Luminescence dynamics of $CsPbBr_3$ quantum dot-based color converters

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Abstract— The excitation density dependent characteristics of a green-emitting $CsPbBr_3$ quantum dot color converter for GaN LEDs and lasers is reported. The bandwidth is found to increase with the excitation reaching up to 55 MHz at a 185 W/cm^2 pump density.

Keywords— Perovskites, Quantum Dots, micro LED, GaN, Visible Light Communications, bandwidth

I. Introduction

Thanks to their narrow emission linewidth and comparatively fast luminescence dynamics, colloidal semiconductor nanocrystals are alternatives to phosphors for certain applications requiring color conversion of GaN-based sources. Their short luminescence lifetime (tens of ns) in particular makes them preferable for applications necessitating high-speed modulation of light, as is the case for example in visible light communications (VLC) [1]. We have previously reported on CdSeS/ZnS quantum dots (QDs) [1] for VLC pumped by microsize LEDs (µLEDs). Herein, we study the dynamics of luminescent recombination for $CsPbBr_3$ QDs [2].

$CsPbBr_3$ QDs first reported only 3 years ago [2] have drawn significant attention, e.g. for VLC [3], because their luminescence lifetime is in principle shorter than for II-VI and III-V nanocrystals [4]. The dynamics of $CsPbBr_3$ QDs however is not fully understood and is rendered complex due to possible multi-excitonic interactions in QDs [4]. The latter can reduce the conversion efficiency and accelerate the luminescence lifetime, and are expected to become significant at high excitation density, as can be the case for color conversion of laser diodes (LDs). Furthermore, it has been reported that in weakly confined $CsPbBr_3$ QDs with sizes of 7 nm or more, the carrier dynamics are bulk-like [5]. In such cases, the luminescence lifetime of the color converters (and hence their modulation bandwidth) is expected to vary with the excitation level. Understanding how could lead to optimization of the performance of the color converters. In this context, we study the luminescence dynamics of a practical $CsPbBr_3$ color converter under different excitation regimes obtained via optical pumping with a µLED and a LD.

II. Materials and Methodology

A. Sample fabrication

$CsPbBr_3$ QDs (10 nm) were commercially sourced from PlasmaChem, GmbH, with specified emission at 515 ± 15 nm, in paste form. The paste was placed inside a glass vial, its mass measured and Poly(methyl methacrylate) (PMMA) was added at a 5% weight ratio of QDs to PMMA to provide a polymeric matrix. The mixture was then dispersed in toluene to make a solution of PMMA+QDs in toluene at 250 mg/mL. The solution was left stirring overnight and then poured into a PDMS mold and left to dry. The resulting samples is illustrated in the inset of the left graphic of Figure 2 and presents around 500 µm thickness on the central region, where it was tested.

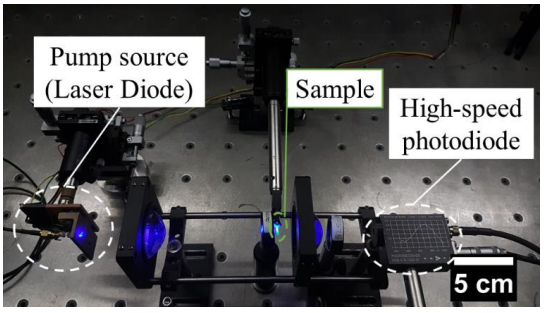

Figure 1 – Setup used in the measurements.

B. Characterization

The setup illustrated in Figure 1 was used to optically pump the sample and collect its emission onto a high–speed photodiode (1.4 GHz bandwidth) for frequency response (dynamics) measurements or onto a power meter and a fiber-coupled Ocean Optics USB4000 spectrometer for, respectively, color-converted power and spectra (static) measurements. The pump source was either a µLED or a LD (OSRAM PL450b) to enable operation under a wide range of excitation density (0.37 - 185 W/cm2). The 100x100µm^2 µLED [1] had a peak emission at 450 nm, the same emission wavelength as the LD. The excitation spot size on the sample was: 0.5 mm^2 (µLED) and 5.5x10^3 mm^2 (LD) as determined by a Beam Profiler (Thorlabs, BC106N-Vis-M).

For frequency measurements, the pump source was driven by a DC bias and an AC modulated signal. A network analyzer provided the AC signal (sine wave) and receives the signal detected by the photodiode, and plots the received electrical power as a function of the frequency (100 kHz to 1 GHz). This frequency response was then fitted with the model function described hereafter, in order to extract the bandwidth. The latter is defined as the frequency at which the converter optical power drops to half (-3dB) of its small frequency value (-6 dB for the electrical response).

The frequency response of the color converter is intrinsically linked to its photoluminescence (PL) decay in the time domain. This PL decay has an associated decay lifetime component. For multi-exponential decays, there are several lifetime components (τ_i) each with their respective weight (α_i), which can be averaged into the average lifetime (τ):

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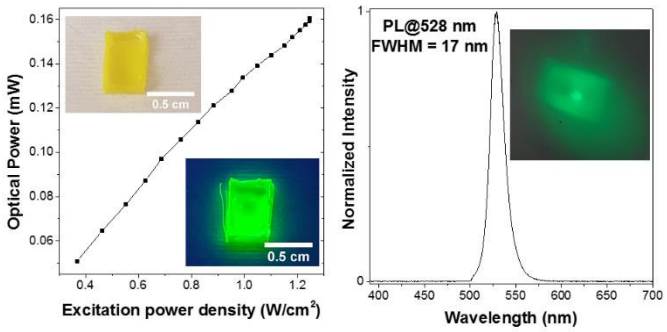

Figure 2 – LEFT: forward converted optical power vs excitation power density; RIGHT: spectral emission.

$$\tau = [\Sigma_i\, \alpha_i \cdot \tau_i^2] \,/\, [\Sigma_i\, \alpha_i \cdot \tau_i] \qquad (1)$$

The relation between the average PL lifetime (τ) and the bandwidth (BW_f) is given by

$$\tau = \sqrt{3} \,/\, (2 \cdot \pi \cdot BW_f) \qquad (2)$$

The frequency response (FR) is then be modulated by (3).

$$FR(f) = 2 \cdot Log[\sqrt{\{n(f)^2 + D(f)^2\}}] \qquad (3.1)$$

$$n(f) = [\Sigma_i\, \{\alpha_i \cdot \omega \cdot \tau_i^2\} / \{1 + \omega^2 \cdot \tau_i^2\}] \,/\, [\Sigma_i\, \alpha_i \tau_i] \qquad (3.2)$$

$$D(f) = [\Sigma_i\, \{\alpha_i \cdot \tau_i^2\} / \{1 + \omega^2 \cdot \tau_i^2\}] \,/\, [\Sigma_i\, \alpha_i \tau_i] \qquad (3.3)$$

III. Results and Discussion

Figure 2 summarizes the static measurements. We can observe that the forward converted optical power (i.e. the optical light collected by the system at the detector) reaches 0.16 mW for a 1.24 W/cm^2 excitation density (µLED excitation), corresponding to a forward color conversion efficiency of 2.4% for absorption of the pump of 97%. The optical power increases linearly with the pump power density. The PL emission is centered at 528 nm, which is red-shifted by several nm compared to the intrinsic PL due to reabsorption, as seen in CdSe/ZnS QDs [1]. The emission linewidth (full-width half maximum) is 17 nm.

Figure 4 plots the frequency response of the color converter for two different excitation power densities. To retrieve the bandwidth, the frequency response is modeled as explained in section II and a double exponential decay is considered.

The bandwidths versus excitation power density are plotted in Figure 3. The averaged lifetime is also plotted. We observe an increase from 25 MHz to 33 MHz between 0.37 W/cm^2 and 1.25 W/cm^2 excitation density, which we attribute to a reducing re-absorption effect within the sample as the excitation increases. At higher excitation densities (22 to 184 W/cm^2) the bandwidth also increases, albeit at a smaller rate, from over 35 MHz, up to 55 MHz. This corresponds to a decrease in the average PL lifetime from 12 to 5 ns, which is faster than the typical lifetime of equivalent color converters made with II-VI QDs [1]. Note that it was verified that the carrier density scales linearly with the excitation power density. This acceleration of the dynamics could be the combination of simple carrier-dependent radiative recombination and of non-radiative recombination and which effect dominates will be discussed.

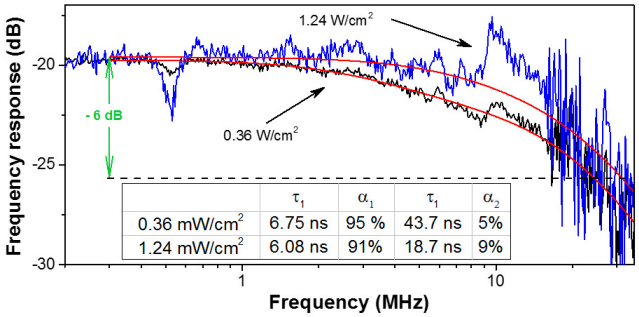

Figure 3– Frequency response of the color converter for two different excitation power densities.

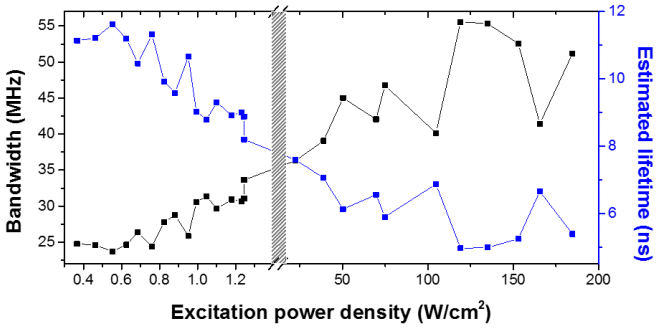

Figure 4 – Perovskite QDs' bandwidths for different excitation power densities.

IV. Conculsions

In conclusion, the luminescent recombination dynamics of inorganic perovskite quantum dots were studied. Unlike what was previously reported, the frequency response modelling indicate that a double exponential decay governs the luminescence recombination dynamics of perovskite quantum dots. Presenting bandwidths up to 35 (55) MHz under µLED (Laser Diode) excitation, and 17 nm linewidth in its emission, perovskite quantum dots are good candidates for applications such as Visible Light Communications

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