Effect of a Rubidium Chloride Carrier Confinement Layer on the Characteristics of CsPbBr₃ Perovskite Light-Emitting Diodes

Chi-Ta Li¹, Kuan-Lin Lee², Sea-Fue Wang¹* and Lung-Chien Chen²*

Abstract
This work describes the effect of a rubidium chloride (RbCl) interlayer in CsPbBr₃ perovskite light-emitting diode (LED) structures. RbCl crystallites exhibited polyhedral structures and lattice parameters similar to those of CsPbBr₃ perovskite crystallites. The lattice mismatch between the RbCl interlayer and CsPbBr₃ active layer was only approximately 2%. The devices exhibited the best quality and performance when RbCl was used as the nucleation and carrier confinement layer. The crystallite sizes of CsPbBr₃ with 0.2-, 0.5-, and 1-nm-thick RbCl bottom layers were 55.1, 65.4, and 55.1 nm, respectively. The full width at half maximum (FWHM) of the photoluminescence (PL) emission peak for CsPbBr₃ with the RbCl bottom layer was 0.096 eV.

Keywords: CsPbBr₃, RbCl carrier confinement layer, Perovskite, Light-emitting diodes

Background
Halide perovskite materials have been extensively studied and are often applied in different photocatalytic and photovoltaic devices owing to their high absorption coefficient and low-cost processing [1–6]. Perovskite is a light-emitting diode (LED) material that shows potential for use as a display light source in the future because of its impressive properties, including high color purity, high photoluminescence quantum yield, and low nonradiative recombination ratio [7–9]. A common engineering method used to boost the luminance of perovskite LEDs is to modify the interfaces between the cathode, electron transport layer, perovskite active layer, hole transport layer, and anode, thereby maximizing carrier injection to the fullest extent possible, except for optimizing the perovskite grain size and conductivity of the layers.

Rubidium chloride (RbCl) has been used as an electron transport layer (ETL) with organic light-emitting diodes (OLEDs) to increase electroluminescent efficiency by lowering the effective electron-injecting barrier height and enhancing the electron-hole pair recombination rate [10–12]. Alkali metal cations have also been used to prevent phase segregation of perovskite materials and dopants in PEDOT:PSS used in perovskite solar cell structures, thereby modifying the interface between PEDOT:PSS and the perovskite active layer [13–15]. In addition, RbCl has been employed with the solution method to dope CsPbBr₃ perovskite films used for blue LEDs [16]. However, interface engineering is important for optoelectronic device structures. Therefore, in this work, we investigate the effect of the RbCl layer used as an ETL in CsPbBr₃ perovskite light-emitting diodes to improve carrier injection and the buffer layer between PEDOT:PSS and CsPbBr₃ perovskite active layers to increase the power conversion efficiency.
Methods
Materials and Syntheses
CsPbBr₃ perovskite LEDs were fabricated on indium tin oxide (ITO)-coated glass substrates (Ruilong Ltd., Taiwan). Cesium bromide (CsBr, 99.99%), lead iodide (PbI₂, 98%), dimethyl sulfoxide (DMSO, 99.9%), rubidium chloride (RbCl, 99.8%), polyethylene oxide (PEO, Mw 400,000), and 1,3,5-benzinetyl)-tris(1-phenyl-1-H-benzimidazole (TPBi, 99%) were obtained from UniRegion Bio-Tech Ltd. (Taiwan).

First, a CsPbBr₃ perovskite solution was prepared: 96 mg of cesium bromide (CsBr) and 110 mg of lead bromide (PbBr₂) were dissolved in 1 mL of dimethyl sulfoxide (DMSO) and then stirred and degassed at 70 °C overnight to produce solution A. Then, 10 mg of polyethylene oxide (PEO) was dissolved in 1 mL of DMSO and stirred and degassed at 70 °C overnight to produce solution B. Then, 0.5 mL of solution A and 20 mg of TPBi powder were added to solution B and stirred until it became completely transparent.

Device Preparation
ITO glass substrates were cleaned with acetone, alcohol, and isopropanol by ultrasonic cleaning for 15 min. PEDOT:PSS was spin-coated on the ITO substrate at 5000 rpm for 60 s and then baked at 140 °C for 15 min. For structure 2, the CsPbBr₃ perovskite solution was spin-coated on the PEDOT:PSS layer at 3000 rpm for 60 s and baked at 80 °C for 10 min. The RbCl upper layer was deposited on the CsPbBr₃ perovskite layer by the thermal evaporation method. Subsequently, 13-nm-thick TPBi and 100-nm-thick Ag were sequentially deposited by thermal evaporation on the RbCl upper layer. The whole LED structure and process flow are shown in Fig. 1a. For structure 3, the RbCl layer was deposited on the PEDOT:PSS layer by the thermal evaporation method. The CsPbBr₃ perovskite solution was spin-coated on the RbCl bottom layer at 3000 rpm for 60 s and baked at 80 °C for 10 min. Subsequently, 13-nm-thick TPBi and 100-nm-thick Ag were sequentially deposited on the CsPbBr₃ perovskite by thermal evaporation. The whole LED structure and process flow are shown in Fig. 1b. In this work, three thicknesses (0.2, 0.5, and 1 nm) were employed for the RbCl layer.

Characteristics
The morphologies of CsPbBr₃ films with and without the RbCl layer were observed using field-emission scanning electron microscopy (FESEM, ZEISS Sigma, ZEISS, Munich, Germany). Crystallite sizes and lattice parameters were estimated using X-ray diffraction (X’Pert PRO MRD, PANalytical, Almelo, Netherlands). Optical characteristics were measured by a fluorescence spectrophotometer (F-7000, Hitachi, Tokyo, Japan). The optoelectronic properties of LEDs were measured using a Keithley 2420 source meter and PR-670 spectroradiometer (JADAK, New York, USA). All characterizations were measured at room temperature.

Results and Discussion
Three structures were studied in this work, as shown in Fig. 2a. Figure 2b–h show top-view FESEM images of the three structures. Figure 2b shows the morphology of structure 1, which is a control sample without the RbCl layer, for comparison with other structures. Figure 2c–e are top views of structure 2 with various thicknesses of the RbCl upper layer. The particle sizes on the surface are larger than those of the control sample without the RbCl layer. Figure 2f–h are top views of structure 3 with various thicknesses of the RbCl bottom layer. The insets of FESEM images in Fig. 2b–h are particle size distribution histograms. The average particle sizes were 120, 180–230, and 80–120 nm for structures 1, 2, and 3, respectively. The particle on the surface were smaller and denser than those of the control sample without the RbCl layer. This may be because the RbCl bottom layer assists nucleation of the CsPbBr₃ perovskite film.

Figure 3 presents the XRD patterns for various structures and thicknesses of the RbCl layers. For the structure without a RbCl layer, six clear diffraction peaks at 15.28°, 21.43°, 30.42°, 35.28°, 37.63°, and 50.73° were observed. They correspond to the (110), (112), (220), (210), (211), and (044) planes of orthorhombic CsPbBr₃ crystallites, respectively [17–19]. For the structure with a RbCl layer, one diffraction shoulder at 30.72° was observed that corresponds to the RbCl dopant due to diffusion effect [20, 21]. The ionic Rb⁺ and Cs⁺ have similar ionic radii and the Rb⁺ substitution could stabilize the orthorhombic CsPbBr₃ phase, as a resulting of diffraction peak of orthorhombic RbPbBr₃ [20, 22]. To compare CsPbBr₃ film quality, crystallite sizes were estimated by Scherrer’s equation [23, 24]. The crystallite sizes of CsPbBr₃ without and with 0.2-, 0.5-, and 1-nm-thick RbCl bottom layers were 53.5, 55.1, 65.4, and 55.1 nm, respectively. Therefore, the RbCl bottom layer improved the CsPbBr₃ crystalites due to their similar polyhedral structures.

Figure 4 shows absorbance spectra for CsPbBr₃ films with and without RbCl layers. The absorption edges of all samples appeared at 520 nm in the absorbance spectra. The optical band gap of the samples was calculated to be approximately 2.385 eV. This result is consistent with the band gap of the CsPbBr₃ film. The band gap of the RbCl layer is approximately 4.8 eV. Thus, it was transparent to visible light. Additionally, a noticeable absorption
band was seen at 425 nm and is attributed to absorption by the trans-isomers of 4-(nitrophenyl)azo groups in the PEDOT:PSS layer [25, 26]. Photoluminescence (PL) emission spectra of the CsPbBr₃ films with and without the RbCl layer are shown in Fig. 5a. The emission peaks in the PL spectra
Fig. 2  a Sketch of the three structures studied in this work. Top-view FESEM images of b structure 1, c–e structure 2 with various RbCl layer thicknesses, and f–h structure 3 with various RbCl layer thicknesses. The insets in FESEM images are particle size distribution histograms.

Fig. 3  XRD patterns of various structures with different thicknesses of the RbCl layer.

Fig. 4  Absorption spectra of CsPbBr₃ films with and without the RbCl layer.
of all samples are at 518 nm. This peak corresponds to a band gap of 2.394 eV [27, 28]. Clearly, the intensities for CsPbBr$_3$ films with the RbCl bottom layer are higher than those for CsPbBr$_3$ film alone and CsPbBr$_3$ films with the RbCl upper layer. The PL intensity responds to the carrier lifetime caused by defect-induced recombination. The FWHM of the emission peak of CsPbBr$_3$ with the RbCl bottom layer is 0.096 eV. It is less than 0.1 eV for CsPbBr$_3$ with the RbCl upper layer and 0.126 eV for CsPbBr$_3$ without the RbCl layer owing to the better crystallite quality. The charge carrier recombination kinetics of CsPbBr$_3$ films with and without a RbCl layer were investigated by time-resolved photoluminescence (TRPL) measurements, as shown in Fig. 5b. Table 1 lists the parameters obtained from fits of the TRPL spectra. The RbCl bottom layer obviously improved the carrier lifetime, and the carrier lifetime was increased slightly by the RbCl upper layer. In other words, RbCl positioned as the bottom layer of the CsPbBr$_3$ film had a better impact than the upper layer on the quality of CsPbBr$_3$ films.

Figure 6a and b are plots of the energy levels of structure 2 and structure 3. In structure 2, the RbCl layer was formed as an electron transport layer on the CsPbBr$_3$ active layer. In structure 3, the RbCl layer was inserted as a carrier confinement layer under the CsPbBr$_3$ active layer to improve the efficiency of electron–hole recombination and enhance the performance of CsPbBr$_3$ perovskite LEDs [29]. Figure 6c–f plot the electroluminescence (EL), current density, luminescence, and external quantum efficiency of CsPbBr$_3$ perovskite LEDs with and without a RbCl layer. Remarkably, the performance of CsPbBr$_3$ LEDs with RbCl bottom layers was superior to that of CsPbBr$_3$ LEDs without and with a RbCl upper layer owing to improvement in crystallite quality for the CsPbBr$_3$ active layer and carrier confinement effect of the RbCl bottom layer, although the turn-on voltage increased from 5 to 5.5 V due to insertion of the RbCl layer, as shown in Fig. 6d. Another factor of performance improvement may be contributed to that Rb$^+$ dopant reduces the surface defects and non-radiative recombination of CsPbBr$_3$ active layer due to passivation, and then increases the carrier lifetime, as shown in Fig. 5b [16, 20, 21]. As shown in Fig. 6c, the emission peaks for all devices appeared at approximately 514 nm and were consistent with the peaks in the PL spectra, as shown in Fig. 5. The inset of Fig. 6c shows a photograph of an operating LED. The intensities of the EL spectra for CsPbBr$_3$ LEDs with RbCl bottom layers were higher than those of CsPbBr$_3$ LEDs without and with a RbCl upper layer. The best luminescence and external quantum efficiency were 9718 cd/m$^2$ at a bias of 8.5 V and 1.29% at a bias of 7.5 V, respectively. These values constituted improvements of 33% and 262%, respectively. In addition, in this work, CsPbBr$_3$ LEDs with RbCl upper layers did not show the effects of an electron transport layer, similar to an OLED structure.
according to Fig. 6c–f. It means that the RbCl impossibly behaves as an electron transport layer in perovskite LEDs.

**Conclusions**

In summary, the effect of rubidium chloride (RbCl) interlayers in CsPbBr₃ perovskite structures of light-emitting diodes (LED) was studied. When using RbCl as the nucleation layer, the CsPbBr₃ perovskite exhibited the best
quality and performance. The crystallite sizes of CsPbBr₃ with 0.2-, 0.5-, and 1-nm-thick RbCl bottom layers were 55.1, 65.4, and 55.1 nm, respectively. The performance of CsPbBr₃ LEDs with RbCl bottom layers was superior to those of CsPbBr₃ LEDs without and with RbCl upper layers. The best luminescence and external quantum efficiencies were 9718 cd/m² at a bias of 8.5 V and 1.29% at a bias of 7.5 V, respectively. These values constituted improvements of 33% and 262%, respectively. This may be due to several factors: the crystallite quality of the improved CsPbBr₃ active layer, stable CsPbBr₃ crystalline, surface passivation strategy of the CsPbBr₃ active layer, and the carrier confinement effect of the RbCl layer.

Abbreviations
RbCl: Rubidium chloride; CsPbBr₃: Cesium lead tri-bromide; CD₃Br: Cesium bromide; PbBr₂: Lead bromide; DMSO: Dimethyl sulfoxide; PEO: Polyethylene oxide; FESEM: Field-emission scanning electron microscopy; ITO: Indium tin oxide; PEDOT:PSS: Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate; LED: Light-emitting diode; OLED: Organic light-emitting diode.

Acknowledgments
This work was supported by the Ministry of Science and Technology (Taiwan) under contract No. 110-2221-E-027-125.

Authors’ Contributions
C-TL and K-LL prepared the samples and performed all measurements. S-FW conceived the original idea and helped to analyze and interpret the data. L-CC wrote the manuscript. All authors approved this manuscript.

Funding
This work was supported by the Ministry of Science and Technology (Taiwan) under contract No. 110-2221-E-027-125.

Availability of Data and Materials
All the data are fully available without restrictions.

Competing interests
The authors declare that they have no competing interests.

Received: 22 July 2021 Accepted: 16 December 2021 Published online: 03 January 2022

References
1. Schanze KS, Kamat PV, Yang P, Bisquert J (2020) Progress in perovskite photocatalysis. ACS Energy Lett 5:2602–2604
2. Teh YW, Chee MK, Kong XY, Yong S-T, Chai S-P (2020) An insight into perovskite-based photocatalysts for artificial photosynthesis. Sustain Energy Fuels 4:973–984
3. Kojima A, Teshima K, Shirai Y, Miyasaka T (2009) Organometal halide perovskite as visible-light sensitizers for photovoltaic cells. J Am Chem Soc 131(17):6050–6051
4. National Renewable Energy Laboratory (2021) Best research-cell efficiencies. Available online: https://www.nrel.gov/pv/assets/pdfs/best-research-cell-efficiencies.20200104.pdf. Accessed 4 Jan 2021
5. Liu Z, Kruckemeier L, Krogeimer B, Klingebel B, Marquez J, Levinson S, Öz S, Mathur S, Rau U, Unold T, Kirchhart T (2019) Open-circuit voltages exceeding 1.26 V in planar methylammonium lead iodide perovskite solar cells. ACS Energy Lett 4(1):110–117
6. Gao B, Meng J, Lu J, Zhao R (2020) CH₃NH₃PbI₃ perovskite solar cells with efficiency over 22% fabricated by green antisolvent method. Mater Lett 274:127995
7. Zhang Q, Tavakoli MM, Gu L, Zhang D, Tang L, Gao Y, Guo J, Lin Y, Yeung S-F, Poddar S (2019) Efficient metal halide perovskite light-emitting diodes with significantly improved light extraction on nanophotonic substrates. Nat Photon 10:727
8. Park J, Jang HM, Kim S, Jo SH, Lee TW (2020) Electroluminescence of perovskite nanocrystals with ligand engineering. Trends Chem 2:837–849
9. He Q, Klee E, Liang X, Xiang W (2021) Ultrastable PbV films-protected CsPbBr₃/3CsPbBr₆ perovskites with high color purity for nearing Rec. 2020 standard. Chem Eng J 419:129529
10. Lu Z, Deng Z, Du H, Li D, Zou Y, Xu D, Chen Z, Wang Y (2009) The effect of rubidium chloride on properties of organic light-emitting diodes. Solid State Electron 53:1154–1158
11. Lu Z, Wang Y, Zou Y, Du H, Chen Z, Deng Z (2010) The effect of alkaline metal chlorides on the properties of organic light-emitting diodes. J Lumin 130:387–391
12. Lu Z, Deng Z, Hou Y, Xu H (2012) Similarities and differences of alkaline metal chlorides applied in organic light-emitting diodes. Thin Solid Films 525:105–109
13. Zhang S, Tang M-C, Fan Y, Li R, Nguyen NV, Zhao K, Anthopoulos TD, Hacker CA (2020) Role of alkali-metal cations in electronic structure and halide segregation of hybrid perovskites. ACS Appl Mater Interfaces 12:34402–34412
14. Liu X, Li B, Zhang N, Yu Z, Sun K, Tang B, Shi D, Yao H, Ouyang J, Gong H (2018) Multifunctional RbCl dopants for efficient inverted planar perovskite solar cell with ultra-high-fill factor, negligible hysteresis and improved stability. Nano Energy 53:567–578
15. Wang H, Xu Y, Wu J, Chen L, Yang Q, Zhang B, Xie Z (2020) Bright and color-stable blue-light-emitting diodes based on three-dimensional perovskite polycrystalline films via morphology and interface engineering. J Phys Chem Lett 11:1411–1418
16. Wang HL, Zhao XF, Zhang BH, Xie ZY (2019) Blue perovskite light-emitting diodes based on RbX-doped polycrystalline CsPbBr₃ perovskite films. J Mater Chem C 7:5596–5603
17. Zhang L, Yuan F, Dong H, Jiao B, Zhang W, Hou X, Wang S, Gong Q, Wu Z (2018) One-step co-evaporation of all-inorganic perovskite thin films with room-temperature ultralow amplified spontaneous emission threshold and air stability. ACS Appl Mater Interfaces 10:40661–40671
18. Tenailleau C, Aharon S, Cohen B-E, Etgar L (2019) Cell refinement characteristics of CH₃NH₃PbI₃ perovskite nanocrystals and thin films. Nanoscale Adv 1:147–153
19. Zhou M, Zheng Z, Fu Q, Chen Z, He J, Zhang S, Yan L, Hu Y, Luo W (2017) Growth and characterization of all-inorganic lead halide perovskite semiconductor CsPbBr₃ single crystals. Cryst Eng Commun 19:6707–6703
20. Todorovic P, Ma DX, Chen B, Quintero-Bermudez R, Saidaminov MI, Dong YT, Lu ZH, Sargent EH (2019) Spectrally tunable and stable electroluminescence enabled by rubidium doping of CsPbI₃ nanocrystals. Adv Opt Mater 7:1901440
21. Geng YX, Yang BB, Xiang YR, Shi MM, Hu RR, Guo CF, Li YF, Zou J (2021) Preparation and research of perovskite quantum dots power based on RbCl doped CsPbBr₃. Chem Sel 6:8422–8425
22. Xiao JW, Liang Y, Zhang SY, Zhao YZ, Li YJ, Chen Q (2019) Stabilizing RbPbBr₃ perovskite nanocrystals through Cs⁺ substitution. Chem Eur J 25:2957–2963
23. West AR (2014) Solid state chemistry and its applications. Wiley, Hoboken
24. Chen L-C, Tseng Z-L, Chen C-C, Chang SH, Ho C-H (2016) Fabrication and characteristics of CH₃NH₃PbBr₃ perovskite solar cells with molybdenum-selenide hole-transport layer. Appl Phys Exp 9:122301
25. Kalachyova V, Guselnikova O, Postnikov P, Fitl P, Lapcak L, Svorcik V, Kral E, Hacker CA, Jia B (2019) The optical properties of Cs₄PbBr₆-CsPbBr₃ perovskite nanocrystals. Cryst Eng Commun 19:6797–6803
26. Liu X, Chen D, Li X, Jia B (2020) Progress in perovskite photovoltaics. ACS Energy Lett 5:2602–2604
27. Toledano P, Ma DX, Chen B, Quintero-Bermudez R, Saidaminov MI, Dong YT, Lu ZH, Sargent EH (2019) Spectrally tunable and stable electroluminescence enabled by rubidium doping of CsPbI₃ nanocrystals. Adv Opt Mater 7:1901440
28. Yeung CL, Charlesworth S, Ipalp B, Bowen J, Preece JA, Mendes PM (2013) Different formation kinetics and photoluminescence behavior of self-assembled monolayers of thiols and dithiols bearing azobenzene moieties. Phys Chem Chem Phys 15:11014–11024
29. Gan Z, Zheng F, Mao W, Zhou C, Chen W, Bach U, Tapping P, Kee TW, Davis JA, Jia B (2019) The optical properties of Cs₅PbBr₁₇-Cs₅PbBr₁₅ perovskite composites. Nanoscale 11:14676–14683
28. Sun C, Wei J, Zhao J, Jiang Y, Wang Y, Hu H, Wang X, Zhang Y, Yuan M (2021) Hard and soft Lewis-base behavior for efficient and stable CsPbBr$_3$ perovskite light-emitting diodes. Nanophotonics 10:2157–2166

29. Jiang J, Sun X, Chen XC, Wang BW, Chen ZZ, Hu Y, Gao YW, Zhang LF, Ma Y, Gao L, Zhanf FS, Jin L, Chen M, Ma ZW, Zhou YY, Padture NP, Beach K, Terrones H, Shi YF, Gao D, Lu TM, Wertz E, Feng J, Shi J (2019) Carrier lifetime enhancement in halide perovskite via remote epitaxy. Nat Commun 10:4145

Publisher’s Note
Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.