Multi-Cation Blue Perovskites Light-Emitting Diodes with Enhanced Luminescence

Yongwei Wu¹, Guang Yang¹, Pei Jiang², Bo He³, Miao Duan², Yongming Yin¹, Dongze Li², Shujih Chen², Hang Zhou¹, Chia-yu Lee² and Shengdong Zhang¹

¹Peking University, Shenzhen Graduate School, Shenzhen, China
²TCL China Star Optoelectronics Technology Co. Ltd., Shenzhen, China

*Corresponding author e-mail: sdlwyyw@gmail.com

Abstract. 2D perovskites, typically with a standard formula of L₂Aₙ₋₁MₓX₃n₊₁, have recently attracted significant attention due to their promising optoelectronic properties. Normally, they contain a mono cation (e.g., butylammonium (BA⁺) or phenylethylammonium (PEA⁺) for “L” and methylammonium (MA⁺) or formamidinium (FA⁺) for “A”). In this work, multiple cation-substitution strategy was used to improve the luminescence and emission efficiency of perovskite thin films. As a result, brightly blue emission with a high photoluminescence quantum yield of 26% was achieved. Finally, the according perovskite light-emitting diodes reached a brightness of 110 cd/m², and a maximum external quantum efficiency of 0.79%.

1. Introduction
Metal halide perovskites (MHPs) are recently emerging as a promising candidate for a series of optoelectronic applications [1-4]. In particular, due to their high photoluminescence quantum yield (PLQY), facile color tunability, solution processability, and sharp emission, perovskite light-emitting diodes (PeLEDs) have attracted significant attention. Very recently, green-emitting, red-emitting, and near-infrared-emitting PeLEDs have obtained impressive external quantum efficiencies (EQEs) exceeding 20%, which represents an important step toward the commercial applications [5-7]. Blue emissions, as one of the most important prerequisites, however, tremendously impede the progress in commercialization of PeLEDs. Blue emissions are generally considered to be in the range of ~450–500 nm, which usually require higher excitation energy or working voltage than their near-infrared, red and green counterparts.

Composition engineering on halide anions is a proven strategy to tune the bandgap of 3D perovskites. When partially replacing Br with Cl in an AMBr₃ perovskite system (where A represents monovalent cations, such as methylammonium (MA⁺) or formamidinium (FA⁺) and M represents divalent metal cations, such as lead (Pb²⁺) or tin (Sn²⁺)), it can enlarge the bandgap of perovskite and hence a hypsochromic shift from green to blue can be obtained. However, the migration of the halogen ions enables phase segregation into Cl-rich and Br-rich phases under illumination and voltage bias. Consequently, the electroluminescence (EL) wavelength undesirably transforms from blue to green when device be turned on by electrical field.

Recently, modulating the quantum-well structure to achieve reduced dimensional, i.e. 2D perovskites, has been developed as another effective approach to generate blue PeLEDs [8, 9]. Their
reduced-dimensional structure has a standard formula of \( L_2A_{n-1}M_nX_{3n+1} \), where \( L \) is a spacer cation such as butylammonium (BA\(^+\)) or phenylethylammonium (PEA\(^+\)). By keeping the quantum-well structures stay in an extremely low thickness region \((n \leq 3)\), the bandgap of 2D perovskites can be well tuned from ca. 2.7 eV \((n = 3)\), to 2.9 eV \((n = 2)\), and 3.1 eV \((n = 1)\). In addition, many other interesting properties, such as simple design of spacer cations, higher activation energy of ion migration, and more make 2D perovskites attractive. However, unfavorable characteristics have been also identified, such as the undesired orientation of the layered structures, which can cause charge-transport problems and charge accumulation. Thus PeLEDs obtained through this strategy commonly exhibit extremely low luminescence and efficiency, together with broad multiple emission peaks, because of the inefficient internal energy transfer.

As bulk polycrystalline film, multiple cation-substitution strategy has been proven to be an effective method to boost the crystallinity and optoelectronic property of perovskite films. By incorporating a second organic spacer cation isopropylammonium (IPA\(^+\)) into the perovskite of PEA\(_2\)A\(_{1.5}\)Pb\(_{2.5}\)Br\(_{8.5}\), Sargent’s group successfully developed a mixing-cation 2D perovskite with single emission peak and color-stable blue emission. Studies also have shown that cesium (Cs\(^+\)) ions are effective in assisting the crystallization of perovskite due to entropic stabilization. By partially replacing MA\(^+\) with Cs\(^+\), Liu et al. reported that both the grain size and surface quality of 2D perovskite films are effectively improved, resulting in reduced trap state density, superior charge carrier mobility. However, the synergetic doping of multi-caiton, such as Cs\(^+\) and IPA\(^+\), into perovskite thin films is seldom explored in the entire PeLED community, especially for blue emission of 2D perovskites.

Here, multi-cations were introduced to PEA\(_2\)FA\(_{1.5}\)Pb\(_{2.5}\)Br\(_{8.5}\) to form PEA\(^+\)-IPA\(^+\)-Cs\(^+\)-FA\(^+\) 2D perovskites. We find that the films exhibit smooth, compact surface morphology compared to the pristine 2D perovskites of PEA\(_2\)FA\(_{1.5}\)Pb\(_{2.5}\)Br\(_{8.5}\). In addition, bright blue thin film with a quantum yield of 26% was also achieved. Finally, the PeLEDs are up to a luminescence of 110 cd/m\(^2\), and a maximum EQE of 0.79%.

2. Results and Discussion

2.1. Optical properties

Blue emission 2D perovskites of PEA\(^+\)-IPA\(^+\)-FA\(^+\)-Cs\(^+\) were fabricated using a one-step solution-based process. Their compositions were controlled through the ratios of PEABr: IPABr: FABr: CsBr: PbBr\(_2\) in dimethyl sulfoxide (DMSO) and a targeted average perovskite formula of \((PEA_mIPAk)_2(FA_{1-x}Cs_x)_{1.5}Pb_{2.5}Br_{8.5} \) \((0 \leq x \leq 1)\) was gently accomplished.

Fig 1a shows PL spectra of the perovskite films. Pristine PEA\(_2\)(FA\(_x\)Cs\(_{1-x}\))\(_{1.5}\)Pb\(_{2.5}\)Br\(_{8.5}\) \((x = 0.8)\) perovskite emits green light (at 522 nm); the addition of IPABr, as expected, sharply shifts the PL peak to 489 nm with a FWHM of around 28 nm. In particular, by tuning the values of \(x\) (controlled by the fractions of FABr and CsBr), significant PL enhancement is observed (Fig 1b) and as summarized in Table 1, an optimized PLQY of 26% were obtained with the PL peak at 484 nm. UV−Vis absorption spectra were used to characterize the optical bandgap and excitonic features of these perovskites and as shown in Fig 1b, multiple excitonic absorption peaks are observed, corresponding to the perovskite phases with different \(n\) values, which are consistent with previous reports, confirming that 2D perovskites contain a variety of \(n\) phases rather than a single component. The extremely similar absorption profile of different \(x\) values perovskites indicates that the varied FA and Cs fractions have little effect on the formation of different \(n\) phases.
Figure. 1 Optical properties of multi-cation 2D perovskites films. (a) PL of 2D perovskites with and w/o IPA; (b) PL of 2D perovskites with different Cs ratios; Inset: UV-Vis absorption of 2D perovskites with different Cs ratios.

Table. 1 Different x values perovskites and their corresponding optical properties

| Items  | PL Peak (nm) | FWHM (nm) | PLQY (%) |
|--------|--------------|-----------|-----------|
| x 0.8  | 490          | 28        | 11        |
| x 0.7  | 487          | 30        | 17        |
| x 0.6  | 485          | 28        | 26        |
| x 0.5  | 481          | 29        | 18        |

2.2. Morphology
The morphology of perovskite thin films is another important factor governing the luminescence property and final performance of perovskite LEDs. Therefore, we used a scanning electron microscope (SEM) to characterize the morphology of perovskite thin films with different cations and different ratios. Figure 2a shows that the pristine PEA$_2$FA$_{1.5}$Pb$_{2.5}$Br$_{8.5}$ film has a rough and uneven morphology with obvious pinholes. However, after the introduction of IPABr and CsBr, perovskite films with better morphology and coverage were obtained. As the CsBr ratio increased, more and more dense and uniform film is observed, suggesting improved crystal quality of the perovskite thin film. Particularly for the x = 0.7 and 0.6 case, smooth, compact, uniform full coverage film was obtained, correlated well with their low trap density and high PLQY. However, when we further increased the CsBr ratio with x = 0.5, the film morphology became rough. It is likely that too much Cs induces decreased solubility and speeds up the crystal process, resulting in relatively uneven morphology, with a similar phenomenon also being observed in previous reported 2D perovskites.

Figure. 2 SEM images of multi-cation 2D perovskites films. (a) x = 1 w/o IPA; (b) x = 0.8; (c) x = 0.7; (d) x = 0.6; (e) x = 0.5.
2.3. Device performance

Encouraged by the above results, we further fabricated PeLEDs using 2D perovskite with the ratio of x = 0.6. Compared to 3D perovskites, 2D perovskites exhibit lower conductivity and thus their LED architecture usually requires thinner active layers. As indicated in Figure 3a, we configured PeLEDs as the structure: ITO/PEDOT: PSS/perovskite film/TPBi/LiF/Al. Both devices emitted bright sky-blue light with the emission peak at 491 nm, which is a little redshift according to their photoluminescence (Figure 3b and Table 1). The narrow emission was also successfully inherited from perovskite film’s PL with the FWHM around 28 nm. Particularly, the provskite of (PEAmIPAk)2(FA1-xCsx)1.5Pb2.5Br8.5 with x = 0.6 displays a significant luminance of 110 cd m⁻², and EQE of 0.79%. Notably, the result represents one of the most luminescent and efficient blue PeLEDs reported so far.

![Figure 3](image)

**Figure. 3** Device structure and performance. (a) Device structure of multi-cation 2D perovskites LEDs; (b) EQE-V-L characteristic curves of the PeLEDs; Inset: EL spectra of the PeLEDs.

3. Conclusion

In summary, we demonstrated an approach to obtain highly luminescent blue PeLEDs. The approach focuses on 2D perovskite and multi-caiton mixing for ‘A-site’ cation and organic cation spacer. We herein introduced multi-cations to PEA₂FA₁.₅Pb₂.₅Br₈.₅ to form PEA⁻̂IPA⁻̂Cs⁻̂FA⁺ 2D perovskites. The resultant smooth and uniform film displays highly bright blue emission. Efficient PeLEDs have been successfully fabricated from these perovskite films and the devices show highly luminescent emission and high EQE.

Acknowledgments

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