Bethe-Salpeter equation (BSE). The resulting high-energy absorption bands agree well with previous experimental absorption spectra,³⁸ which is due to Pb²⁺(6s)Br⁻(4p)→Pb²⁺(6p) interband transitions (see Figure S4). As compared to the RPA method, the excitonic band centered at 380 nm can be well reproduced by the BSE method. Moreover, the deduced band gap for Cs₄PbBr₆ appears to be 3.88 eV, which greatly differs from our experimental evidence. The apparent mismatch between the theoretical and experimental evidences motivated us to investigate in further depth the origin of the optical properties of Cs₄PbBr₆ single crystals.

Thus, to shed light on the mechanism behind the high PLQY, we performed temperature dependent steady-state and time-resolved PL measurements together with structural analysis by combining temperature dependent XRD and Electron Diffraction (ED) analyses (Figure 3). The PL spectra of Cs₄PbBr₆ single crystals were collected between 80 K and 360 K. As shown in Figure 2c, the PL intensity and position of Cs₄PbBr₆ single crystals change with temperature. To gain insight into the origin of the PL we investigate the exciton binding energy, by plotting the integrated PL emission intensity with respect to 1/T (see Figure 4b). The exciton binding energy can be estimated by fitting the experimental data to the following equation:^{17, 39}

$$I(T) = \frac{I_0}{1 + Ae^{-E_b/k_b T}} \quad (1)$$

where I_0 is the estimated integrated PL intensity at 0 K, E_b is the exciton binding energy, and k_b is the Boltzmann constant. This fitting gives an exciton binding energy of 159 ± 18 meV. This value is higher than that in 3D organo-metal halide perovskites,^{39, 40} but comparable to previous findings for oD-PRS powders,^{16, 17} which suggest a different origin of the PL respect to 3D bulk perovskites. We also observed a thermal broadening of the PL FWHM, which has been attributed in 3D perovskites to exciton-phonon coupling,³⁹ and a blue shift of the emission with increasing temperature, which has been attributed to the emission from higher-energy states that are populated by electrons through the interaction with phonons.^{17, 43-44}

Subsequently, we measured the PL lifetime of the Cs₄PbBr₆ single crystals as a function of temperature (Figure S5). In hybrid perovskites, the PL lifetime increases with decreasing temperature, due to exciton thermal quenching.⁴⁵ However, Cs₄PbBr₆ single crystals show the opposite behavior, i.e. the PL lifetime decreases at lower temperature, a feature independent of excitation power densities (see Figure 4e). Such a behavior was already

observed in CdSe colloidal quantum dots.^{46, 47} This trend can be explained by considering the almost negligible electron/phonon interaction at low temperatures, where radiative recombination dominates over non-radiative recombination.

All these phenomena differentiate the optical properties of Cs₄PbBr₆ single crystals distinctively from those of the bulk 3D perovskites family. To clarify the origin of these properties, we thoroughly investigated the structure of Cs₄PbBr₆ by means of temperature dependent XRD and Electron Diffraction (ED). In Figure 3a we report the XRD powder patterns of Cs₄PbBr₆ in a range of temperature from 230 °C to 430 °C. Initially, the XRD peaks are in good agreement with the Cs₄PbBr₆ reflections. However, as the temperature rises above 280 °C secondary reflections corresponding to CsPbBr₃ start to appear (see inset in Figure 3a). Notably, this thermally-induced CsPbBr₃ phase is preserved when the temperature is decreased to ambient conditions, a sign of irreversible conversion. In Figure 3b (top panel) we calculated the sizes of CsPbBr₃ crystallites from the XRD data (see Supporting Information for the calculations). We observed that the CsPbBr₃ phase appears at 280 °C with crystals smaller than 10 nm that subsequently grow when the temperature is further increased. In order to validate the detection limit of our XRD setup, we tested

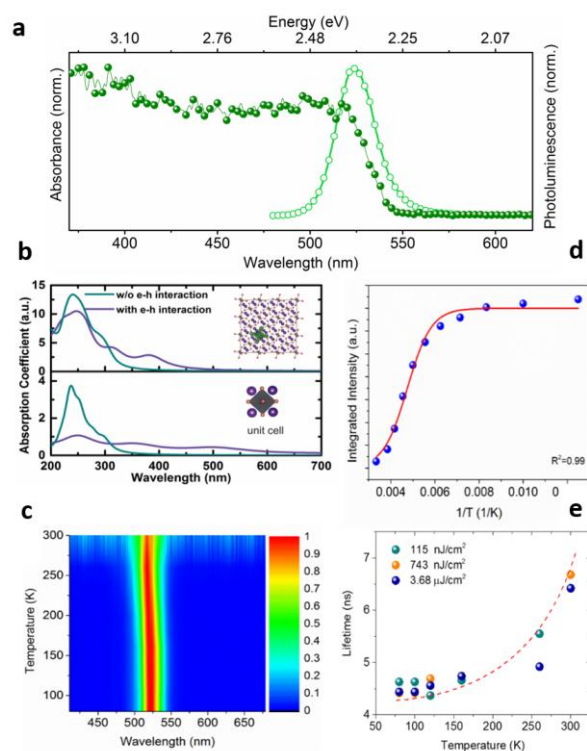


Figure 2. a) Absorption spectrum (full dots) and PL spectrum (hollow dots) of Cs₄PbBr₆ single crystal. b) Calculated absorption coefficient of Cs₄PbBr₆ single crystal and its single unit without and with electron-hole (*e-h*) interactions together the exciton wavefunction shown in the inset. c) PL color map as a function of temperature, d) integrate PL intensity, e) average PL lifetime at different temperatures for different excitation fluences, dot line is used as a guide for the eye.

its sensitivity by detecting 0.5 wt% of pre-synthesized CsPbBr₃ nanocrystals, which were intentionally mixed with 99.5 wt% of Cs₄PbBr₆ at room temperature (see Figure S6).

Additionally, we investigated the PL spectra of the annealed pristine Cs₄PbBr₆ samples (see Figure 3b bottom panel). We observed that the PL quickly quenches by raising the temperature as reported in ref¹⁷. Furthermore, we

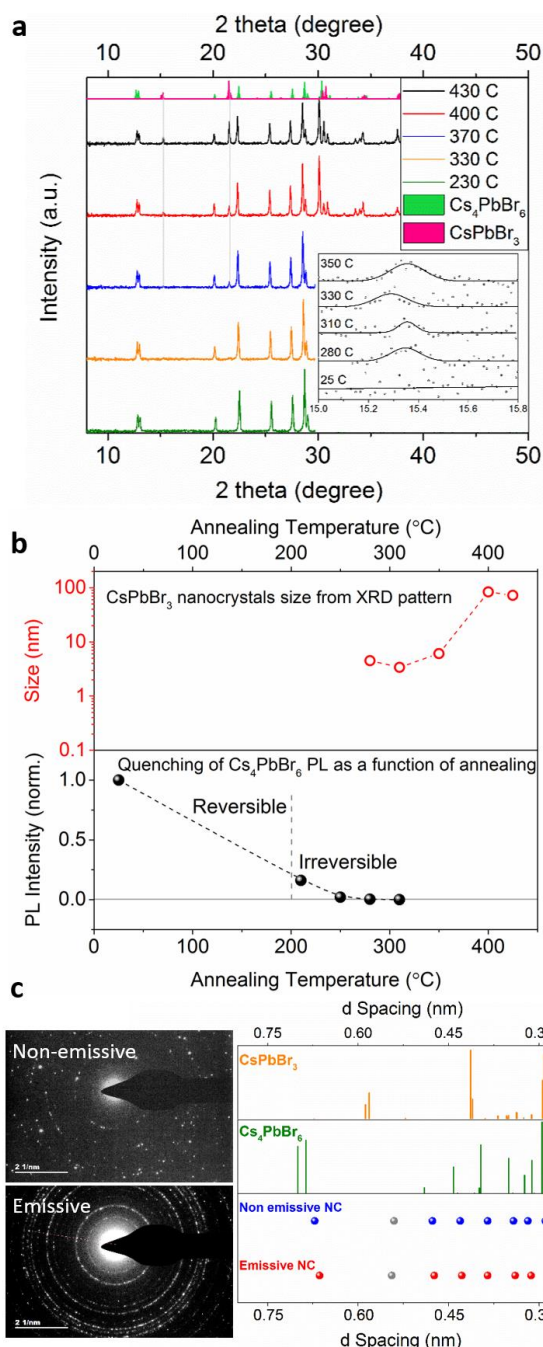


Figure 3. a) XRD powder spectrum of Cs₄PbBr₆ during the heating process. In the inset is reported a detailed investigation centered on the peak at 15 degrees. b) CsPbBr₃ nanocrystals sizes calculated from the XRD pattern at different temperatures (top panel, red); quenching of the PL as a function of temperature for Cs₄PbBr₆ (bottom panel, black). c) ED pattern for non-emissive (blue dots) and emissive (red dots) Cs₄PbBr₆ nanocrystals together with the calculated reflection for Cs₄PbBr₆ (green) and CsPbBr₃ (orange).

found that the quenching of the PL was totally reversible until 180 °C. Finally, we noticed that for samples annealed at temperatures higher than 180 °C, the PL quenches irreversibly. Thus, we deduce that: *i*) formation of the CsPbBr₃ phase and quenching of the PL could be connected and *ii*) the irreversible quenching of the PL, induced by the formation of the nanometric-sized CsPbBr₃ phase is contrary to the hypothesis that the PL is originating from nanocrystals impurities.⁴⁸⁻⁵⁰ Therefore, to unravel the origin of these phenomena, we took advantages of the latest results on Cs₄PbBr₆ nanocrystals.^{49, 51} Cs₄PbBr₆ nanocrystals exhibits totally different optical properties according to their synthesis protocol: according to ref⁴⁹ Cs₄PbBr₆ nanocrystals show no emission in the visible spectrum. In contrast, according to ref⁵¹, Cs₄PbBr₆ nanocrystals show strong green emission with quantum-like behavior. Thus, we synthesized both non-emissive and green-emissive Cs₄PbBr₆ nanocrystals and investigated their structural properties by ED (Figure 3c). The ED patterns of emissive and non-emissive nanocrystals both identically match with Cs₄PbBr₆, except for an extra spots at 0.54 nm which can be assigned to a forbidden reflection. No reflections related to CsPbBr₃ were detected for either sample. The ED results enable us to draw two important conclusions: first, we can exclude the presence of CsPbBr₃ nanocrystals embedded in the Cs₄PbBr₆ matrix, since CsPbBr₃ fingerprint reflection are missing from the ED pattern; second, the origin of the quantum emission is not related to any particular crystalline phase due to the identical ED patterns of emissive Cs₄PbBr₆ and non-emissive Cs₄PbBr₆.

Taken together, all these results point towards a PL mechanism in Cs₄PbBr₆ that is likely independent of the absence or presence of CsPbBr₃ nanocrystals.

As we could not find evidence for a role for CsPbBr₃ inclusions in our emission scenario, we looked for another plausible interpretation of the quantum behavior of bulk Cs₄PbBr₆ crystals. Another hypothesis for the origin of the quantum photoluminescence of Cs₄PbBr₆ crystals is the presence of shallow and deep energy defects.^{52, 53} These types of defects, in perovskite semiconductors, are widely accepted with the presence of sub-bandgap states whose energies are related to the formation energy of the defect itself.⁵³⁻⁵⁵ Among the possible types of defects, halogen vacancies are the most prevalent defects under halogen-poor conditions.⁵⁴ Thus, we posit that bromide vacancies may behave as radiative recombination centers by forming sub-bandgap states where excitons get trapped. Indeed, the formation of the CsPbBr₃ phase at high temperature could be connected to these point defects, which are well known to act as initialization centers for more extended defects such as dislocations.⁵³ The migration and coalescence of defects, under annealing conditions, leads to the nucleation and clusterization of a CsPbBr₃ phase, which is accompanied by the irreversible suppression of the PL (Figure 4).

In conclusion, we unraveled the remarkable optical properties of Cs₄PbBr₆ oD-PRS single crystals. Our crystals display narrow PL emission centered at 524 nm and PLQY values higher than 40%. Time-resolved and temperature-dependent PL, combined with DFT calculations, reveal a direct correlation between these properties and those of

quantum confined structures. Thanks to the structural analysis of emissive and non-emissive oD-PRS we were able to provide new insights on the hotly debated origin of the optical properties of oD-PRS, ruling out any role for CsPbBr₃ nanocrystals or inclusion. These findings provide key insights needed to engineer the emissive properties of this rapidly emerging class of materials.

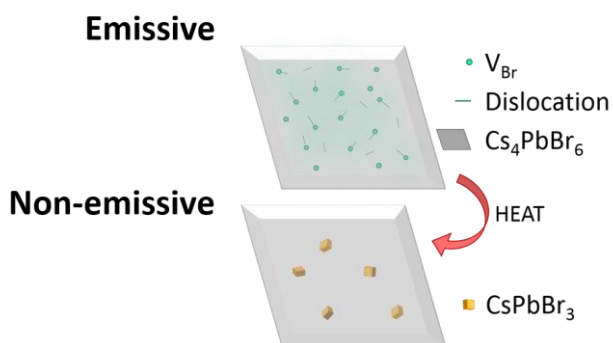


Figure 4. Schematic representation of the possible aggregation mechanism that involves bromide vacancies and CsPbBr₃ aggregates.

ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>. Experimental methods; XRD details; Absorption Spectrum; PL lifetime, and ED.

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The manuscript was written through contributions of all authors.

ACKNOWLEDGMENT

The authors acknowledge the financial support of KAUST and Saudi Aramco (Grant RGC/3/3095-01).

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Table of Contents

