Fabrication of Thin Films from Powdered Cesium Lead Bromide (CsPbBr$_3$) Perovskite Quantum Dots for Coherent Green Light Emission

Saif M. H. Qaid, Hamid M. Ghaithan, Bandar Ali Al-Asbahi, Abdulaziz Alqasem, and Abdullah S. Aldwayyan

ABSTRACT: High-quality thin films were obtained directly by spin-coating glass substrates with suspensions of powdered cesium lead bromide (CsPbBr$_3$) perovskite quantum dots (PQDs). The structural properties of the films were characterized via transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD) analysis, and atomic force microscopy (AFM). The crystal structure of the CsPbBr$_3$ PQDs was unique. The optical behavior of the CsPbBr$_3$ PQDs, including absorption and emission, was then investigated to determine the absorption coefficient and band gap of the material. The CsPbBr$_3$ PQDs were evaluated as active lasing media and irradiated with a pulsed laser under ambient conditions. The PQDs were laser-active when subjected to optical pumping for pulse durations of 70–80 ps at 15 Hz. Amplified spontaneous emission (ASE) by the CsPbBr$_3$ PQD thin films was observed, and a narrow ASE band (~5 nm) was generated at a low threshold energy of 22.25 μJ cm$^{-2}$. The estimated ASE threshold carrier density ($n_{th}$) was ~7.06 × 10$^{18}$ cm$^{-3}$. Band-gap renormalization (BGR) was indicated by an ASE red shift and a BGR constant of ~27.10 × 10$^{-8}$ eV. A large optical absorption coefficient, photoluminescence (PL), and a substantial optical gain indicated that the CsPbBr$_3$ PQD thin films could be embedded in a wide variety of cavity resonators to fabricate unique on-chip coherent light sources.

INTRODUCTION

In the last decade, perovskite materials have become the preferred choice for many photonic applications, due to their unique crystal structures, excellent carrier mobility, high absorption coefficients, and easily tuned direct band gaps. Also, perovskite-based devices can be manufactured using simple and flexible processes with low production costs, such as solution processing.\textsuperscript{1–14} The performance of perovskites as solar light-harvesting materials in photovoltaics\textsuperscript{1–14,19} and photodetectors\textsuperscript{1–14} is extraordinary. Perovskites have also shown promise as active layers for light-emitting diodes (LEDs)\textsuperscript{9,10} and lasing applications.\textsuperscript{1–14}

The large family of lead halide-based perovskites has ABX$_3$ crystal structures. In these materials, A can be Cs$^+$, CH$_3$NH$_3^+$, or HC(NH$_2$)$_2^+$, B represents Pb, and X can be Br$^-$, I$^-$, or Cl$. More recently, three-dimensional (3D) hybrid perovskites have been shown to be promising materials for light-emitting applications.\textsuperscript{5,11,16–19} These perovskites contain much smaller organic cations, such as methylammonium (MA) or formamidinium (FA), although perovskite structures that contain Cs$^+$ are reported to have much better thermal stability and photostability.\textsuperscript{20–22} However, the perovskite band gap can be widened to ~2.3 eV by substituting X = Br$^-$. This will enable the limitations of current fabrication methods to be circumvented for the development of devices that emit true green light.\textsuperscript{20,23} The potential applications of CsPbBr$_3$ are oriented mainly toward LEDs, with few reports for photodetectors and photovoltaics. These are due to their excellent carrier mobility, short radiative lifetimes, high PL quantum yields (PLQYs), narrow full widths, tunable emission wavelengths, color purity, and high absorption coefficients.

Perovskites can be fabricated in various forms, including thin films,\textsuperscript{24} single crystals,\textsuperscript{25,26} nanowires,\textsuperscript{13} and quantum dots (QDs).\textsuperscript{9} Perovskite QDs (PQDs) have more desirable optical properties than their bulk counterparts, and they are chemically robust due to quantum size effects. PQDs are also more attractive platforms than other perovskite structures in terms of enhanced optical gain and stability. These features make PQDs ideal for use in printed optoelectronic devices, such as QD LEDs, QD lasers, QD backlights for liquid crystal...
displayed (LCDs), and lighting.27–29 By combining the advantages of perovskites with a QD structure, PQDs bring perovskite materials into the realm of quantum confinement.30,31 Compared to 3D counterparts commonly used, PQDs have been intensively studied as optoelectronic materials due to their many attractive features, which include size-tunable band gaps enriching the wavelength range of absorption and emission, high PL quantum yields, increased surface–volume ratio, excellent photostability, and versatile chemical processability. Also, compared to 3D, low-dimensional perovskites have high exciton binding energies due to dielectric confinement and the presence of quantum wells due to the enlarged Coulombic force between electrons and holes. Their high exciton binding energies result in high PLQYs, which makes them very promising for lighting applications.1–5,7−14,28,32

In general, the halide perovskites have been studied for quite some time, but the application of perovskites for amplified spontaneous emission (ASE) was not reported until 2014 by Xing et al.11 Since then, the use of perovskites for ASE and lasing has expanded significantly. The first report on random lasing in organo-lead halide perovskite microcrystal networks18 was published only a few months after the demonstration of ASE from MAPbX3 thin films.11 Rapid advancements in the compositions, structures, and engineered morphologies of perovskite micro–nano lasers30,31,35−36 have paved the way for developments in many areas due to the ultracompact physical sizes, which can confine the generated photons inside the nanostructured cavities.37 Then, the laser action will occur when the photons satisfy the resonance conditions and obtain sufficient gain.38 For example, Yakunin et al.38 used femtosecond and nanosecond lasers to stimulate ASE from CsPbX3 NCs thin films. They observed low thresholds of ∼7−15 μJ cm−2 under femtosecond excitation pulses, whereas ASE thresholds rise to ∼450 μJ cm−2 for nanosecond excitation pulses. Also, they observed that the ASE peaks were found to be red-shifted with respect to the PL maxima. They concluded that CsPbX3 NCs (10 nm) exhibit the best balance between optical performance and lowest ASE thresholds compared to CsPbX3 microcrystals and small CsPbX3 QDs (4−8 nm, chemically unstable). Another group from KAUST demonstrated ultra-air- and photostable CsPbBr3 PQDs using an inorganic–organic hybrid ion pair as the capping ligand. They introduce the passivation approach to alleviate the inherent instability of the material when operating under ambient conditions or under high laser fluences. Also, they reported that the ASE thresholds of CsPbBr3 thin films under single-photon and two-photon microscopy using a femtosecond laser system as a pumping laser were 192 and 12 μJ cm−2, respectively.39 In 2019, Yan et al. studied the poor stability and second and nanosecond lasers to stimulate ASE from CsPbX3 thin films. They observed that the ASE thresholds of CsPbBr3 thin films were significantly increased under femtosecond laser excitation with few reports for picosecond laser excitation. In those studies, PQD solutions were used to prepare thin films. Although, for all of these efforts, there are some challenges in this field that need to be solved.

In this work, powdered QDs were used directly to prepare high-quality cesium lead bromide perovskite quantum dot (CsPbBr3 PQD) thin films synthesized via the modified hot-injection method using the combination of oleic acid and oleylamine as a capping agent. We analyzed the structures of the CsPbBr3 PQD thin films through several characterization techniques. Then, the optical properties of the prepared CsPbBr3 PQD films were investigated. We then explored the potential of CsPbBr3 PQD thin films as laser-active media using, for example, a picosecond laser as an optical pumping source. ASE regimes in CsPbBr3 PQD thin films were investigated in terms of PL and carrier density over a range of pumping energies. In this contribution, successful light amplification with a lower threshold of energy density and narrower FWHM has been demonstrated. This will lead to, at the threshold carrier density, the easy increase of the net gain of the material through either optical or electrical means, opening the prospects for attempting the electrically pumped perovskite lasers. The short PL lifetime of the CsPbBr3 PQD thin films indicates that they have great potential as light-emitting materials for QD-based LEDs.

## RESULTS AND DISCUSSION

### Structural Characteristics of the CsPbBr3 PQD Thin Films

Figure 1a is a typical high-resolution transmission electron microscopy (HR-TEM) image that reveals the CsPbBr3 PQD structure. The CsPbBr3 PQDs had a cubic morphology and were quite homogeneous. The lattice fringes of a single QD with an interplanar spacing of ∼0.25 nm are visible in the inset of Figure 1b. This corresponded to the distance between adjacent (200) lattice planes, which was confirmed by performing X-ray diffraction (XRD) analysis. The PQD particles ranged from 3 to 10 nm in size with an average size of 6.5 nm. The size distribution in Figure 1c (inset) indicated that quantum confinement would occur in the PQDs. The elemental composition of the CsPbBr3 thin films was analyzed via EDS. The EDS results in Figure 1d (inset) were consistent with the elemental composition of CsPbBr3. The results also indicated that the synthesis of the PQDs via hot injection41 and a modified hot injection method32 was highly controllable and efficient.

Then, the XRD pattern of the PQDs (Figure 2a) contained strong and distinct peaks at (2θ) 15.33, 21.70, 30.87, 34.45, 37.90, and 43.93° that corresponded to diffractions from the (100), (110), (200), (210), (211), and (220) crystal planes, respectively. All of the peaks were indexed to the cubic phase near 130 °C. The dihedral angle was quite intense, and its appearance further. Also, a lot of researchers have sought to investigate the ASE/laser characterization of CsPbBr3 PQD thin films through femtosecond and nanosecond laser excitation with few reports for picosecond laser excitation. In those studies, PQD solutions were used to prepare thin films. Although, for all of these efforts, there are some challenges in this field that need to be solved and improved.

### Photoluminescence Spectra

The photoluminescence spectra of the CsPbBr3 PQD thin films are shown in Figure 2b. The PQD films were excited with different excitation wavelengths at 395 nm and 405 nm, respectively. As the excitation wavelength increased, the PL intensity of the PQD films decreased. The decrease in PL intensity was due to the Stark effect caused by the electric field of the exciton. The Stark effect is a phenomenon in which the energy levels of a quantum system are split into discrete levels by an external electric field. In the case of the PQD films, the electric field caused by the exciton leads to the splitting of the energy levels, resulting in the decrease in PL intensity.
phase at room temperature. CsPbBr₃ crystallized in the cubic phase during the direct synthesis of the PQDs due to a combination of high temperature, QD surface effects, and surface energy contributions.³⁴,⁴²,⁴⁷,⁵³ The cubic crystal phase was more stable, even at room temperature.⁵³ The average grain size of the CsPbBr₃ nanocrystals (D) and lattice strain (ε) were estimated using the uniform deformation model (UDM), which was a modified Williamson–Hall (W–H) model.⁵⁵ D and ε were determined from the XRD data using eq 1.

\[
\beta_{hkl} \cos \theta = \frac{k \lambda}{D} + 4\varepsilon \sin \theta 
\]

where \(\beta_{hkl}\) represents the peak broadening, \(\lambda\) is the wavelength of the incident X-ray (0.154 nm), and \(k\) is a constant (~0.9). The slope and intercept of the straight line in a plot of \(4 \sin \theta\) vs \(\beta_{hkl} \cos \theta\) (Figure 2b) were equal to \(\varepsilon\) and \(k \lambda/D\), respectively. The values of \(\varepsilon\) and \(D\) were determined from the XRD data using eq 1.⁵⁵⁻⁵⁷

The grain size of the CsPbBr₃ PQD film was 6.2 nm, which was consistent with the HR-TEM results (Figure 1). The large strain value was attributed to the gradual formation of the perovskite layer and hence reducing the strain. The narrow FWHMs of the diffraction peaks indicated that the dislocation density and residual stress in the crystals were both low.⁵⁵ The CsPbBr₃ unit cell (pmm3) is illustrated in Figure S1a and the super-cell in Figure S1b (Supporting Information). The image of a 2 × 2 × 2 CsPbBr₃ super cell with eight formula units in Figure S1b (Supporting Information) was generated using the VESTA software.⁵⁸

Surface Morphologies of the Thin Films. The surface roughness of a film is an important factor that affects its optical characteristics. Achieving high-performance light emission with perovskite films requires excellent surface coverage and smooth layers. Atomic force microscopy (AFM) is a powerful tool for examining the surface morphologies of films. A two-dimensional (2D) planar AFM image of a CsPbBr₃ PQD film is shown in Figure 3a. The 3D topography of the film is visible in Figure 3b, for a film thickness of ~400 nm, which is measured by a Dektak profilometer. The top-down view of the film in Figure 3a shows a generally smooth surface. Topography was

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**Figure 1.** (a) TEM image. (b) High-resolution transmission electron microscopy images. The corresponding scale bar is 2 nm. (c) Particle size distribution of CsPbBr₃ QD. (d) EDS analysis of the elements in the CsPbBr₃ films.

**Figure 2.** (a) XRD pattern of the parent spectra of CsPbBr₃ perovskite QD (red line) and CsPbBr₃ (JCPDS, 01-075-0412 (blue line)) and (b) uniform deformation mode plot concluded from X-ray diffraction (XRD) spectra.
examined over a 5 × 5 μm² area, and the average roughness in the selected area (R_a) was 4.36 nm. The maximum roughness value (R_max) was 64.3 nm, although the root-mean-square (R_q) was only 5.59 nm. This indicated that the surface of the film was smooth and uniform without pinholes and that surface coverage was good. The smooth surface of the film would reduce incident light loss at the air/PQD interface, which would promote ASE and lasing. Smoothness would also be important if the thin films were used as active layers in photonic devices. The HR-TEM, EDS, XRD, and AFM results confirmed that the CsPbBr₃ PQD thin films were successfully fabricated using powdered QDs. The CsPbBr₃ PQDs were small and uniformly distributed in the alloy, and the cubic phase was stable at room temperature.

Optical Properties of the Thin Films. The UV−vis absorption and photoluminescence (PL) spectra of the films were recorded to characterize their optical properties. Absorption measurements provide details about the existing band states of a material, including the absorbance coefficient (α) and band gap (E_g). The recombination of photogenerated electrons and holes in a semiconductor can generate PL, so PL data provide useful information about the efficiency of electron−hole recombination and charge carrier trapping.

The absorption spectra of CsPbBr₃ PQD in Figure S2a (Supporting Information) and later in Figure 5a indicated that absorption decreased as the wavelength increased. Maximum absorption was observed at 325 nm with a shoulder near 508 nm. The band-edge absorption profile showed a very small excitonic peak at the absorption edge. An extended absorption edge indicated that band-to-band electronic transitions contributed to absorption. Broad and strong absorption by the PQDs indicated that their light-harvesting capability was excellent. The light harvesting efficiency (LHE) spectrum is shown in Figure S2b (Supporting Information). The LHE of an optoelectronic device is a critical property that influences its power conversion efficiency (PCE). LHE was calculated as 1−10⁻⁴ and plotted (Figure S2b). The wavelength dependence indicated that the LHE of the CsPbBr₃ PQDs was 80%. The optical absorption coefficient (α) was evaluated as a function of photon energy in the region of the strongest absorption using eq 2 and plotted (Figure 4a) to determine what type of electron transition occurred. We then calculated the band-gap energy of the CsPbBr₃ PQDs, E_g

\[ \alpha = \frac{A}{d} \]

where (d) is the sample thickness. The absorption coefficient of CsPbBr₃ PQD was estimated to be 1.49 × 10⁵ cm⁻¹ at 410 nm, which meant that light at this wavelength penetrated to a depth of 6.71 μm. It was thus possible to make CsPbBr₃ PQD films that were thin and absorbed strongly. This would be crucial for a bilayered device because the PQD films had a
large absorption coefficient in the visible region. The absorption coefficient of the $A^*$ is independent of the photon energy and was in the same range as those of other inorganic semiconductors, such as GaAs, CdSe, and PbSe.$^{62-64}$ The optical band gap ($E_g$) can be determined by examining fundamental absorption at the edge, which is when a photon excites an electron to a higher-energy state.$^{65}$ Tauc plots were constructed from the optical absorption data. We then determined $E_g$ and the type of transition that occurred in the CsPbBr$_3$ PQDs using eq 3.$^{35,61}$

$$\alpha \nu = A^* (\nu - E_g)^n$$  \hspace{1cm} (3)

where $A^*$ is a constant that depends on the transition probability, $h$ is Planck’s constant, and $\nu$ is the frequency of the incident radiation. $A^*$ is independent of the photon energy. The values of $n$ for the direct and indirect band gaps were 2 and 0.5, respectively. The linearity in a plot of $\alpha \nu$ vs $(\alpha \nu)^2$ indicates a direct band gap, while an indirect band gap is indicated by a linear plot of $\alpha \nu$ vs $(\alpha \nu)^{1/2}$. $E_g$ was estimated from the intercept of the line where no absorption occurred ($\alpha = 0$). The line in Figure S3 (Supporting Information) did not cross the $x$-axis, so the transition was not consistent with an indirect band gap. After plotting $(\alpha \nu)^2$ against $\nu$ (Figure 4b), we found that an $n$ of 2 provided the best fit. The CsPbBr$_3$ PQDs thus had a direct band gap for an allowed transition from the first valence band (VB) to the conduction band (CB). When a semiconductor has a direct band gap, the highest level in the VB and the lowest level in the CB have the same wavenumber ($k$). The calculated energy of the direct band gap was approximately 2.38 eV, which was in good agreement with the values in previous reports.$^{30,34,48,66}$

Peaks in the PL emission spectra had narrow FWHMs and indicated a high quantum yield (QY). The absorption edge and PL peak of the CsPbBr$_3$ PQDs were located at ~508 nm and 515 nm, respectively. The ASE peak corresponded to the end of the shallow absorption (Urbach) tail. Under UV irradiation at 365 nm, CsPbBr$_3$ PQDs in a liquid suspension emitted bright green light (Figure 5c, inset). Green photoluminescence was observed at ~515 nm (2.41 eV) with a line width of ~15 nm, and the band-edge PL peak was symmetric.

The FWHM of the PL peak reflected the size distribution and morphology of the PQDs. A PL peak with a narrow FWHM would indicate that the PQD film is uniform. It would also indicate good monochromaticity, which is an important parameter for lighting devices and display applications.$^{41}$

The PL spectra were recorded using excitation wavelengths that ranged from 278 to 460 nm and plotted (Figure S4, Supporting Information). The most intense PL was observed with excitation wavelengths of 278 and 366 nm (Figure S5, Supporting Information). PL intensity varied depending on the excitation wavelength, but the emission maxima were consistently observed near 515 nm with a small red shift. Two types of photoexcitation are possible near the band edge of a semiconductor with a direct band gap. Photoexcitation can involve free electron–hole pairs or bound electron–hole pairs (excitons). The dominant photoexcitation process depends on the magnitude of the Coulombic attraction between the holes and electrons, which can be determined by examining the dielectric properties of the material.$^{67}$ The radiative recombination of free electron–hole pairs is referred to as band-to-band recombination. The PL spectrum of the CsPbBr$_3$ PQDs indicated that photoluminescence resulted from the direct recombination of electrons in the CB and holes in the VB.$^{68,69}$

Photoluminescence quantum yield (PLQY), which is defined as the ratio of emitted photons to absorbed ones, is one of the important photonic parameters including FWHM, PLQY, ASE (or lasing energy density at the threshold), and optical gain.$^{70}$ Generally, high PLQYs in films are desirable and beneficial for achieving a high optical gain. For CsPbBr$_3$ PQDs, the relative PLQYs after overnight in the N-hexane AR solution reached up to 77% by taking rhodamine (R6G) as a reference dye ($\Phi_f = 0.95$ in ethanol). We also confirmed high PLQYs by studying the differential quantum efficiency, which can be deduced from the slope of the PL vs energy density curves, as shown in Figure 7a. Thus, the highest PLQY resulted at the lowest ASE threshold.

The PL lifetime of the CsPbBr$_3$ PQD films was measured to investigate the recombination dynamics. We performed single-exponential fitting, $I(t) = A e^{-t/T}$, of the experimental curves decay on the assumption that competing PL processes would
yield a clean, single-exponent line shape after data were fitted with a mono-, bi-, and tri-exponential function and then the best fit should be selected. The time-dependent PL decay spectrum of the CsPbBr₃ PQDs is shown in Figure 5d. The PL lifetime of the CsPbBr₃ PQD thin films was short, and the PL decay was fast with a lifetime of ∼14.9 ns and exhibited single-exponential distribution with the decay components with different fractional intensities of 18.2 and 14.9 nm for the fraction amplitude (A) and lifetime (τ), respectively. χ² = 0.94, which characterized the best fitting. The method utilizing fractional intensities (A, τ) diminishes the influence of the fastest decay dynamics and increases the reliably of analysis. χ² should be close to unity for the best fit. For the short-lived excited state, lasing with electrically pumped conditions can be realized because the long-lived excited state may accumulate and cause large optical losses via excited-state absorption and the reduction of the singlet-state population. Thus, the hot electrons might be captured before their nonradiative recombination with holes. These results indicate that CsPbBr₃ PQDs have great potential as light-emitting materials for QD-based LEDs. Therefore, the PQD thin films were employed as the optical gain medium for laser fabrication.

**Evaluation of PL with Optical Pumping.** The ASE value of a material is a better benchmark of its intrinsic suitability for gain applications. If no modifications are made, such as sandwiching the thin film between two Bragg mirrors, the gain can be observed by pumping the thin film with a pulsed laser. If stimulated emission is achieved at a certain threshold, two features are typically observed (Figure 5b, inset). The first is that emission by the material as a function of pumping energy will change drastically at the threshold. The second feature is line narrowing in the emission spectrum, which indicates a transition from spontaneous emission to stimulated emission. Other indicators include a reduction in the carrier lifetime. ASE was evaluated at excitation wavelengths of 410, 420, 430, 440, 450, and 460 nm. ASE was clearly observed below 410 nm excitation. The best excitation wavelength, which characterized the best ASE, was 410 nm based on the absorbance spectrum. The evolution of PL from SE to ASE corresponded to a high optical density, was 410 nm based on the absorbance spectrum. The evolution of PL from SE to ASE was fast with a lifetime of ∼14.9 ns and exhibited single-exponential distribution with the decay components with different fractional intensities of 18.2 and 14.9 nm for the fraction amplitude (A) and lifetime (τ), respectively. χ² = 0.94, which characterized the best fitting. The method utilizing fractional intensities (A, τ) diminishes the influence of the fastest decay dynamics and increases the reliably of analysis. χ² should be close to unity for the best fit. For the short-lived excited state, lasing with electrically pumped conditions can be realized because the long-lived excited state may accumulate and cause large optical losses via excited-state absorption and the reduction of the singlet-state population. Thus, the hot electrons might be captured before their nonradiative recombination with holes. These results indicate that CsPbBr₃ PQDs have great potential as light-emitting materials for QD-based LEDs. Therefore, the PQD thin films were employed as the optical gain medium for laser fabrication.

**Figure 6.** (a) Evolution of PL spectra with pulse energy density and (b) 3D diagram of pump–fluence relationship, for the CsPbBr₃ PQD thin film under 410 nm excitation.
the roughness value determined via AFM and would definitely contribute to stronger emission. For a high-efficiency optical output, the sufficient thickness of thin films is needed because the film thickness is an influential factor in their ASE behavior. Thus, it was found that 400 nm would be the optimal film thickness for the best ASE behavior. In our previous work, we warned that while decreasing the film thickness is of practical importance to reduce the ASE threshold pump current, e.g., in electrically driven LEDs, the solution processing of perovskites, newly rediscovered for their potential photonic and photovoltaic applications, can be a restraining factor. Also, the low ASE threshold of the PQDs could be attributed to high optical gain. A detailed calculation of optical gain using the variable stripe length method would be interesting for a separate paper. A low ASE threshold can also be attributed to trapping states with small cross sections, slow Auger recombination, and low rates of bimolecular recombination. The dimensions of quantum dots are comparable to the de Broglie wavelength of electrons, so the energy difference between two adjacent levels exceeds the product of the absolute temperature (T) and the Boltzmann constant (k). This results in quantum confinement, which limits the mobility of electrons and holes. The CsPbBr₃ PQDs combined the advantages of perovskites and quantum confinement. Auger recombination is more likely with quantum confinement because the momentum conservation requirement is relaxed. Another parameter that is strongly influenced by quantum confinement is the biexcitonic binding energy. A biexciton consists of two neutral bound excitons that are red-shifted relative to unbound excitons due to Coulombic effects. When the transition from SE to ASE began, the FWHM of the spectral line suddenly decreased. When the threshold was exceeded, the PL intensity increased dramatically (Figure 7a). The FWHM decreased sharply from over 17 nm to less than 5 nm as the pumping fluence increased, and the emission band at the Fₚₐₙ narrowed. These were clear ASE signatures of ASE. When the sample was excited at twice the ASE threshold energy, the FWHM stabilized at ~5 nm.

The abrupt change in the PL intensity coinciding with a decrease in the FWHM was also accompanied by a sudden wavelength shift from 525 to 534 nm as the pumping fluence increased. The position of the ASE peak varied with the pumping energy density, and the lasing peak at 531 nm shifted to 534 nm with respect to the PL peak (Figure 7b). Many factors could have been responsible for the ASE red shifts, such as a real absorbance effect in single-exciton amplification, defect transitions, and band-gap renormalization (BGR). Band-gap renormalization (BGR) in a perovskite crystal refers to a red shift in the band gap under strong excitation. BGR in semiconductors is a many-body problem involving interactions between large populations of electrons and holes, which ultimately results in a red shift of the band-gap. The ASE peak underwent a red shift of ~4 nm over the entire range of pumping energy densities, which corresponded to a BGR of approximately 12 meV. The dependence of ASE on power is illustrated in Figure 8a as a function of injected carrier density (n). The carrier density was calculated from the absorbance spectrum while taking additional absorption on the surface layer under 410 nm excitation into account. The clear onset of the transition from SE to ASE was observed at a threshold carrier density of approximately 7.06 × 10¹⁸ cm⁻³. At the threshold carrier density, the net gain of the material could be increased easily through either electrical or optical means. The BGR was estimated using eq 4.

\[ \Delta E_{BGR} = (2\gamma n)^{1/3} \]  

where \( \gamma \) is the band-gap renormalization factor. The red shift in the emission peak with increasing pumping power was used to estimate BGR. ASE was expected to appear in the region of maximum gain. \( \Delta E_{BGR} \) during excitation at 410 nm is plotted against \( n^{1/3} \) in Figure 8b. As expected, BGR was induced by an increase in the carrier density and reached a maximum value of ~45 meV, which corresponded to a maximum red shift of ~8 nm at a pumping energy density of ~39 \( \mu J \) cm⁻². The small BGR value was attributed to unconfined photocarriers. BGR did not continue at pumping energy densities above ~22.5 \( \mu J \) cm⁻² because the carrier density did not increase significantly with increasing fluence. Since BGR depended only on the carrier density, the energy shift was almost negligible above 22.5 \( \mu J \) cm⁻² given the spectral resolution of our setup (~0.78
The BGR coefficient was thus estimated at a lower carrier density. The estimated BGR was $\sim 27.10 \times 10^{-8}$ eV cm, which was very close to the reported BGR of GaAs. These results indicated that the PQDs behaved like a typical semiconductor and could be evaluated using the same criteria.

## CONCLUSIONS

CsPbBr$_3$ PQD thin films were successfully obtained directly from powdered QDs. They possessed excellent optical properties and were strong emitters. Amplified spontaneous emission (ASE) by the CsPbBr$_3$ PQDs and optically pumped lasing were observed with excitation under laser irradiation for picosecond pulse intervals. Low-threshold ASE and optically pumped perovskite laser emission were achieved at room temperature. The ASE threshold of the CsPbBr$_3$ PQDs was exceptionally low, which could make them ideal candidates for photonic integration applications. Also, as far as we know, the energy density threshold of ASE reported in this work (22.25 $\mu$J/cm$^2$) is the lowest value reported under picosecond pulsed laser of excitation, which indicates that as-synthesized CsPbBr$_3$ PQDs with good phase purity can be used as lasers. The purity of the cubic phase was attributed to synthesis at a high temperature. The CsPbBr$_3$ PQDs exhibited a narrow emission line, which would be an important feature for both LEDs and lasers. Lasers should emit monochromatic light, while LEDs require narrow emission lines for color purity. The lasing features of the CsPbBr$_3$ PQDs included a low threshold and narrow line width. These were attributed in part to quantum confinement in the CsPbBr$_3$ PQDs, which limited PL losses. Surface coverage was good, and the surfaces of the films were smooth and contained no pinholes and few defects. This could be attributed to the combined contributions of the QD surfaces, a high reaction temperature, and surface energy as indicated by the roughness value. The photon density increased dramatically when the carrier density reached the threshold value, and stimulated recombination became significant. The estimated ASE threshold carrier density was $7.06 \times 10^{18}$ cm$^{-3}$, and the estimated BGR constant of the CsPbBr$_3$ films was $27.10 \times 10^{-8}$ eV cm. The CsPbBr$_3$ PQDs thus combined the advantages of perovskite materials with quantum confinement.

## MATERIALS AND METHODS

### Materials.

High-quality cesium lead bromide (CsPbBr$_3$) QD powder was obtained from Quantum Solutions Company (Thuwal, Saudi Arabia, www.qdot.inc) and was prepared by a modified hot-injection process. N-Hexane AR solution (Avonchem, Cheshire, UK) was used to dissolve the CsPbBr$_3$ PQD powder.

**Fabrication of the CsPbBr$_3$ QD Powder and QD Solution.** The QDs were prepared via modified hot injection as described by Protesescu et al. using the combination of Oleic acid and oleylamine as a capping agent and emitted green light.

In this work, powdered QDs were used directly to prepare high-quality cesium lead bromide perovskite quantum dot (CsPbBr$_3$ PQD) thin films. The powdered CsPbBr$_3$ QDs and precursor materials were dissolved in a certain amount of hexane to get the required concentration. A typical film was prepared by first suspending 50 mg of the CsPbBr$_3$ QD powder in hexane (1 mL). The suspension was left overnight to ensure complete dispersion prior to spin-coating the CsPbBr$_3$ QD film.

**Fabrication of the CsPbBr$_3$ QD Thin Films.** The CsPbBr$_3$ thin films were fabricated by directly coating glass substrates. Therefore, glass microscope slides were used as substrates for thin-film fabrication. The substrates were sonicated by an ultrasonicator in soapy water for 15 min, followed by sonication in water alone for 15 min. The substrates were then sequentially ultrasonicated in acetone and isopropyl alcohol (IPA) for 15 min each and allowed to dry. The QD mixture (100 $\mu$L) was dropped onto the 1 × 2 cm$^2$ glass substrate and spin-coated at 4000 rpm for 30 s. The film thickness could be controlled by adjusting the concentration of the QD suspension. The films were generally not annealed. To remove the solvent, the films were simply dried under vacuum for 1 h.

**Structure and Morphology.** High-resolution transmission electron microscopy (HR-TEM) was conducted using a 2100 HR-TEM (JEOL, Japan) at an accelerating voltage of 200 kV. The HR-TEM was equipped with an energy-dispersive X-ray spectrometer, which was used to perform elemental analysis and generate lateral distribution maps of the elements at selected locations on the samples. Elements in the samples...
emitted X-rays with characteristic wavelengths after excitation by the incident electron beam. A JSM-6380 scanning electron microscope (SEM, JEOL) was also used to examine the morphologies of the films. The crystal phases in the CsPbBr3 PQD films were determined via X-ray diffraction (XRD) analysis using a Miniflex 600 XRD (Rigaku, Japan) equipped with a copper Kα radiation source (λ = 1.5418 Å). Scanning from (2θ) 10–80° was performed at a scan rate of 3° min⁻¹ with a step size of 0.02°.

Surface Characterization. Atomic force microscopy (AFM) was performed using a Multimode V AFM (Veeco, Northern Ireland) in tapping mode to examine the surface morphologies of the thin films. Film thickness was measured using a Dektak 150 stylus profiler (Bruker).

Optical Characterization. A portion of the CsPbBr3 PQD suspension was dispersed on a microscopically glass slide for optical characterization. The absorption spectra of the PQD thin films were recorded at ambient temperature using a V-670 UV–Vis spectrophotometer (JASCO Corp., Japan). The photoluminescence (PL) spectra of the perovskite films were recorded using an FP-8200 fluorescence spectrophotometer (JASCO Corp., Japan) in the wavelength range from 350 to 800 nm.

Time-Resolved PL Measurements. The time-resolved PL measurements were performed using a Shamrock SR-500i spectrometer (Andor) equipped with an MS257 ICCD detector (Oriel Instruments). The samples were optically pumped with an Nd: YAG laser, Solaran, LPS 1500 (3rd harmonic, wavelength: 355 nm, pulse width: 11 ns, repetition rate: 100 Hz, energy density: 1.5 μJ cm⁻²). An optical fiber attached to the ICCD camera and a lens system collected part of the emitted light from the samples.

Laser Experiments. To investigate the ASE and lasing properties of the films, power-dependent ASE spectra were recorded at the sample edges near the ends of the excitation strips using an LT-2215-OPG optical parametric generator (OPG, 3photon, Lithuania). The OPG was constructed with barium borate (β-BaB₂O₄) and had a tunable range of 425–2,300 nm. A LOTUS II Q-switched Nd:YAG picosecond laser (LOTTIS, Belarus) was used for excitation with a pulse duration of 70–80 ps at a repetition rate of 15 Hz. The signals emitted by the samples were directed through an optical fiber and a collimating lens. A QE650 Pro spectrograph (Ocean Optics) with a spectral resolution of 0.78 nm was used as the detector for all lasing and ASE measurements. All measurements were performed in air at room temperature (293 K). A schematic diagram of the laser setup used in the experiment investigate the presence of stimulated emission is shown in Figure S6 (Supporting Information).

ASE Measurements. The pumping laser beam was passed through a plate with an aperture ~2 mm in diameter. The laser beam was focused to have a radius of ~2 mm using a reflective microscope objective lens with a focal length of 10 cm, and the signals emitted by the samples were directed through an optical fiber. The pumping laser energy density was adjusted using a variable neutral density (ND) filter wheel. The energy of the laser was measured using an LM-P-209 coherent thermal sensor head. The laser energy density was attenuated, which enabled us to study the threshold dependence on energy density.

Data Analysis. A custom Python-based program developed in our research group was used to analyze the large amount of data collected in the study. The program enabled us to rapidly obtain Gaussian fits of dual PL emission peaks in multiple data files.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04517. Schematic diagram of the laser setup. More details about the structural and optical properties of CsPbBr3 QD perovskite thin films (PDF)

AUTHOR INFORMATION

Corresponding Author
Sal M. H. Qaid — Department of Physics and Astronomy, College of Science, King Saud University, Riyadh 11451, Saudi Arabia; Department of Physics, Faculty of Science, Ibb University, Ibb 70270, Yemen; orcid.org/0000-0001-8958-8960; Email: sqaid@ksu.edu.sa

Authors
Hamid M. Ghaithan — Department of Physics and Astronomy, College of Science, King Saud University, Riyadh 11451, Saudi Arabia; orcid.org/0000-0001-5126-4477
Bandar Ali Al-Asbah — Department of Physics and Astronomy, College of Science, King Saud University, Riyadh 11451, Saudi Arabia; Department of Physics, Faculty of Science, Sana’a University, Sana’a 70270, Yemen; orcid.org/0000-0002-2308-381X
Abdulaziz Alqasem — Department of Physics and Astronomy, College of Science, King Saud University, Riyadh 11451, Saudi Arabia
Abdullah S. Aldwayyan — Department of Physics and Astronomy, College of Science and King Abdullah Institute for Nanotechnology, King Saud University, Riyadh 11451, Saudi Arabia; K. A. CARE Energy Research and Innovation Center at Riyadh, Riyadh 11451, Saudi Arabia

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c04517

Author Contributions
All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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