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Phase control of quasi-2D halide perovskite by post-treatment and antisolvent treatment techniques

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Abstract. The fabrication of efficient and stable deep blue halide perovskite light-emitting diodes has attracted significant interest nowadays due to their potential applications in next-generation display technologies. Quasi-2D halide perovskite seems to be perfect material for this application, owing to their unique optoelectronic properties and tunability. However, during the deposition from stoichiometrically clear phase solution mixture of phases is forming in the thin film leading to redshift of luminescence peak. This shift occurs due to energy transfer between different phases, affecting the performance and stability of the light-emitting diode. In this study, we explore various approaches for phase control in multiple quantum well structures to achieve stable and efficient emission in the blue region. Additionally, we conduct a comparative analysis of two distinct quasi-2D ligands used in the synthesis of these materials, evaluating their influence on the optical and electronic properties. We study possible ways for synthesis of pure phase quasi-2D perovskite thin films for their implementation in light-emitting diodes.

Keywords: quasi-2D halide perovskite, phase control, photoluminescence, absorption spectroscopy

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Контроль фаз в квазидвумерном галогенидном перовските с помощью методов постобработки и обработки антирастворителем

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Аннотация. Данное исследование изучает различные подходы для контроля фаз в квази-двумерных перовскитных тонких пленках для получения стабильного излучения в синей области видимого спектра. Мы сравниваем различные подходы, а также квазидвумерные лиганды для их дальнейшего применения в изготовлении светодиодов.

Ключевые слова: квазидвумерный галогенидный перовскит, фазовый контроль, фотолюминесценция, абсорбционная спектроскопия

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Introduction

Quasi-2D halide perovskites are currently attracting significant interest due to their remarkable properties and diverse applications in photonics and optoelectronics. One of the most promising areas is in perovskite light-emitting diodes (PeLEDs), where the incorporation of quasi-2D perovskites has enabled the achievement of brightness exceeding 10^5 cd/m^2 and external quantum efficiency (EQE) over 30% [1]. Moreover, these materials are valuable for the development of efficient and stable deep blue PeLEDs [2]. For instance, the excitonic peak of the widely used phenethylammonium (PEA)-based quasi-2D perovskite phase $PEA_2MA_{n-1}Pb_nBr_{3n+1}$, where $n = 2$, exhibits a deep blue luminescence wavelength around 450 nm [3]. Another unstudied but promising ligand for stable PeLED applications is methyl-phenethylammonium (MePEA) [4]. However, even a stoichiometric $n = 2$ solution can result in a mixture of phases during deposition, leading to a redshift in the luminescence peak due to energy transfer between these phases. Consequently, effective phase control in quasi-2D halide perovskites is crucial for the development of stable blue PeLEDs.

Materials and Methods

$PEA_2FAPb_2Br_7$ and $MePEA_2FAPb_2Br_7$ quasi-2D perovskite were prepared using stoichiometric mixtures of 0.3 mmol PbBr2 (>99.9%), 0.15 mmol FABr (>99.9%) and 0.3 mmol MePEABr or PEABr (>98%) in dimethyl sulfoxide. The solution was deposited and stored in a glove box filled with nitrogen atmosphere. Halide perovskite thin films were deposited via spin-coating method using a one-step spin-cycle with 2000 rpm to obtain a film with thickness of 60–80 nm. For antisolvent treatment 0.3 ml of toluene was dripped during the spin-coating deposition. For post-treatment techniques diluted polar solvent with toluene was deposited on formed perovskite thin film [5]. Absorption spectra were measured using a UV-Vis-NIR spectrophotometer UV-3600 Plus (Shimadzu). The instrument is equipped with a grating–grating dual-monochromator system, which minimizes stray light and allows for high-accuracy spectral measurements. A deuterium lamp was employed as the radiation source for the ultraviolet region, while a tungsten–halogen lamp provided illumination for the visible and near-infrared regions. Spectral detection across the range of 185–3300 nm was achieved using three detectors: a photomultiplier tube for the ultraviolet–visible region, and InGaAs and cooled PbS detectors for the near-infrared region. Photoluminescence (PL) spectra were obtained using a QE pro Ocean optic spectrometer

connected to the Axio Imager.A2m (Carl Zeiss SMT) optical microscope via fiber optic, with optical pumping provided by a UV lamp emitting at a wavelength of 350 nm. Atomic force microscopy (AFM) was made on AIST-NT SmartSPM 1000.

Results and Discussion

In this work, we study approaches for phase control in quasi-2D perovskite, using two treatment techniques. The first technique involves antisolvent treatment. We examined two types of quasi-2D ligands, PEA and a novel MePEA, and demonstrated that this antisolvent method is effective for both ligands.

Although we employ a stoichiometric solution for quasi-2D perovskite with $n = 2$, the thin film deposited via the spin-coating technique consists of a mixture of different phases, as illustrated in Fig. 1, *a* and 1, *b* (green curves). In addition to the $n = 2$ phase, we clearly observe an excitonic peak corresponding to $n = 1$ and another peak associated with the bandgap of bulk $FAPbBr_3$ perovskite. Due to energy transfer between these quasi-2D phases, peak shifts closer to the wavelength of bulk $FAPbBr_3$, as shown in Fig. 1, *c* and 1, *d* (green curves).

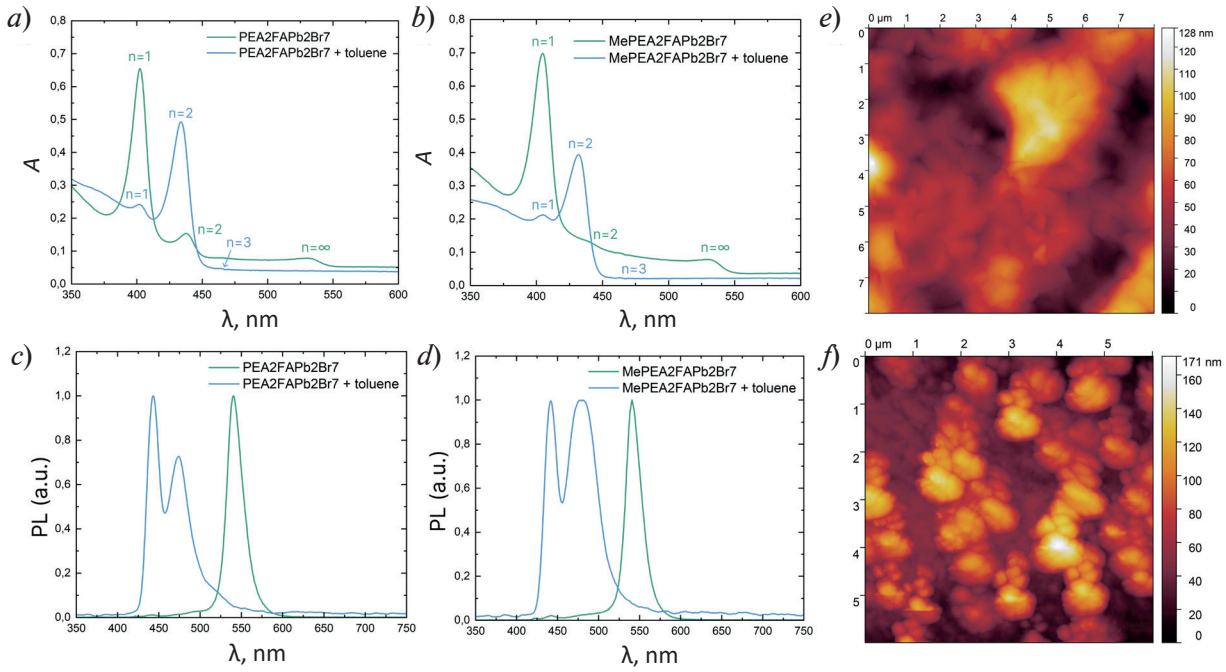

Fig. 1. Antisolvent treatment technique. Absorption spectra for $PEA_2FAPb_2Br_7$ with and without toluene treatment (*a*). Absorption spectra for $MePEA_2FAPb_2Br_7$ with and without toluene treatment (*b*). Normalized PL spectra for $PEA_2FAPb_2Br_7$ with and without toluene treatment (*c*). Normalized PL spectra for $MePEA_2FAPb_2Br_7$ with and without toluene treatment (*d*). AFM image of $PEA_2FAPb_2Br_7$ thin film without toluene treatment (*e*). AFM image of $PEA_2FAPb_2Br_7$ thin film with toluene treatment (*f*)

There are several methods to control the phase formation in quasi-2D perovskite thin films. By dripping toluene at a specific time during the spin-coating process, we can promote the formation of the quasi-2D phase with $n = 2$, as illustrated in Fig. 1, *a* and 1, *b* (blue curves), while reducing or even washing away unwanted phases. This approach enables us to achieve blue photoluminescence with two distinct peaks at 450 nm ($n = 2$ phase) and 470 nm ($n = 3$ phase), as shown in Fig. 1, *c* and 1, *d* (blue curves). Furthermore, while removing higher n phases, this method also reduces the amount of the $n = 1$ phase (peak near 400 nm in the absorption spectra), which contains many dielectric quasi-2D ligands that can decrease the electrical conductivity of the thin films. The full width at half maximum (FWHM) values of the absorption spectra were analyzed to evaluate the effect of toluene treatment on the optical properties of the films. For the $PEA_2FAPb_2Br_7$ samples (Fig. 1, *a*), the untreated film exhibited FWHM values of 12.76 nm

for the $n = 1$ peak and 11.73 nm for the $n = 2$ peak. After toluene treatment, the corresponding values were 8.48 nm ($n = 1$) and 14.45 nm ($n = 2$). For $MePEA_2FAPb_2Br_7$ (Fig. 1, *b*), the untreated sample displayed a FWHM of 15.15 nm for the $n = 1$ peak, while the $n = 2$ peak was barely distinguishable. Following toluene treatment, in general, the MePEA-based films exhibited slightly larger FWHM values than the PEA-based films, although the differences were relatively small.

Similar trends were observed in the photoluminescence (PL) spectra (Fig. 1, *c* and 1, *d*). For $PEA_2FAPb_2Br_7$, the untreated sample showed a single emission peak with a FWHM of 22.93 nm. In contrast, the toluene-treated film exhibited two emission peaks: one at 443 nm (FWHM = 14.17 nm) and another at 473 nm (FWHM = 30.10 nm). For $MePEA_2FAPb_2Br_7$ PL spectra on Fig. 1, *d* FWHM is 22.29 nm, and for $MePEA_2FAPb_2Br_7$, the untreated film displayed an emission peak with a FWHM of 22.29 nm. Upon toluene treatment, two peaks emerged at 442 nm (FWHM = 22.61 nm) and 481 nm (FWHM = 45.96 nm). Notably, the toluene-treated MePEA-based films exhibited broader PL emission compared to the PEA-based counterparts.

Additionally, atomic force microscopy (AFM) was employed to compare the morphology of thin films before and after toluene treatment. Fig. 1, *e* and 1f display images of $PEA_2FAPb_2Br_7$ thin films: one without toluene treatment (Fig. 1, *e*) and the other with treatment (Fig. 1, *f*). Both films exhibit relatively similar morphological characteristics; however, small difference is observed in the average grain sizes. The average grain size in the perovskite film after toluene treatment is smaller compared to the thin film without treatment. This reduction in grain size may influence the material's properties and performance in potential device applications.

The second method involves post-treatment, originally described in work [5]. This approach also reduces the intensity of unwanted excitonic peaks in the absorption spectrum; however, it decreases the intensity of all peaks, albeit at different ratios. In this technique a polar solvent (DMF) is mixed with antisolvents (toluene) to make a 15% DMF solution in our case. This mixture is deposited on the surface of the fully-formed perovskite film for a few seconds. After that, the substrate rotates at high speed. This brief exposure helps to reduce certain unwanted quasi-2D phases, especially the low-n phases, without damaging the thin film itself. A 15% DMF solution in toluene can significantly reduce the $n = 1$ phase in PEA-based perovskite, while the $n = 2$ phase remains largely unchanged, as illustrated in Fig. 2, *a*.

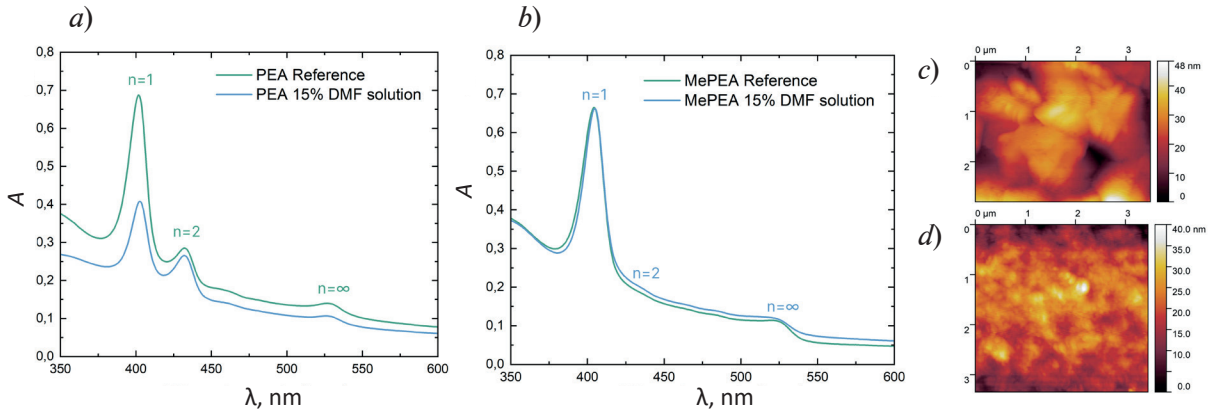

Fig. 2. Post-treatment technique: $PEA_2FAPb_2Br_7$ post-treatment with 15% DMF solution (*a*). $MePEA_2FAPb_2Br_7$ post-treatment with 15% DMF solution (*b*). AFM image of AFM image of $PEA_2FAPb_2Br_7$ thin film before solvent post-treatment (*c*). AFM image of AFM image of $PEA_2FAPb_2Br_7$ thin film after solvent post-treatment (*d*)

Quasi-2D perovskites that use a methyl-substituted PEA derivative, known as MePEA, show improved stability against moisture and polar solvents compared to traditional PEA-based quasi-2D perovskites. When exposed to a 15% DMF solution, which can greatly decrease the $n = 1$ phase of the PEA-based thin film, the MePEA-based perovskite thin film remains mostly unaffected, as illustrated in Fig. 2, *b*. This demonstrates that MePEA-based perovskite films have enhanced structural stability compared to PEA-based quasi-2D halide perovskites.

Furthermore, the AFM images of PEA-based thin films (Fig. 2, *c* and 2, *d*) reveal an improved morphology following solvent post-treatment. This technique effectively dissolves and removes some of the thin film's surface. Such uniformity is crucial for future device applications, as it can significantly influence charge transport, reduce defects, and improve overall device performance. The observed morphological enhancements suggest that solvent post-treatment could be a promising strategy for optimizing PEA-based materials in various optoelectronic applications.

Conclusion

Our research demonstrates effective methods for controlling the formation of quasi-2D phases in halide perovskites. This approach enables us to achieve clearer quasi-2D perovskites, shifting the luminescence peak to a deep blue region, in contrast to the initial green luminescence, while also reducing the presence of the highly dielectric $n = 1$ phase in the thin film. Furthermore, we compared two different quasi-2D ligands and discovered a new property of MePEA-based perovskite films, which exhibit greater structural stability against solvent influence. These findings represent significant progress toward the development of efficient and stable deep blue PeLEDs.

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REFERENCES

1. **Bai W., et al.,** Perovskite light-emitting diodes with an external quantum efficiency exceeding 30%, Adv. Mater. 35 (39) (2023) 2302283.

2. **Zhou N., et al.,** Co-Interlayer Engineering for Homogenous Phase Quasi-2-D Perovskite and High-Performance Deep-Blue Light-Emitting Diodes, Adv. Optical Mater. 12 (18) (2024) 2302273.

3. **Kim J., et al.,** Spectrally Stable Deep-Blue Light-Emitting Diodes Based on Layer-Transferred Single-Crystalline Ruddlesden–Popper Halide Perovskites, ACS Applied Materials & Interfaces. 16 (5) (2024) 6274–6283.

4. **Alahbakhshi M., et al.,** Highly efficient quasi 2D blue perovskite electroluminescence leveraging a dual ligand composition, Adv. Funct. Mater. 33 (28) (2023) 2214315.

5. **Ding S., et al.,** Phase dimensions resolving of efficient and stable perovskite light-emitting diodes at high brightness, Nature Photonics. 18 (4) (2024) 363–370.

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