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Suppressed phase segregation in $CsPbIBr_2$ based PeLEC

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Abstract. In this work we describe some strategies to suppress phase segregation in perovskite light-emitting electrochemical cells based on mixed halide $CsPbIBr_2$ perovskite. Lead halide perovskites are widely used class materials used for creating optoelectronic devices. However, appearing phase segregation causes peak separation on photo- and electro luminance spectra, which limit efficiency and color rendering of devices based on lead halide perovskite materials. Improving crystallinity of perovskite film by annealing temperature controlling can affect halide separation. Mn^{2+} doping was used to enhance materials stability of lead halide perovskite. Another strategy is crystal grains passivation by polymers, i.e. polyethylene oxide and polyvinylidene fluoride, which reduce crystal defect density that cause phase segregation. All these strategies were applied in this work and demonstrate single peaks on photo- and electro luminance spectra. Suggested solution of phase segregation problem allows to create more stable and effective $CsPbIBr_2$ based perovskite light-emitting electrochemical cells that work in red range of visible spectrum (620-680 nm).

Keywords: $CsPbIBr_2$, perovskite, PeLEC, phase segregation, mixed anion

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Материалы конференции
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Подавленная фазовая сегрегация в $CsPbIBr_2$ PeLEC

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Аннотация. В данной работе предложены способы подавления фазовой сегрегации в светоизлучающих ячейках на основе свинцово-галогенидных перовскитов со смешанным типом аниона. Оптимальный температурный режим отжига, легирование ионами марганца, а также пассивация кристаллических зерен полимерной матрицей позволяют улучшить стабильность перовскитного материала за счет улучшения кристаллической структуры перовскитных пленок.

Ключевые слова: $CsPbIBr_2$, перовскит, PeLEC, фазовая сегрегация, смешанный анион

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Introduction

Lead-halide perovskites (LHP) are semiconductor materials used as an active layer in light-emitting devices and solar cells. The advantages of LHP are the simplicity of synthesis and the high external quantum efficiency of the devices. Perovskite light-emitting electrochemical cell (PeLEC) is one of the possible device types based on LHP. PeLECs stand out due to their high luminance (~100 000 cd/m^2 for "green" PeLEC) and simple device design. [1].

Using of PeLECs is a relatively new approach to fabricating light-emitting devices. For the synthesis of all-inorganic lead-halide PeLECs operating in the red spectral range, it is necessary to use mixed anion (halide) ($CsPbI_xBr_{3-x}$) compositions to achieve luminance at the desired wavelength [2].

However, perovskites with a mixed halogen composition have a lower photoluminescence quantum yield and quantum efficiency compared to perovskites with single halogen, which is due to the occurrence of phase segregation, i.e., spatial separation of the different halide ions and formation of narrow and wide band gap areas. Phase segregation leads to trap states density increase and changes the band gap width, limiting the structure's external quantum efficiency and photoluminescence quantum yield. The domains with different bandgaps cause two or more peaks in the photo- (PL) and electroluminescence (EL) spectra [3].

There are several ways to suppress phase segregation:

1) improving crystallinity to reduce trap state density, which occurs on crystal surfaces and grain boundaries [4];

2) surface and grain boundary passivation (modification), for example, by polyethylene oxide (PEO) and polyvinylidene fluoride (PVDF) [1];

3) B-site doping, for example, by Mn^{2+}, Sn^{2+}, or Ba^{2+} [5].

In this work, we apply these techniques for reducing phase segregation in the all-inorganic $CsPbIBr_2$-based PeLECs, operating in a red spectral range. Improving the crystallinity of perovskite grains by temperature control, doping with Mn and passivation by the mixed polymer matrix PEO/PVDF allow to suppress phase segregation.

Materials and Methods

For studying the phase segregation phenomenon, two types of samples were fabricated. The first type is films, which consist of a perovskite-polymer layer on glass. The second type is devices, which consist of glass substrates with an indium tin oxide (ITO) layer (as a bottom electrode), a polystyrene sulfonate (PEDOT:PSS) layer (as a hole transport layer (HTL)), a perovskite-polymer layer, LiF (as a buffer layer), 2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (as an electron transport layer (ETL)), and LiF/Al layers (as top contact). Fig. 1 shows the PeLEC device structure.

To create the perovskite light-emitting layer, a perovskite-polymer solution was made. It contains: 1) 0.4 molar concentration solution of $CsPb_xMn_{1-x}IBr_2$, 2) a solution of PEO with a molecular weight of 10^6 and a concentration of 20 mg/ml, 3) a solution of PVDF with a molecular weight of 534000 and a concentration of 40 mg/ml, and 4) a solution of lithium salts (10 mg/ml). Dimethyl sulfoxide (DMSO) was used as a solvent for all solutions. These four solutions were

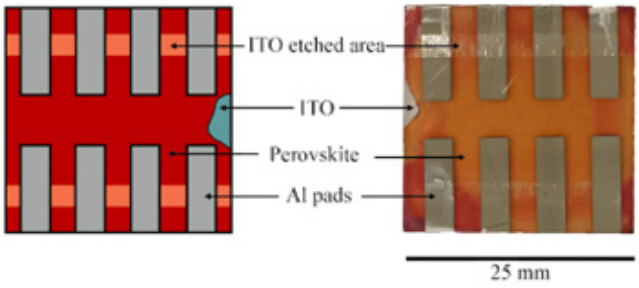

Fig. 1. Sample scheme (left panel) and photo (right panel) from the back (Al contact side)

stirred (300 rpm, 60 °C, 1 day). Then all the solutions had been mixed and stirred (300 rpm, 25 °C, 1 day). All solutions were made in a dry N_2 atmosphere in the glovebox system. The film was fabricated via composite solution drop-casting and spin-coating at 1000 rpm for 1 min. Then vacuum treatment was performed (10^{-3} bar ,1 min). In the final step, samples were annealed at (T_{ann})=70 or 80 °C for 5 min. To study the effects of improving crystallinity, polymer passivation and B-site doping films with different T_{ann} (70 and 80 °C), PEO:PVDF ratios (1:4 and 1:9) and Mn^{2+} amount (0 and 5%) were used. Sample notation and description are presented in Table 1.

Table 1

Sample notation and description

Notation	T_{ann}	Mn, %	PEO:PVDF ratio
S1	80	0	1:9
S2	80	5	1:9
S3	70	5	1:9
S4	70	5	1:4

For light-induced phase segregation analysis, PL spectra and PL optical images were obtained. Scanning electron microscopy (SEM) was performed to compare the film's morphology. To study electrical-field induced phase segregation, EL spectra measurements were obtained.

Results and Discussion

Fig. 2, *a* shows PL spectra of perovskite-polymer films. Among all the samples, only S4 demonstrated one PL peak, which shows that the proposed composition and treatments suppress phase segregation. Sample S4 presents the most homogenous surface morphology through all the obtained film, which is clearly seen on PL optical images (Fig. 2, *b*).

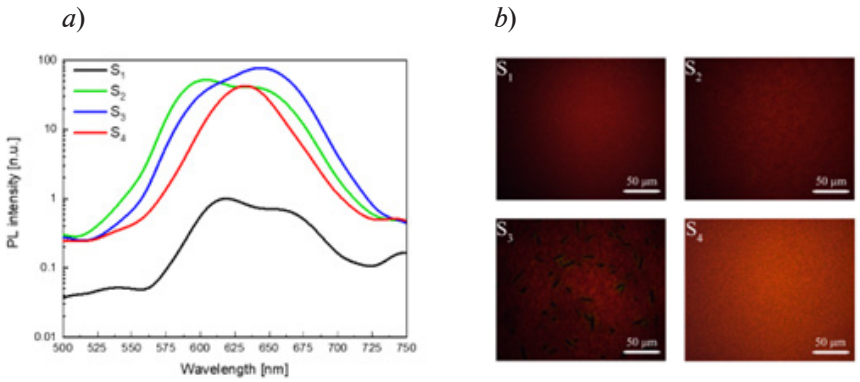

Fig. 2. PL spectra (*a*), PL optical images (*b*)

For a more detailed surface studying, SEM images were analyzed (Fig. 3, *a*). Sample S4 does not have long polymer-rich domains compared with other samples, which means better PEO:PVDF distribution and perovskite crystal passivation.

Sample S4 demonstrates outstanding properties due to its composition and technological treatment. A device was made based on the S4 film to study electrical-field induced phase segregation. Fig. 3, *b* shows dynamic EL spectra of developed device. As well as PL spectra, EL spectra demonstrate single peak, which indicates prevented phase segregation. It should be noted that EL peak position has a red shift compared with PL peak, which can be explained by increasing defect state density caused ion migration under applied voltage.

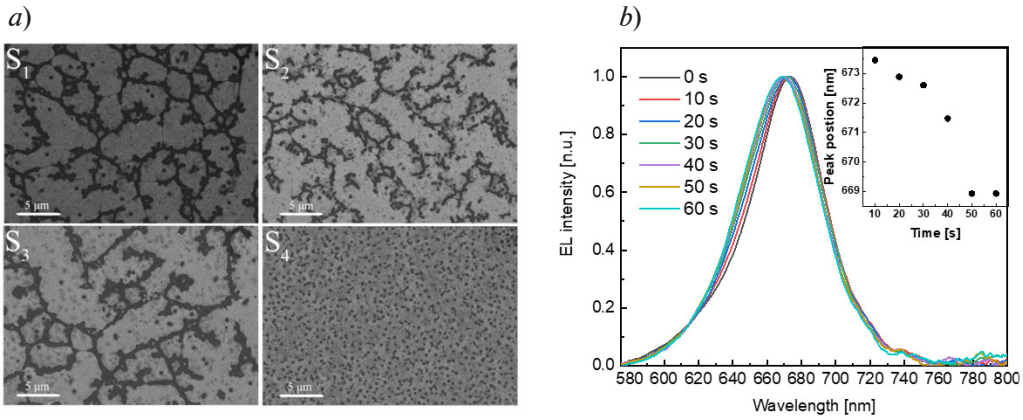

Fig. 3. SEM images (*a*), dynamic EL spectra (*b*)

Conclusion

We have described a method for suppressing phase segregation in inorganic mixed lead-halide PeLEC. B-site doping by Mn and PEO:PVDF passivation allows to obtain PeLEC stable to photo and electrical-field induced phase segregation.

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