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# Revealing the Origin of Luminescence Center in 0D Cs<sub>4</sub>PbBr<sub>6</sub> Perovskite

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Supporting Information

ABSTRACT: 0D perovskite Cs<sub>4</sub>PbBr<sub>6</sub> has attracted considerable attention recently because of its highly efficient green photoluminescence (PL) and highly debated opposing mechanisms: embedded CsPbBr3 nanocrystals versus intrinsic Br vacancy states. Here we provide sensitive but noninvasive methods that can not only directly correlate luminescence with the underlying structure, but also distinguish point defects from embedded nanostructures. We first use correlated Raman-PL as a passive structure-property method to identify the difference between emissive and nonemissive Cs<sub>4</sub>PbBr<sub>6</sub> crystals and reveal the existence of CsPbBr<sub>3</sub> nanocrystals in emissive Cs<sub>4</sub>PbBr<sub>6</sub>. We then employ a diamond anvil cell to probe the response of luminescence centers to hydrostatic pressure. The observations



of fast red-shifting, diminishing, and eventual disappearance of both green emission and Raman exclude Br vacancies as possible luminescent centers. The resolution of this long-lasting controversy paves the way for further device applications of low dimensional perovskites, and our techniques are applied to other emerging materials.

# INTRODUCTION

The lack of deep-level, carrier trapping, and defect states in  $CsPbX_3$  (X = I, Br, Cl) determines in part the defect-tolerant electronic and optical properties of these all-inorganic perovskites and make them auspicious materials for highefficiency low-cost solar cells and many other optoelectronic devices.<sup>1-4</sup> As such, recent observations of apparently deeplevel and highly luminescent states in low-dimensional lead halide perovskites such as 0D Cs<sub>4</sub>PbBr<sub>6</sub><sup>5-9</sup> and 2D  $CsPb_2Br_{5,}^{10-15}$  have attracted a lot of attention as well as intensive debates. Among them, the debate on the origin of bright green luminescence in the otherwise wide bandgap Cs<sub>4</sub>PbBr<sub>6</sub> is more intense and involving a large community, as can be seen from four recent critical reviews representing two opposing opinions.<sup>6-9</sup> Because of the extreme similarity of its

green emission with that of CsPbBr3 nanocrystals, it is believed that the embedded CsPbBr3 nanocrystals are responsible for the highly efficient photoluminescence (PL).<sup>8,9,16-19</sup> This opinion is further strengthened by direct imaging of CsPbBr<sub>3</sub> nanocrystals in Cs<sub>4</sub>PbBr<sub>6</sub>.<sup>20–29</sup> Nevertheless, the other group offers a totally different theory, attributing the strong PL to Br vacancies and regarding the green emission as an intrinsic property of  $Cs_4PbBr_6$ . This Br vacancy theory is supported by their density functional theory (DFT) simulation and most importantly, the observation of pure Cs<sub>4</sub>PbBr<sub>6</sub> single crystals without embedded CsPbBr3 nanocrystals by high

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**Figure 1.** Failure to detect  $CsPbBr_3$  nanocrystals in  $Cs_4PbBr_6$  with transmission electron microscopy (TEM). (a,b) Optical images of emissive and nonemissive  $Cs_4PbBr_6$  nanocrystals. (c,d) Optical images of large size emissive  $Cs_4PbBr_6$  single crystals under (c) white light and (d) UV light. (ei) Photoluminescence (PL) image, low and high magnification TEM images, selected area (indicated by the white circle in (g) electron diffraction and lattice fringe images of an emissive  $Cs_4PbBr_6$  nanocrystal (indicated by the red arrows in (e) and (f)). (j–l) PL, TEM, and electron diffraction images of  $Cs_4PbBr_6$  nanocrystals obtained from large single crystals as in (c,d).

resolution transmission electron microscopy (TEM).<sup>7</sup> It is also supported by their observation that the appearance of CsPbBr<sub>3</sub> in initially bright Cs<sub>4</sub>PbBr<sub>6</sub> will quench its PL,<sup>30</sup> although this counterintuitive observation has been questioned.<sup>8</sup> The Br vacancy theory also has problem because the calculated deeplevel defect states are not reproduced by other DFT simulation and are rarely found experimentally in lead halide perovskites.<sup>9</sup>

Structure-property relation is the essential goal of materials science. The unsettling nature of this controversy indicates the challenge of controversy and limitation of existing efforts. Although simulation has become more powerful in predicting material properties, experimental evidence is still pivotal to fundamental understanding and is the test for any theoretical contenders. The root cause for the dispute is the lack of oneto-one correlation between luminescence and structure, and an experimental technique that can distinguish luminescence from point defects versus nanoinclusions. For example, the structure of a single Cs<sub>4</sub>PbBr<sub>6</sub> nanocrystal was confirmed by high resolution TEM, but the PL of the same exact nanoparticle was not reported or confirmed, even though this nanocrystal was selected from an ensemble of emissive nanocrystals,<sup>7,14,37,38</sup> so one-to-one relationship was not solidly established.<sup>15</sup> On the other hand, it is well-known that lead halide perovskites are very sensitive to electron beams and can easily get damaged,<sup>39</sup> thus the TEM evidence from both sides could be questionable. Here we report a resolution of this controversy and identification of the origin of luminescent centers in Cs<sub>4</sub>PbBr<sub>6</sub>. This has been achieved by using a combined confocal Raman-PL technique in conjunction with a diamond anvil cell (DAC) that can directly correlate structural information with luminescent property at the same length scale. Since the

complete Raman spectrum of  $Cs_4PbBr_6$  was unknown at the time of this study, we recorded and assigned all Raman active modes. The response of PL and Raman scattering of  $Cs_4PbBr_6$  to hydrostatic pressure helped us to elucidate whether the PL comes from point defect or extended structures.

## RESULTS AND DISCUSSION

We synthesized both green PL emissive and nonemissive Cs<sub>4</sub>PbBr<sub>6</sub> (shortly emissive and nonemissive) based on reported methods so that similar experiments from opposing sides can be checked under the same conditions.<sup>28,30,5</sup> CsPbBr<sub>3</sub> micropowders and highly luminescent CsPbBr<sub>3</sub> nanocrystals were also prepared as PL and Raman references for comparison.<sup>16,40,41</sup> Figure 1a,b shows optical images of emissive and nonemissive Cs<sub>4</sub>PbBr<sub>6</sub> nanocrystal suspensions. The nonemissive Cs<sub>4</sub>PbBr<sub>6</sub> nanocrystals appear transparent, confirming it as a wide bandgap semiconductor. However, no difference in their X-ray (XRD) patterns (Figure SF1 of the Supporting Information, SI) is observed<sup>5,7,30-36</sup> except with a wider line width of nonemissive Cs<sub>4</sub>PbBr<sub>6</sub> due to its smaller crystal size (Figure SF2). Like emissive Cs<sub>4</sub>PbBr<sub>6</sub> nanocrystals, large size Cs4PbBr6 crystals also exhibit a yellow color under white light and strong green color under UV. To overcome the low sensitivity of XRD, we employed TEM to identify possible  $CsPbBr_3$  nanoinclusions in  $Cs_4PbBr_6.$  In contrast to previous work,  $^{7,14,37,38}$  here we performed TEM and PL on the same emissive single crystals.<sup>42</sup> Figure 1e-l confirms their excellent Cs<sub>4</sub>PbBr<sub>6</sub> structure with clear crystal facets, and similar to XRD, no embedded CsPbBr<sub>3</sub> nanocrystals were detected. However, it is important to point out that after exposure to electron beams, green emission from these nanocrystals either

decreased significantly or disappeared, indicating a severe structural damage.

After failing to detect CsPbBr<sub>3</sub> nanocrystals in Cs<sub>4</sub>PbBr<sub>6</sub>, we turned to Raman spectroscopy, a noninvasive and sensitive optical technique. Since to the best of our knowledge there has been no report on the complete Raman spectra of Cs<sub>4</sub>PbBr<sub>6</sub> but only partial ones,<sup>32,43</sup> we provide a more detailed analysis of the experimental Raman spectrum. In addition to the need of proper assignment of Raman active phonons, this analysis is helpful in discerning intrinsic from inclusion Raman features. We choose nonemissive Cs<sub>4</sub>PbBr<sub>6</sub> as a reference for Raman spectrum. Its Raman at 80 K is shown in Figure 2a.



**Figure 2.** Raman spectra of CsPbBr<sub>3</sub> microcrystals, nonemissive, and emissive  $Cs_4PbBr_6$  at 80 K and room temperature (RT). (a) Polarized spectra of nonemissive  $Cs_4PbBr_6$  at 80 K with all  $4A_{1g} + 10E_g$  Raman modes marked with vertical bars. II stands for parallel and + for orthogonal incident and scattered light polarizations, respectively. (b) Raman spectra of emissive  $Cs_4PbBr_6$  and  $CsPbBr_3$  at 80 K. (c) Raman spectra of nonemissive  $Cs_4PbBr_6$  at RT. (d) Raman spectra of emissive  $Cs_4PbBr_6$  at RT. (d) Raman spectra of emissive  $Cs_4PbBr_6$  at RT. (d) Raman spectra of emissive  $Cs_4PbBr_6$  is evidenced by the second order Raman band at 310 cm<sup>-1</sup> in (d) and Cs phonon peaks of  $CsPbBr_3$  at 80 K. Raman spectra in (a,b) and (d) are excited with 632.8 nm laser. The scattering intensity scale is the same for all spectra in a given panel.

 $Cs_4PbBr_6$  crystallizes in a trigonal crystal structure characterized by the space group Rc (No. 167).<sup>44</sup> The rhombohedral unit cell is the primitive cell (PC) of this compound and contains two formula units of  $Cs_4PbBr_6$ ,  $N_{cell} =$ 22 atoms per PC and  $3N_{cell} = 66$  degrees of vibrational freedom. The irreducible representations of the  $\Gamma$ -point phonon modes are  $4A_{1g} + 10E_g + 6A_{2g} + 5A_{1u} + 7A_{2u} +$  $12E_u$  and only the  $A_{1g}$  and  $E_g$  phonons are Raman active.<sup>21</sup> The three acoustic phonons are represented by  $A_{2u} + E_u$  symmetry modes, the remaining  $5A_{2u} + 11E_u$  modes are infrared (IR) active, whereas  $5A_u + 6A_{2g}$  modes are neither IR nor Raman active. One experimental approach to discerning different symmetry modes is to measure the polarized Raman spectra. The Raman tensor,  $R_S = |\alpha_{ij}|$  with i, j = x, y, z, of active modes  $S = A_{1g}$  and  $E_{g}$ , has the following nonzero components:<sup>45</sup>  $R_{A_{1g}}$  $(\alpha_{xx} = \alpha_{yy} = a, \alpha_{zz} = b) R_{E_{g,1}} (\alpha_{xx} = -\alpha_{yy} = c, \alpha_{yz} = \alpha_{zy} = d)$ And  $R_{E_{g,2}}(\alpha_{xy} = \alpha_{yx} = -c, \alpha_{xz} = \alpha_{zx} = -d)$  The analysis of Raman scattering activity  $I_S = [\vec{e}_s \times R_S \times \vec{e}_I]^2$ , where  $\vec{e}_I$  and  $\vec{e}_S$  are the incident and scattered light polarizations, suggests that for polycrystalline or randomly oriented nanocrystals of Cs<sub>4</sub>PbBr<sub>6</sub>,<sup>46</sup> as in the case of most of our samples, the depolarization ratio for  $A_{1g}$  modes is as follows: $0 \leq \frac{I_{A_{1g}}^+}{I_{A_{1g}}^+} \leq \frac{3}{4}$ 

and  $\frac{I_{E_g}}{I_{E_g}^{\parallel}} = \frac{3}{4}$  for the  $E_g$  modes, where || stands for parallel and +

for orthogonal  $\vec{e}_I$  and  $\vec{e}_S$  respectively. This allowed us to distinguish the four  $A_{1g}$  modes in Figure 2a by their markedly smaller depolarization ratio. Our experimental assignment of the Raman modes is further confirmed by DFT lattice dynamics calculations as seen in Table SF1.

With Raman standard of  $Cs_4PbBr_6$  at hand, we can identify the Raman difference between emissive and nonemissive  $Cs_4PbBr_6$ . As shown in Figure 2b, the Raman spectrum of emissive  $Cs_4PbBr_6$  is identical to that of nonemissive  $Cs_4PbBr_6$ in Figure 2a except that the spectrum of emissive  $Cs_4PbBr_6$ contains an additional Raman band at ~29 cm<sup>-1</sup> that replicates the doublet at 28–30 cm<sup>-1</sup> in CsPbBr<sub>3</sub>,<sup>47,48</sup> indicating presence of CsPbBr<sub>3</sub> in Cs<sub>4</sub>PbBr<sub>6</sub>. Figure SF9 shows the difference in atomic displacements of Cs that are involved in 28–30 cm<sup>-1</sup> doublet in CsPbBr<sub>3</sub> and those in Cs4PbBr<sub>6</sub>. Under 632.8 nm laser excitation the Raman scattering in both compounds is nonresonant. This allowed us to estimate trace amount of CsPbBr<sub>3</sub> in the emissive Cs<sub>4</sub>PbBr<sub>6</sub>. On the basis of the relative Raman intensity, the concentration of CsPbBr<sub>3</sub> is estimated to 0.2% by volume, which is below typical XRD sensitivity.

The observation of Raman difference and identification of CsPbBr<sub>3</sub> in Cs<sub>4</sub>PbBr<sub>6</sub> proves that Raman is the right method to solve this controversy, however, the low temperature used is usually not very convenient; hence we explore room temperature Raman spectra for finer details. Figure 2c shows the RT Raman spectra of nonemissive Cs<sub>4</sub>PbBr<sub>6</sub> excited with 632.8 nm (1.96 eV) and 488 nm (2.54 eV) laser lines. The spectra are identical to that of low temperature except that lines become broader. The good signal-to-noise ratio and lack of strong background in the spectrum excited with the 488 nm laser demonstrate that no green PL is excited in this sample. Figure 2d shows Raman spectrum of emissive Cs<sub>4</sub>PbBr<sub>6</sub>. The feature at  $\sim 29$  cm<sup>-1</sup> stemming from CsPbBr<sub>3</sub> becomes indistinguishable, but this agrees with the stronger background due to dynamic-disorder scattering from Cs coupled to Br anharmonic motion in CsPbBr<sub>3</sub> at RT,<sup>47</sup> as also shown in Figure 2d. A close look at the 200-400 cm<sup>-1</sup> spectral range displayed in the insets of Figure 2c,d, however, reveals a Raman band around 310 cm<sup>-1</sup> in the emissive sample, whereas this band is absent in the nonemissive one. The band at 310  $\rm cm^{-1}$  is at the same position as in the second-order phonon Raman scattering in  $\rm CsPbBr_3^{-32,47,48}$  also shown in Figure 2d for comparison.

Because there was no Raman spectral overlap with  $Cs_4PbBr_6$ and relatively large wavenumber, the 310 cm<sup>-1</sup> line is a convenient spectral signature to identify CsPbBr<sub>3</sub> at RT. However, due to the low concentration of CsPbBr<sub>3</sub> in Cs<sub>4</sub>PbBr<sub>6</sub> and weak intensity of second-order phonon Raman scattering, the detection of 310 cm<sup>-1</sup> line requires a high signal-to-noise ratio. To better understand this challenge, we chose CsPbBr<sub>3</sub> nanocrystals (100 nm in average diameter, Figure SF3) and emissive  $Cs_4PbBr_6$  and performed confocal Raman-PL on the same spot and under the same condition. Figure 3a shows PL of CsPbBr<sub>3</sub> nanocrystals and Cs<sub>4</sub>PbBr<sub>6</sub>



**Figure 3.** Room temperature PL and Raman of CsPbBr<sub>3</sub> nanocrystals and emissive  $Cs_4PbBr_6$ . (a) PL spectra under 473 nm laser excitation. (b) Raman spectra under 633 nm laser excitation. (c) Diamond anvil cell for confocal pressure Raman-PL. (d) Pressure evolution of Raman of emissive  $Cs_4PbBr_6$ . The weaker appearance of closely spaced  $E_g$  and  $A_{1g}$  lines at 88 cm<sup>-1</sup> is due their closeness to the spectral cutoff of a dichroic beam splitter.

under 473 nm laser excitation, and their same spot Raman spectra with 632.8 nm laser are shown in Figure 3b. Both samples exhibit very similar PL, with slightly stronger PL for  $Cs_4PbBr_6$ , but the 310 cm<sup>-1</sup> CsPbBr<sub>3</sub> feature in  $Cs_4PbBr_6$  is orders of magnitude weaker than in the CsPbBr<sub>3</sub> nanocrystals as seen in the inset of Figure 3b. Because of higher PL quantum yield for smaller CsPbBr<sub>3</sub>, the stronger PL but much weaker Raman indicates that CsPbBr<sub>3</sub> in  $Cs_4PbBr_6$  must be much smaller than the 100 nm CsPbBr<sub>3</sub> nanocrystals, in agreement with the TEM of Cs<sub>4</sub>PbBr<sub>6</sub> nanocrystals in Figure 2.

The observation of CsPbBr<sub>3</sub> Raman in emissive Cs<sub>4</sub>PbBr<sub>6</sub> is a significant step toward the resolution of the controversy, however, it cannot completely rule out the existence of other green emitters such as Br vacancies suggested as a sole source of green PL in Cs<sub>4</sub>PbBr<sub>6</sub><sup>7</sup>. In order to distinguish between presumably different green PL emitters, we study the Raman and PL response of Cs<sub>4</sub>PbBr<sub>6</sub> to hydrostatic pressure using a high-throughput Raman/PL spectrometer. Figure 3c shows the schematic of experimental setup, and Figure 3d shows the evolution of Raman under pressure to up to 5 GPa. The Raman is still dominated by two peaks, the weaker appearance of  $E_g/A_{1g}$  line at 88 cm<sup>-1</sup> is due to the spectral cutoff of a dichroic beam splitter, a complete Raman spectrum evolution recorded on a triple spectrometer with cutoff at 10 cm<sup>-1</sup> is shown in Figure SF4. The disappearance of this line indicates a phase transition of Cs<sub>4</sub>PbBr<sub>6</sub> around 3 GPa, in agreement with previous report.43

Figure 4 shows the corresponding pressure evolution of green PL and 310 cm<sup>-1</sup> Raman band. The PL intensity increases initially and then decreases gradually until a quick disappearance at ~2.0 GPa. In the meantime, the PL peak has



**Figure 4.** (a,b) Evolution of PL spectrum and peak position of emissive  $Cs_4PbBr_6$  crystals under hydrostatic pressure. (c) Zoomed-in view of evolution of Raman spectrum near 300 cm<sup>-1</sup> from Figure 3d. (d) Optical images of green emission under increasing pressure.

been shifting to longer wavelength until a turn to shorter wavelength at ~2.0 GPa. The 310 cm<sup>-1</sup> Raman band follows the same trend and disappears at around the same pressure of 2.0 GPa. These PL and Raman responses to pressure are nearly identical to that of CsPbBr<sub>3</sub> nanocrystals, as reported in the literature<sup>49,50</sup> as well as observed in our own measurement (Figures SF5–SF8). The strong correlation between PL and Raman, i.e., the diminishing and disappearance of PL and Raman at the same pressure reveals that CsPbBr<sub>3</sub> nanocrystals are the sole source for the green PL.

We further argue that the observed pressure responses of PL and Raman cannot be explained by Br vacancies or other lead halide structures such as Cs<sub>2</sub>PbBr<sub>4</sub>. The effect of hydrostatic pressure on point-defect states or luminescent centers has been investigated in many semiconductors.<sup>51–56</sup> The consensus is that localized states such as Br vacancies are very stable under hydrostatic pressure, especially if they are already deep level states. First, their optical activity will remain more or less the same and certainly will not disappear suddenly as long as its host material maintains the same structure. Second, the pressure induced energy shift should be less than the bandgap shift of the host material. The bandgap of Cs<sub>4</sub>PbBr<sub>6</sub> decreases only by 10 meV under 1 GPa,<sup>43</sup> but the observed PL shift is 20 meV, that is, twice the bandgap shift. As revealed both by Raman and bandgap evolution, Cs<sub>4</sub>PbBr<sub>6</sub> remains stable until the phase transition at 3 GPa, but the PL already disappears at 2 GPa, way before the phase transition. On the basis of these two reasons, we can safely rule out Br vacancies as the source for green PL in Cs<sub>4</sub>PbBr<sub>6</sub>. Cs<sub>2</sub>PbBr<sub>4</sub> is ruled out because it does not have the Raman signature of CsPbBr<sub>3</sub> at 310 cm<sup>-1</sup>.<sup>57,58</sup>

Having concluded that CsPbBr<sub>3</sub> nanoinclusions are the sole PL source, we comment on their size and try to understand some minor but confusing observations. Unlike CsPbBr<sub>3</sub> colloids or free-standing nanocrystals in Figure SF5 and refs 49,50, we always observe a PL enhancement under initial small

pressure as shown in Figure 4a. We believe that this is due to different dielectric environment or local strain experienced by the embedded CsPbBr<sub>3</sub> inclusions. Due to the same reason, the PL of CsPbBr<sub>3</sub> nanoinclusions exhibits a red shift compared to that of colloids.<sup>22,23,26,59,60</sup> Because of shorter PL peak wavelength, we believe that CsPbBr<sub>3</sub> nanocrystals in our case are smaller than reported nanoinclusions, which are less than 5 nm.<sup>33</sup> We also stress again that previous TEM evidence for pure emissive Cs<sub>4</sub>PbBr<sub>6</sub> is not solidly justified, because it lacks a report of PL from the same nanocrystals before and after TEM imaging.<sup>7</sup> The observation of decreasing PL with increased CsPbBr<sub>3</sub> nanocrystal concentration in Cs<sub>4</sub>PbBr<sub>6</sub> is due to the reduced PL quantum yield for larger size and lower quality CsPbBr<sub>3</sub><sup>7</sup>.

One challenge for material sciences is that samples from different growers could be different even though they have followed the same recipes, i.e., our emissive Cs<sub>4</sub>PbBr<sub>6</sub> might not be exactly identical to those reported. However, our combined confocal Raman-PL and pressure Raman-PL techniques are generalizable. As demonstrated, they are sensitive and noninvasive, and can be easily adopted by any scientists with the proper equipment. In fact, in most cases, pressure Raman-PL with a DAC is not necessary because both Raman and PL can be quantitative if they are carefully calibrated against a reference sample such as CsPbBr<sub>3</sub> nanocrystals. A quick Raman can tell whether Br vacancies are solely responsible for the green PL, and a careful analysis of Raman and PL can tell the contribution of CsPbBr<sub>3</sub> nanocrystals to the total PL emission. A PL source other than CsPbBr<sub>3</sub> nanocrystals can be introduced only when the green PL cannot be accounted for by CsPbBr<sub>3</sub> nanocrystals with a near unity PL quantum yield.

## CONCLUSIONS

In summary, we have identified CsPbBr<sub>3</sub> nanocrystal inclusions in Cs<sub>4</sub>PbBr<sub>6</sub> as dominant green PL source in this compound. The complete Raman spectra of pristine Cs<sub>4</sub>PbBr<sub>6</sub> are presented, and the observed spectral lines are assigned to certain phonons in accordance with DFT lattice dynamics. We reveal the Raman signatures of emissive Cs<sub>4</sub>PbBr<sub>6</sub>. These are the doublet at 28-30 cm<sup>-1</sup> at low temperature and the Raman band at 310 cm<sup>-1</sup> at RT, shown to stem from CsPbBr<sub>3</sub> nanocrystal inclusions. No indication of Br vacancies related PL was found. The problem we faced in our attempt to find out whether intrinsic point defects can produce green PL in Cs<sub>4</sub>PbBr<sub>6</sub> is that all tested emissive samples showed presence of CsPbBr<sub>3</sub>. For future quests in searching for alternative origins of green PL in Cs<sub>4</sub>PbBr<sub>6</sub> we suggest a mandatory Raman test. The resolution of this long-lasting controversy paves the way for device applications of low dimensional perovskites, and our comprehensive optical technique integrating structure-property with dynamic response can be applied to other materials to understand their luminescence centers.

## EXPERIMENTAL DETAILS

**Photoluminescence (PL) and Raman Spectroscopy.** Raman spectra in Figure 2 were measured using a Horiba JY T64000 triplegrating Raman spectrometer. The spectrometer is capable of measuring Raman as low as  $10 \text{ cm}^{-1}$ . A 632.8 nm He–Ne laser and a 488 nm Ar<sup>+</sup> gas laser were used as excitation sources. Room temperature PL and Raman spectra in Figure 3a,b were measured using a HORIBA iHR320 Spectrometer equipped with a Synapse CCD. A 473 nm laser was used for PL and a He-Ne laser was used Raman measurement. A 365 nm UV LED (Thorlabs, CS2010) was used to excite samples in Figure 1a, b, d, e, and j.

**High-Pressure Diamond Anvil Cell.** High-pressure optical measurements were carried out with a diamond anvil cell (Diacell OmniDAC-LT model, Almax Easylabs). The culet of type-Ia ultralow fluorescence diamonds is 600  $\mu$ m. Samples were loaded into a 250- $\mu$ m diameter hole in a BeCu gasket preindented to 70  $\mu$ m, together with ruby microspheres for pressure calibration. Silicone oil was used as a pressure-transmitting medium. All the measurements were performed at room temperature.

**High-Pressure Optical Measurements.** High-pressure PL-Raman spectra were measured using a Horiba Triax 550 spectrometer equipped with a Spectrum One CCD. A 20X Mitutoyo Plan Apo objective was used as a confocal microscope to excite and collect PL-Raman spectra. For PL spectra in Figures 4a and SF5, a 351 nm continuous wave laser (Innova 300C, Coherent) with a power of 10 mW after neutral density filter was used as an excitation source. The PL spectra were collected with an exposure time of 1 s. For Raman spectra in Figures 3d, SF4, and SF7, the He–Ne laser was used as excitation source. A 632.8 nm dichroic beam splitter was used to maximize optical excitation and collected efficiency. The Raman spectra were collected with an exposure time of 30 s.

## ASSOCIATED CONTENT

## **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.9b03426.

Synthesis of various types of  $Cs_4PbBr_6$  and  $CsPbBr_3$ , scanning electron microscopy, X-ray diffraction measurements, transmission electron microscopy, photoluminescence (PL) and Raman measurements, XRD of various types of  $Cs_4PbBr_6$  and  $CsPbBr_3$ , TEM of nonemissive  $Cs_4PbBr_6$  nanocrystals, SEM of  $CsPbBr_3$  nanocrystals, Raman spectra of emissive  $Cs_4PbBr_6$  under pressure, pressure-dependent PL and Raman spectra of  $CsPbBr_3$ nanocrystals, and density functional perturbation theory (DFPT) lattice dynamics of  $Cs_4PbBr_6$  and  $CsPbBr_3$ (PDF)

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#### Notes

The authors declare no competing financial interest.

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