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Effect of the precursor's stoichiometry on the optoelectronic properties of methylammonium lead bromide perovskites

Giulia Longo [a], Alan Wong [b], Michele Sessolo [a,*], Henk J. Bolink [a]

[a] Instituto de Ciencia Molecular, Universidad de Valencia, C/ Catedrático José Beltrán, 2, 46980 Paterna, Spain
[b] NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, Gif-sur-Yvette, 91191 Paris, France

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ABSTRACT

Methylammonium lead bromide ($MAPbBr_3$) perovskites have been widely studied in applications such as lasers and light-emitting diodes, thanks to their favorable bandgap, efficient charge transport, and the possibility of processing by simple solution methods. The film morphology has a large impact on the optical and electronic properties of the material; hence the deposition methods and the type of precursors used are crucial in the preparation of efficient optoelectronic devices. Here we studied the effect of the precursor´s stoichiometry of solution processed $MAPbBr_3$ thin films on their optical and electronic properties. We found a drastic effect of the stoichiometry on the resulting thin film morphology, and suggest the use of excess MA cations to enhance the photo- and electroluminescence of hybrid perovskites.

1. Introduction

Organic inorganic (hybrid) perovskites are known since the beginning of the last century [1–6], but their unique optical and electronic properties have been unveiled mostly during the last thirty years. One of the advantages of hybrid perovskite over inorganic semiconductors is the possibility to obtain high quality semiconducting films by simple solution or sublimation methods. Initially, most works focused on layered (or 2D) perovskites due to the interesting properties arising from the high exciton binding energy, in the order of hundreds of meV [7–10]. Later on, three dimensional (3D) perovskites have also emerged [11,12], but it is in the last five years when hybrid 3D perovskites have been widely investigated, mainly due to the promising photovoltaic performances of methylammonium lead iodide $MAPbI_3$ [13–17]. During this short period, the power conversion efficiency of perovskite solar cells rapidly increased up to 22% (close to Silicon photovoltaic performances), thanks to a continuous optimization of the perovskite absorber and of the device structure [18]. The analogous bromide compound, the $MAPbBr_3$ perovskite, has been recently investigated because of its favorable optical properties (green emission, intense photoluminescence) and its potential for the development of light-emitting diodes (LEDs) and lasers [19–22]. Since the first report of room temperature electroluminescence from 3D perovskite LEDs [19], several works have addressed the issues related with the achievement of efficient LEDs with hybrid perovskites. Most of the efforts has been directed towards the optimization of the charge transport layers, either organic or inorganic, in order to efficiently inject and confine carriers in the perovskite film [23,24]. Within this perspective, the challenge is to efficiently inject holes into the low-lying valence band of the $MAPbBr_3$ (-5.9 eV), which strongly limits the choice of the hole transport layers. One of the most promising strategies is the use of a Nafion®-modified PEDOT:PSS layer, substantially increasing the work function of the anode (up to -6.0 eV) [25]. Another property differentiating perovskites from organic semiconductors, is the relatively small exciton binding energy, implying that mostly free carriers are present at room temperature [26]. Since recombination between free carriers is a bimolecular process, the LED operation is less efficient compared to organics where the recombination is purely excitonic. As a consequence, the photoluminescence quantum yield (PLQY) is found to be proportional to the excitation intensity [21], meaning that high current densities are needed for electroluminescence, hence reducing the device power conversion efficiency. High PLQY can be achieved by limiting the growth of the perovskite crystals, enhancing the probability of radiative recombination [27,28]. Recently, highly efficient perovskite LEDs have been demonstrated by overcoming all the device and material limitations discussed above, i.e. charge injection, recombination and morphology [29]. The morphology of perovskite thin films has been found to be of crucial importance for the performance of optoelectronic devices, since it severely affects the perovskite electrical and optical properties. In order to tune the morphology of perovskite thin-films, different deposition techniques have been developed [14,28,30–33]. Importantly, the

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[*] Corresponding author.
E-mail address: michele.sessolo@uv.es (M. Sessolo).

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nature and stoichiometry of the precursor materials has a large effect on the final film composition and morphology [34].

Here, we report on the influence of the precursor's stoichiometry on the optoelectronic properties of $MAPbBr_3$ perovskite thin films. Thin films were prepared by solution processing of stoichiometric and non-stoichiometric precursors solutions with a single-step deposition (direct spin-coating of the solution followed by thermal annealing). The morphology and optical properties of the layers were investigated and the perovskite thin films were incorporated in multilayer LEDs employing organic semiconductors as charge transport layers.

2. Experimental methods

Methylammonium bromide (MABr, Dyesol), lead bromide ($PbBr_2$, $\geq$98% Sigma Aldrich), dimethylformamide (DMF, anhydrous, 99.8%, Sigma Aldrich), PEDOT:PSS (Clevios P VP AI4083), Nafion® (Nafion® perfluorinated resin solution, 5 wt. % in lower aliphatic alcohols and water, Aldrich), 1,3-Bis[3,5-di(pyridin-3-yl) phenyl]benzene (BmPyPhB, Lumtec) were used as-received without further purification.

2.1. Thin film preparation for optical characterization

Solution of stoichiometric ($MABr/PbBr_2=1$) and non-stoichiometric ($MABr/PbBr_2=3$) precursors at 70 mg/ml were prepared in DMF using stock solutions of the organic and inorganic components. These solutions were used to deposit the thin-film by spin-coating on glass substrates. The stoichiometric (F1) and non-stoichiometric (F3) films were annealed at 90 °C for 15 min. All the processes were performed in a nitrogen filled glove box.

2.2. Powders precipitations and device preparation

For solid state nuclear magnetic resonance (NMR) and x-ray diffraction (XRD) analysis, powder samples were prepared by precipitation of a 40 wt% solution of stoichiometric (P1) and non-stoichiometric precursors (P3), upon addition of chlorobenzene as precipitating agent. The polycrystalline materials obtained were dried at 70 °C for 48 h. Part of the P3 powder was further annealed at 115 °C for 24 h. The ^{13}C magic angle spinning (MAS) spectra were acquired on a Bruker Avance 300 MHz, with sample spinning at 10 kHz using a ^{1}H-decoupling experiment. A long recycle-delay of 60 s was used to ensure a reliable quantitative measurement. The ^{13}C chemical shift is referenced to an alanine $–CH_3–$ at 20.5 ppm.

Solutions at 40 wt% were also employed to prepare the optoelectronic devices reported in this work. For the hole injection layer, a blend of PEDOT:PSS and Nafion® was used as this is known to increase the electrode work function and hence improve hole injection.[35] A blend of the suspensions (PEDOT:PSS/Nafion® 1 mL:1.20 mL) was spin-coated on top of an ITO patterned glass substrate, and then annealed at 150 °C for 15 min. The perovskite active layers were deposited in a nitrogen filled glovebox by spin-coating the precursors solutions followed by annealing at 100 °C for 15 min. The electron transport (hole blocking) layer (BmPyPhB) and the top metal electrode (5 nm Ba capped with 100 nm Ag) were thermally evaporated in a high vacuum chamber with a base pressure of 10^{-6} mbar. Devices were not encapsulated and were characterized in the nitrogen filled glove box.

3. Results

The absorption and the photoluminescence spectra of $MAPbBr_3$ perovskite thin films on glass substrates for the two sets of samples (F1, MA/Pb=1 and F3, MA/Pb=3) are reported in Fig. 1.

The absorption spectra for the two samples presented similar features, with a steep absorption onset at 537 nm for the stoichiometric (F1) and 530 nm for the non-stoichiometric (F3) perovskite films, consistent with the $MAPbBr_3$ perovskite bandgap. The F3 sample showed a higher absorbance in the visible range. The photoluminescence spectra were collected with an integrating sphere equipped with a low intensity excitation source (Xe lamp) and a monochromator, using an excitation wavelength of 365 nm. While sample F3 showed weak but clear photoluminescence centered at 527 nm, no emission was observed for the F1 film.

In order to correlate the difference in the optical properties of the two perovskite samples with the material composition, solid state ^{13}C NMR analysis were performed on polycrystalline perovskite powders (Fig. 2), obtained by precipitation of concentrated solutions and annealed at 70 °C for 48 h.

The stoichiometric perovskite sample (P1) showed a single peak at 30.8 ppm, while an additional peak at 27.9 ppm was observed for the non-stoichiometric perovskite (P3). For comparison, the NMR spectra of the pure MABr precursor was also collected, showing a single signal at 27.9 ppm. Hence, the peak at higher chemical shift corresponds to the MA cation coordinated to the lead bromide (in the $MAPbBr_3$) in the perovskite structure, and the peak at lower chemical shift indicates the presence of a large amount of free MABr in the P3 sample. Fig. 2b reports the NMR spectrum of the non-stoichiometric perovskite sample with and without an additional thermal treatment at 115 °C for 24 h in air. Interestingly, in both samples the peak related to the free MABr is present and its

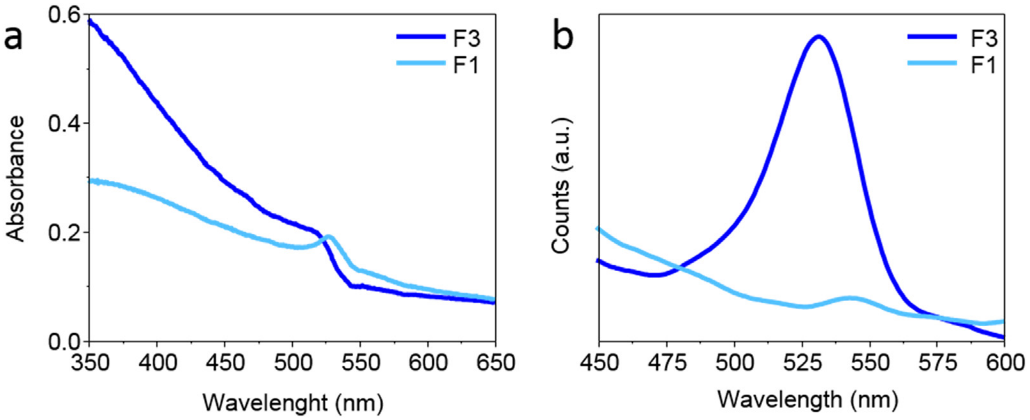

Fig. 1. (a) Absorption and (b) photoluminescence spectra of stoichiometric (F1) and non-stoichiometric (F3) $MAPbBr_3$ perovskite thin films.