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## Physical performance limitations of luminescent down-conversion layers for photovoltaic applications

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## ABSTRACT

An optical model is presented to determine the constraints imparted by self-absorption on the luminescence emitted from down-conversion (DC) materials. An analytical formula was derived demonstrating that, for a given DC material, an optimal thickness exists that maximizes the intensity of the emitted radiation, while minimizing the impact of self-absorption. This defines a new limit for the optical efficiency of a DC material that is governed by its geometry. Subsequently, the model was validated through experimental analysis of a specific down-converting borate glass co-doped with  $\text{Ce}^{3+}$ – $\text{Yb}^{3+}$ , whose optimal thickness has been determined to be 0.83 mm. The model clarifies the origin of the disparity between the theoretical and the experimental efficiencies reported for some materials. The results from this work assist with the design and implementation of DC layers for photovoltaic devices, as well as providing a framework for optimization of DC materials to other fields of optics and photonics.

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## 1. Introduction

Luminescent materials have been studied extensively over past decades because of their potential applications in a wide area of technological processes, such as lasers, LED, plasma displays, detectors, bioimaging [1,2]. Recently, considerable interest has been generated in developing luminescent materials to reduce losses in photovoltaic (PV) devices. The performance of a single junction PV device – such as those based on silicon with a bandgap of  $E_g = 1.1$  eV – is greatly limited by transmission losses of near-infrared (NIR) radiation – photons with energy  $E_{ph} < E_g$  – and lattice thermalization losses following the absorption of ultraviolet (UV) photons with energy  $E_{ph} \gg E_g$ . In order to minimize thermalization losses, different approaches have been pursued, such as tandem solar cells [3], multiple exciton generation [4], and hot-carrier solar cells [5]. In this paper, the focus is on another technique based on spectral conversion by luminescent down-converting materials [6,7].

Down-conversion (DC) is an optical process that can occur in some materials doped with rare earth elements, and consists of the absorption of a single high energy photon followed by the

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emission of two or more photons of lower energy. Thus, the internal photoluminescent quantum yield (iPLQY) of the DC process – defined as the ratio of emitted photons compared to the number of absorbed photons – can theoretically achieve values of 200% or more. Despite the definition, the iPLQY of the process is also affected by non-radiative losses, which consequently limit to achievable values much lower than the theoretical ones. For completeness we also define the external photoluminescent quantum yield (ePLQY) as the ratio of emitted photons divided by the number of incident photons.

In a solar cell, the thermalization losses become greater as the difference between the bandgap of the semiconductor and the absorbed photon energy increases. Thus, if it was possible to convert the high energy photons to lower energy photons, ideally close to  $E_g$ , and with a iPLQY > 100% then the higher flux of photons incident on the PV device will increase the generated photocurrent and consequently will improve the energy conversion efficiency of the device [6].

A similar strategy has been already implemented in PV by using luminescent down-shifting (similar to DC but with maximum iPLQY of unity) with up to 9% enhancements being reported on thin-film PV modules [8]. Based on such results, DC should be even more efficient with 200% iPLQY values. For a single junction silicon solar cell, the maximum theoretical energy conversion efficiency, given by the Shockley–Queisser (S–Q) limit, has been established to be  $\eta = 30\%$ . [9] A theoretical study carried out by Trupke et al. [6]

indicated that the  $S$ – $Q$  limit could be increased up to  $\eta=38.6\%$  (under one sun illumination) if an ideal DC material is adhered to the front surface of a silicon PV device.

Due to the promise of improved performance for the mainstay PV technology, DC research has attracted much attention over the last decade. The majority of publications have been mainly focused on materials chemistry studies of promising materials (for reviews see [10,11]), and, to date, no practical demonstration of DC-enhanced solar cell performance have been achieved.

DC has also been employed in lightning technology, such as mercury-free fluorescent tubes, as well as plasma displays [12]. Materials based on trivalent rare-earth ( $RE^{3+}$ ) ions have been studied and high values of iPLQY approaching 190% were measured for systems based on  $Gd^{3+}$  and  $Eu^{3+}$  [13–15]. Despite the high iPLQY values, the DC mechanism for this particular system is based on conversion of vacuum ultraviolet ( $\lambda < 200$  nm) photons into visible (VIS) photons. This process is not relevant for either space- or terrestrial-based PV applications where the solar spectrum begins at  $\lambda=200$  nm or 300 nm, respectively. It is also important to highlight that the ePLQY of this system is only 32% due to, firstly, the weak absorption of the  ${}^6G_J$  level of the  $Gd^{3+}$  ion and, secondly, the strong parasitic absorption in the  $LiGdF_4$  host [16].

A more promising way to apply DC to PV devices are UV/VIS to NIR DC materials, typically based on co-doped system  $RE^{3+}$ – $Yb^{3+}$ . The UV/VIS light is absorbed by a  $RE^{3+}$  sensitizer ion, which then transfers its energy to two neighboring  $Yb^{3+}$  activator ions and exciting them from the  ${}^2F_{7/2}$  ground state to the excited level  ${}^2F_{5/2}$  ( $\sim 1.2$  eV). The resulting NIR ( $\lambda=980$  nm) emission from the latter level corresponds to photon energies close to the bandgap of a silicon solar cell. The advantage of the  $Yb^{3+}$  ion originates from the absence of intermediate levels between the  ${}^2F_{5/2}$  level and the ground state, which increases the probability of radiative emission. Moreover, the UV/VIS light could be transmitted for energies higher than 1.2 eV due to the absence of levels higher energy levels.

A good co-dopant ion for  $Yb^{3+}$  is  $Ce^{3+}$ , due to its high absorption at short wavelengths. In a  $Ce^{3+}$ – $Yb^{3+}$  system, the UV pump excite the  $Ce^{3+}$  ion into the  $5d$  manifold which after a Stokes shift into the  $4f$  manifold allowing the DC to occur via cooperative energy transfer (CET) to the  $Yb^{3+}$  ions [17]. CET in borate glasses is a non-resonant energy transfer assisted by phonons with a maximum phonon energy in the range of 1310–1380  $cm^{-1}$  [18].

The performance of  $RE^{3+}$ – $Yb^{3+}$  co-doped materials have been investigated through the theoretical evaluation of the energy transfer efficiency (ETE) from  $RE^{3+}$  ions to  $Yb^{3+}$  ions via time-dependent photoluminescence (PL) measurements [10]. This evaluation method, proposed by Vergeer et al. [19], consists in measuring the decrease of the lifetime decay of the excited level of the  $RE^{3+}$  ions with the increasing concentration of  $Yb^{3+}$  ions. The ratio of the measured lifetime (corresponding to a specific concentration value) compared to the natural lifetime (measured in an undoped sample) allows the theoretical ETE of the process, relative to each  $Yb^{3+}$  concentration, to be estimated.

From the literature, the theoretical ETE estimations are very close to the maximum theoretical of 200% [19–22]. However, achieving such ETE values typically require  $Yb^{3+}$  concentrations of greater than 20 mol%, which also promotes other losses mechanisms such as quenching of the emitted radiation [23,24]. This is a non-radiative relaxation phenomena that, firstly, decreases the intensity of the fluorescence and, secondly, results in self-absorption of the emitted radiation due to the overlapping absorption and emission spectra. These two loss mechanisms represent the main reasons that DC materials have not yet demonstrated the desired performance enhancement for PV devices [25]. Self-absorption of  $Yb^{3+}$  have been modeled through a rate equation model to describe its impact on lifetime measurements [26].

Our approach will instead focus on studying the effect of self-absorption on the ePLQY considering an optical model based on Beer–Lambert law. Therefore, this study aims to quantify the losses due to the self-absorbed radiation in order to facilitate the design of future DC-PV devices. An optical model has been developed and an analytical formula has been derived to demonstrate that an optimal thickness exists for the DC layer, which can minimize the fraction of emission lost to self-absorption. The model has been validated by performing spectroscopic measurements for different  $Yb^{3+}$  doping levels and different thickness on a specific DC system based on a transparent glass system, comprised of borate glasses co-doped with  $Ce^{3+}$  and  $Yb^{3+}$  ions.

## 2. Materials and methods

### 2.1. Experimental

#### 2.1.1. Synthesis

Borate glasses [ $70B_2O_3$ – $7BaO$ – $8CaO$ – $(15-x)La_2O_3$ ] co-doped with  $Ce^{3+}/Yb^{3+}$  were prepared using the melt-quenching method. The  $Ce^{3+}$  concentration has been fixed to 0.5 mol%, while different  $Yb^{3+}$  concentrations 1%, 2%, 5%, and 10% were prepared, as described in [17]. An un-doped borate glass sample was also fabricated as a reference sample. The glass samples were polished down to dimensions of 20 mm  $\times$  20 mm  $\times$  2.2 mm. Seven smaller samples (6 mm  $\times$  6 mm) were cut from the 0.5%  $Ce^{3+}$ –1%  $Yb^{3+}$  glass sample and each one was optically polished to different thicknesses ranging from 0.29 mm to 2.18 mm.

#### 2.1.2. Characterization

Absorption spectra were measured with a spectrophotometer (Perkin-Elmer, Lambda 950 UV/VIS/NIR) with a resolution of 1 nm over the 250–1200 nm wavelength range. Any effects from the host matrix were accounted for via the undoped reference sample. Fluorescence spectra were obtained using a calibrated spectrofluorometer (Edinburgh Instruments, FLS920) equipped with a xenon lamp excitation source, an integrating sphere (Jobin-Yvon), and a liquid nitrogen cooled NIR photo-multiplier tube (Hamamatsu, R5509-72). The uncertainty for the calibrated data is  $\pm 3\%$  and the measurement accuracy of the technique is typically 10% [27]. All the measurements on the samples have been performed at room temperature (25 °C).

### 2.2. Modeling

A 1D optical model has been developed in order to describe the self-absorption of the emitted down-converted radiation. Consider a DC layer of length  $L$  divided into  $N$  slabs (see Figs. 1 and 2), where  $\alpha$  and  $\beta$  are the absorption coefficients relative to the wavelengths of the pump and the emitted radiation, respectively. It is assumed that all the incident photons, which are absorbed by the donor (sensitizer) ions, transfer their energy to two acceptors (activator) ions with an efficiency  $\eta_{ET}$ .

The emission is considered to be isotropic, thus statistically the emitted photons will be equally distributed between the front and back side. The probability for the emitted photons to exit from the material is then taken into account and depends on the number of slabs that the emitted photons have to pass through. The probability for an incident photon to be absorbed in the  $i$ th slab is

$$p_a^i(\alpha, L, N) = e^{-\alpha i \frac{L}{N}} - e^{-\alpha(i+1) \frac{L}{N}} = e^{-\alpha i \frac{L}{N}} (1 - e^{-\alpha \frac{L}{N}}). \quad (1)$$

The probability for an emitted photon (from the  $i$ th slab) to be transmitted outside the sample, such that it is not reabsorbed, in

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