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Electric field-induced segregation in a sky-blue perovskite light-emitting diode based on CsPbBr₂Cl:PEO composite

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Abstract. Perovskite light-emitting diodes (pero-LEDs) is a rapidly developing technology that is supposed to supersede existing ones in the near future. In comparison with organic and A^{III}B^V analogues, pero-LEDs possess the following advantages: very narrow spectral linewidth of electroluminescence (EL), spectral tunability in the whole visible range and the possibility of a cost-effective large-scale fabrication by means of wet chemistry techniques. CsPbX₃ (X = Cl, Br, I) are the most robust perovskites suitable for LEDs production due to their excellent optical properties. There are numerous reports describing green and red electroluminescence of such tribromide and triiodide materials, respectively, whereas a blue color is not easy to achieve. The main obstacles in the way of development of blue pero-LEDs based on chlorine salts are poor solubility of perovskite precursors in the same organic solvents as well as light- and an electric field-induced phase instability of mixed-halide (CsPbBr_{3-x}Cl_x) materials. The latter leads to red-shift of EL spectrum with the increase in applied voltage. In this work, we present a design of a single-layer sky-blue pero-LED based on CsPbBr₂Cl-poly(ethylene oxide) (PEO) thin film, study the morphology of the emissive layer, its phase instability under UV illumination and in the electric field.

1. Introduction

Last decade light-emitting diodes based on organic molecules (OLED), quantum dots (QLED), and perovskites (pero-LED) aspire to supersede well established, however, hazardous and expensive A^{III}B^V technology. The outstanding performance was achieved for diodes emitting green and red light, whereas high efficiency and long-term stability of blue electroluminescent (EL) devices still remain challenging. The main drawback of organic blue light-emitting diodes stems from the bimolecular triplet-polaron annihilation (TPA).[1] Simply put electroluminescence is a result of radiative decay of excitons formed by electrons and holes injected into the emissive layer from electrodes. According to quantum spin statistics, singlet and triplet excitons are formed with a ratio of 1:3.[2] Singlet excitons, which are also called "bright", undergo fast radiative decay. On the contrary, triplet excitons are "dark", because they



have a much longer lifetime than that of "bright" ones, and therefore mostly experience non-radiative relaxation via defect states. However, when the triplet exciton located on an excited molecule transfers its energy to a nearby charged molecule (polaron) it results in the formation of a high-energy polaron. During the thermalization, the latter capable of breaking chemical bonds in the molecule on which it resides. Thus, besides quantum spin statistics dictating the EL efficiency cannot exceed 25%, numerous defects which, to some extent, deactivate singlet excitons are produced. Similar "dark" excitons are responsible for low photo- and electroluminescence quantum efficiency in conventional colloidal quantum dots made from cadmium chalcogenides.[3] On the contrary, cesium lead halide perovskites (CsPbX_3 ; $\text{X} = \text{Cl, Br, I}$) possess "bright" triplet excitons[4] which energy can be altered from 1.72 to 3.1 eV by halide anion exchange in the crystal lattice.[5] For this reason, mixed-halide $\text{CsPbBr}_{3-x}\text{Cl}_x$ ($1 \leq x \leq 3$) perovskites yielding narrow-band emission in 410–480 nm range are promising candidates for the development of blue light electroluminescent devices.

In the meanwhile, mixed-halide perovskites have been shown to demonstrate light- and electric field-induced phase instability which originates from anion migration (segregation) in the crystal lattice.[6,7] As a result, new perovskite domains enriched with one sort of halogen atoms are formed. The low band gap domains act as excitonic funnels, and hence change the luminescence peak position and its intensity.

Herein, we fabricate pristine CsPbBr_2Cl and composite $\text{CsPbBr}_2\text{Cl}:\text{PEO}$ (PEO - poly(ethylene oxide)) thin films and study their structure, photo-, and electroluminescence. The polymer is found to be preventing the perovskite from light-induced segregation. However, stable blue electroluminescence ($\lambda_{\text{max}} = 480 \text{ nm}$) from a single-layer ITO/ $\text{CsPbBr}_2\text{Cl}:\text{PEO}$ (300 nm)/Ga-In (ITO – indium tin oxide; Ga-In – gallium–indium eutectic) pero-LED operating at 2.8 V bias experiences more than 20 nm redshift at 3.2 V. These observations manifest that an electric field-driven segregation in the studied composite film occurs when the field in the single-layer structure exceeds $1 \times 10^5 \text{ V/cm}$.

2. Results

To obtain CsPbBr_2Cl thin film (70 nm), CsPbBr_3 film on a glass substrate was exposed to HCl vapor (0.2 mg/cm^3) for 8 s at 120°C and then gradually heated up to 200°C to eliminate crystal lattice defects. The tribromide film was deposited by spin-casting a perovskite solution (mixture of PbBr_2 (110 mg) and CsBr (70 mg) in 3 ml of anhydrous dimethyl sulfoxide) at 2500 rpm for 5 min and subsequent gradual annealing of the sample on a hotplate from 50°C up to 150°C .

$\text{CsPbBr}_2\text{Cl}:\text{PEO}$ film with a thickness of 300 nm was deposited onto an ITO substrate by spin-casting a perovskite-polymer solution (mixture of PbBr_2 (14.6 mg), CsCl (7 mg), and PEO (10 mg) in 1.4 ml of methanol:dimethyl sulfoxide mixed in the ratio 1:6) at 2500 rpm for 1 min. Then, the film was gradually annealed on a hotplate from 50°C up to 200°C to give dense-packed small perovskite grains covered with a thin polymer layer. Note that the preparation of the solutions and spin-casting were carried out in a N_2 -filled glove box, whereas the chemical vapor anion exchange procedure was conducted outside the glove box.

According to fluorescence microscopy images, both films have a pinhole-free surface morphology. However, in the case of composite film, CsPbBr_2Cl aggregates were observed which confirms that perovskite precursors are not ideally dispersed in PEO (Fig. 1a). A room-temperature crystal phase was determined by X-ray powder diffraction (XRD). XRD patterns revealed that both samples contain the same perovskite adopting an orthorhombic crystal structure (Fig. 1b).[8] Under continuous-wave UV light excitation ($\lambda_{\text{ex}} = 360 \text{ nm}$, $P = 10 \text{ W/cm}^2$) the polymer-free sample demonstrated extremely fast segregation for 1 s, while polymer-stabilized CsPbBr_2Cl grains did not show any spectral changes over 1000 s (Fig. 1c). Such a behavior can be explained in terms of the surface free energy of the perovskite submicron

grains and its contribution to their Gibbs free energy. The polymer-free grains stick together which reduces their surface energy, whereas separate grains coated with a polymer shell have the surface energy exceeding the volume one. Thus, a volume phase of the core-shell submicron particles is stabilized by their high surface energy.

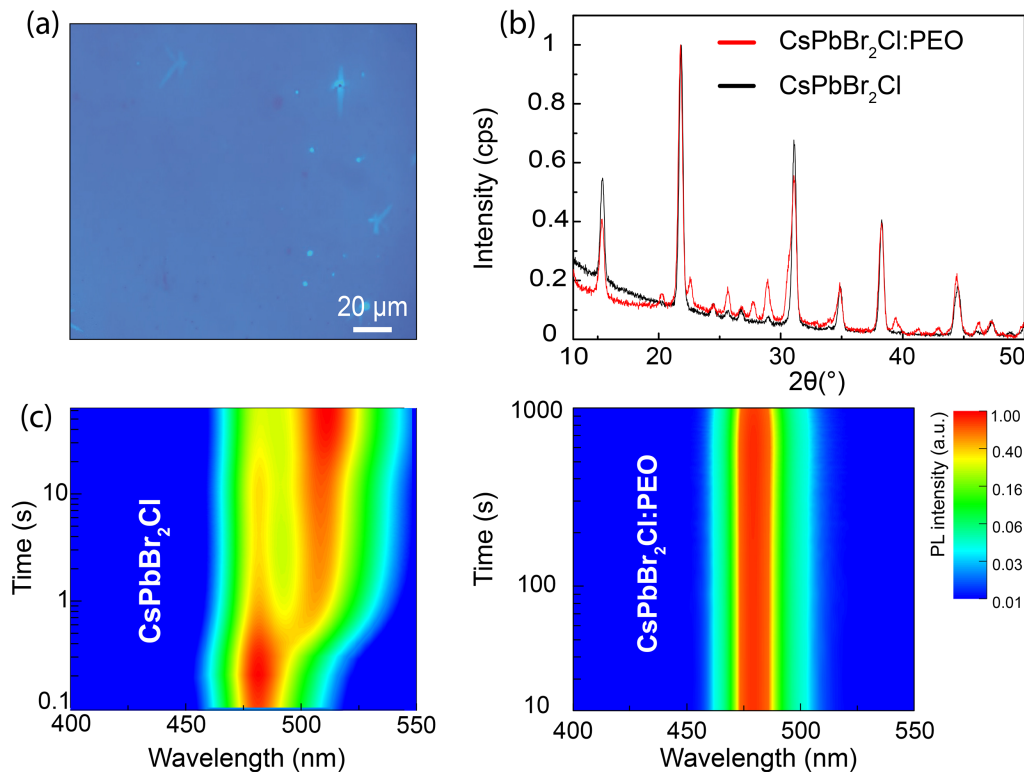


Figure 1. (a) Fluorescence microphotograph of the perovskite-polymer film. (b) XRD patterns of the samples. (c) Photoluminescence dynamics for the films illuminated with intense UV light.

Encouraged by the enhanced phase stability of the perovskite-polymer composite, we deposited a Ga-In electrode on top of the film (Fig. 2a) and examined its electroluminescence. The working mechanism (Fig 2b) of the manufactured pero-LED can be described as follows: i) a voltage applied between two electrodes creates electrostatic field which, in turn, invokes a partial dissociation of the perovskite into cations (Cs^+) and anions (Cl^- and Br^-) drifting in a solid electrolyte (PEO) towards the cathode (Ga-In) and anode (ITO), respectively; ii) PIN diode is formed; iii) holes and electrons tunnel through the thin energetic barriers and recombine radiatively in the region of intrinsic perovskite. The model that governs similar pero-LED operation is called the electrochemical doping (ECD).[9] According to this model, there is a non-zero electrostatic field in the intrinsic semiconductor region. The examined pero-LED showed stable sky-blue emission with $\lambda_{max} = 480$ nm and luminance (L) of about 50 cd/m^2 at 2.8 V bias (Fig. 2c). Further increase in the applied voltage led to a luminance enhancement along with a redshift of EL spectrum. For instance, at 3.2 V the diode gave intense light ($L \approx 500 \text{ cd/m}^2$) corresponding to a greenish-blue emission at 505 nm (Fig. 2c).

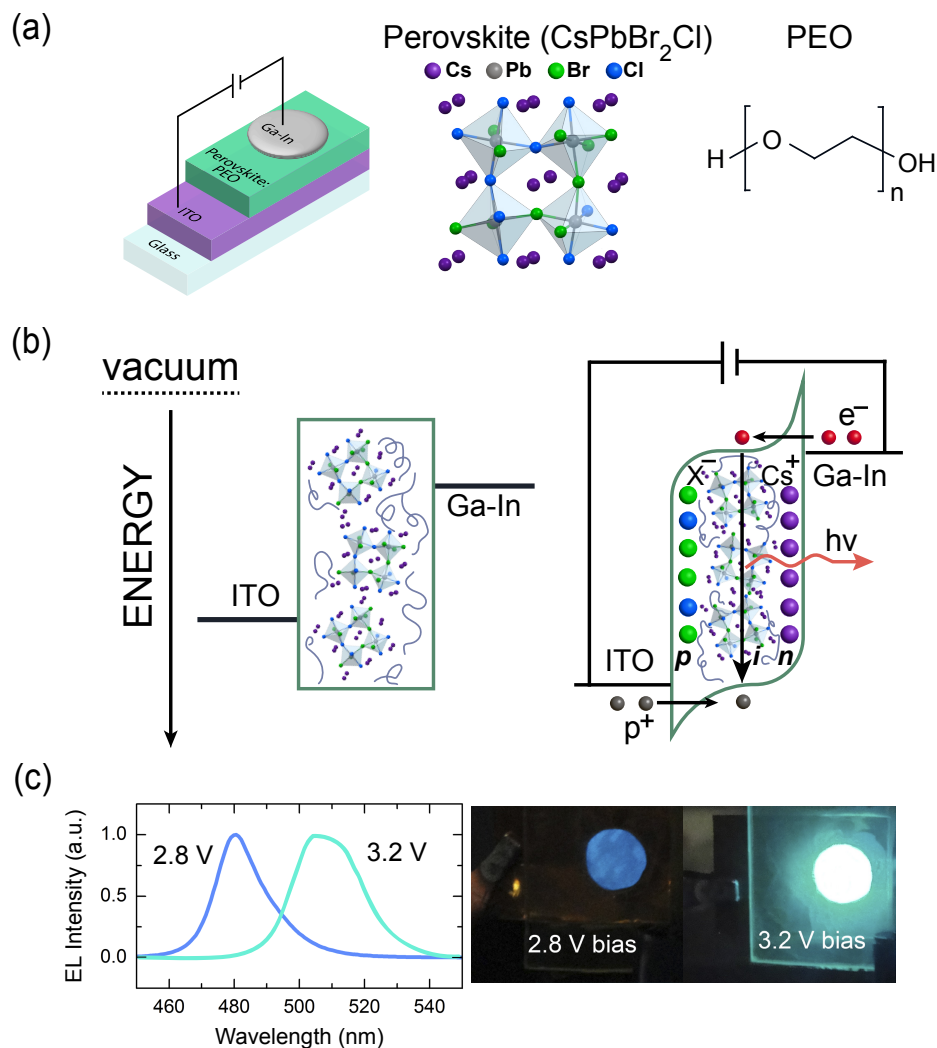


Figure 2. (a) The scheme of a pero-LED based on CsPbBr₂Cl:PEO thin film. (b) The working mechanism of the pero-LED. (c) The EL spectra and photographs of the fabricated device operating at different bias.

3. Conclusion

In summary, we fabricated CsPbBr₂Cl and CsPbBr₂Cl:poly(ethylene oxide) thin films of 70 and 300 nm thickness, respectively. A polymer shell was found to be preventing the volume phase of the mixed-halide perovskite micrograins from light-induced segregation. The phase-stable perovskite-polymer film was utilized for the manufacturing of a single-layer pero-LED which working mechanism is well described within an electrochemical doping (ECD) model.[9] The device exhibited a sky-blue electroluminescence at 2.8 V bias. A redshift of the emission spectrum was observed with increase in the applied voltage. In accordance with these findings the electric field-driven segregation in CsPbBr₂Cl perovskite occurs when the field in the perovskite-polymer layer exceeds 1×10^5 V/cm. Therefore, we assume that no stable and bright blue EL can be achieved when a pero-LED operation is governed by the ECD model since there is a non-zero field in the light-emitting perovskite region which suffers from the field-induced phase instability. From this point of view, the electrodynamic model [9] manifesting a free field intrinsic perovskite

region seems to be more promising for the successful operation of single-layer pero-LEDs based on cesium lead mixed-halide perovskites.

4. Acknowledgment

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