Enhancement of Upconversion for Photovoltaics with β-NaYF$_4$:Er^{3+} and Concentrating Integrated Optics

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Abstract: The internal photoluminescence quantum yield of β-NaYF$_4$:Er^{3+} is determined under broadband excitation and a photovoltaic-upconverter system with concentrating integrated optics is proposed to enhance the near-infrared response of silicon solar cells.

OCIS codes: (190.7220) Upconversion, (220.1770) Concentrators; (350.6050) Solar energy

1. Introduction

Up-conversion is one of the promising processes to surpass the Shockley-Queisser limit [1] for single-junction solar cells [2,3]. Among the rare earths that have been identified for their luminescence properties, erbium has been identified as the most promising to improve the sub-bandgap response of silicon solar cells [4]. Fluorides have been identified as ideal hosts for upconversion due to low phonon energy, with highest performance when applied on a photovoltaic-up-conversion (PV-UC) device [5,6,7]. Due to the non-linear nature of upconversion process, high power densities are needed for best performance, which correspond to solar concentrations in the range of 500-1200 X [8] for concentrating photovoltaic (CPV) systems.

In this paper we investigate the performance of trivalent erbium doped sodium yttrium fluoride (β-NaYF$_4$:Er^{3+}) embedded in a fluorinated polymer matrix of perfluorocyclobutyl (PFCB) which has exhibited the highest PLQY under monochromatic excitation [9] to the best of our knowledge. We use a series of broadband excitation spectra from 50 to 200 nm at FWHM to cover the absorption spectrum of Er^{3+} as shown in Figure 1. We also examine the geometrical concentration of an upconversion system with integrated optics and investigate whether this solar concentration will lead to an adequate power density to excite the upconverter under the sun.

2. Experimental

A 1000 W quartz tungsten halogen (QTH) lamp (Oriel, 66187) was used as the excitation source, while a series of short and long wave-pass filters (Edmund Optics) have been used to adjust the desired spectral windows on Figure 1. In addition, a 300 µm thick silicon wafer and a long wave-pass filter centered at 1200 nm were used to block wavelengths below 1100 nm.

Fluorescence measurements were performed in a fluorescence spectrometer (Edinburgh Instruments, FLS920) equipped with a Jobin-Yvon integrating sphere, Czerny-Turner monochromators and a LN$_2$-cooled NIR photomultiplier tube (Hamamatsu, R5509-72).

The output of the QTH lamp was guided into the fluorescence spectrometer via a multimode optical fiber (Thorlabs, BFL48-1000). The integrated power was measured with a thermal detector (Thorlabs, S302C) of maximum calibration uncertainty ±5%, and the profile of the beam was characterized with an IR camera (Electrophysics, Micronviewer 7290A).

β-NaYF$_4$ microcrystals microcrystalline powder with 25% Er^{3+} concentration have been prepared at the University of Bern following the method described in reference [10], and casted in PFCB polymer matrix in-house, at a phosphor to polymer weight ratio of 84.9%.

3. Internal photoluminescence quantum yield

The upconversion efficiency of a luminescent material is determined by the internal photoluminescence quantum yield (iPLQY) which is defined as the ratio of emitted photons to the absorbed excitation photons.

Figure 1 shows the excitation spectrum of Er^{3+} in β-NaYF$_4$ on the right Y axis and the power density on the left Y axis as a function of wavelength. The spectral windows were selected in order to investigate the cumulative effect of the broadband excitation on wavelengths other than the main resonant peaks at 1508 and 1523 nm.

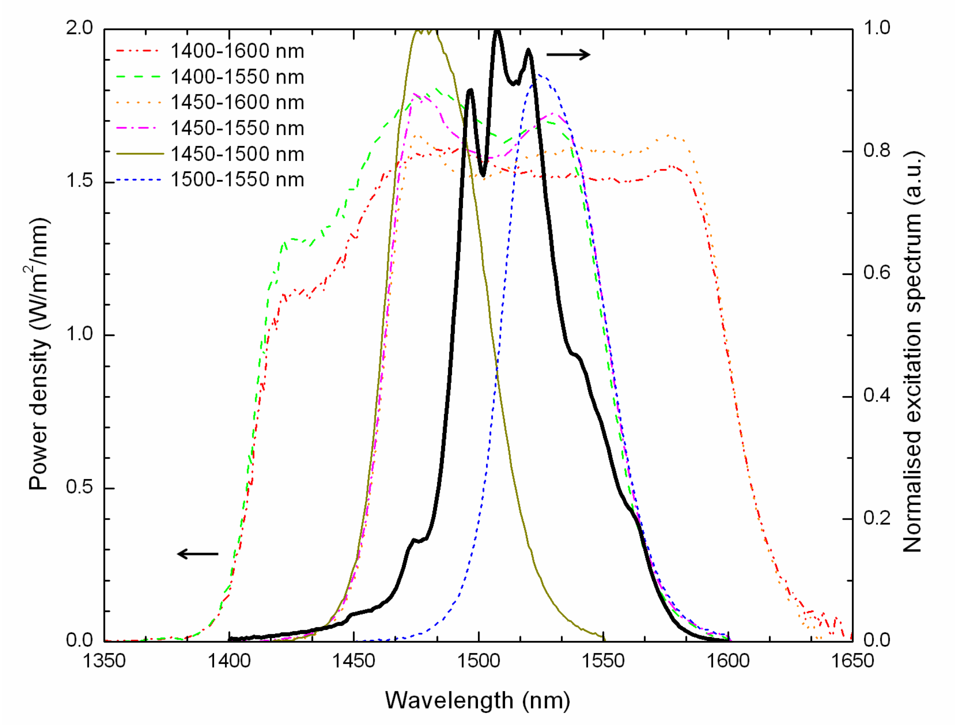

Figure 1: The excitation spectrum under monochromatic excitation (black solid line) of β-NaYF$_4$:Er^{3+} resulting to the $^4I_{11/2} \Rightarrow {}^4I_{15/2}$ transition (980 nm emission). The broadband spectra used to excite the samples for iPLQY measurements are shown for comparison.

The iPLQY values evaluated under broadband excitation (Figure 1) are summarised in Table 1. The highest iPLQY is given with the broadest excitation of 200 nm, which covers all the excitation spectrum of Er^{3+} and encompasses more photons per unit area. A decrease by 0.35% is shown by removing the excitation between 1400-1450 nm, and a decrease by 1.66% after removal of the 1550-1600 nm excitation. After reduction to the 1500-1550 nm excitation the iPLQY is reduced by a further 0.65%, which results to 1.61%. We also observe an improvement of 0.05% by extending the excitation 1450-1550 nm to 1400-1550 nm, indicating the additional emission by exciting the absorption tail of Er^{3+}.

Table 1: iPLQY corresponding to the excitation spectra of Figure 1

Spectral range of excitation (nm)	FWHM (nm)	iPLQY (%)
1400-1600	200	4.27
1400-1550	150	2.21
1450-1600	150	3.92
1450-1550	100	2.26
1450-1500	50	0.58
1500-1550	50	1.61

4. Geometrical concentration with integrated optics

Figure 2 shows a schematic of the system with integrated optics which consists of: a lens of diameter *D* and focal length *f*, a bifacial silicon solar cell, a dielectric taper of acceptance angle *α* and the upconverter, in this case β-NaYF$_4$:Er.

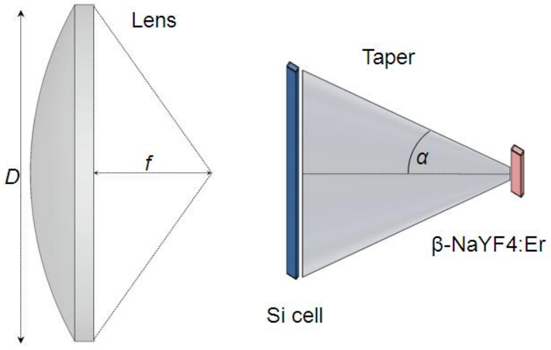

Figure 2: Schematic of the PV-UC device with integrated optics

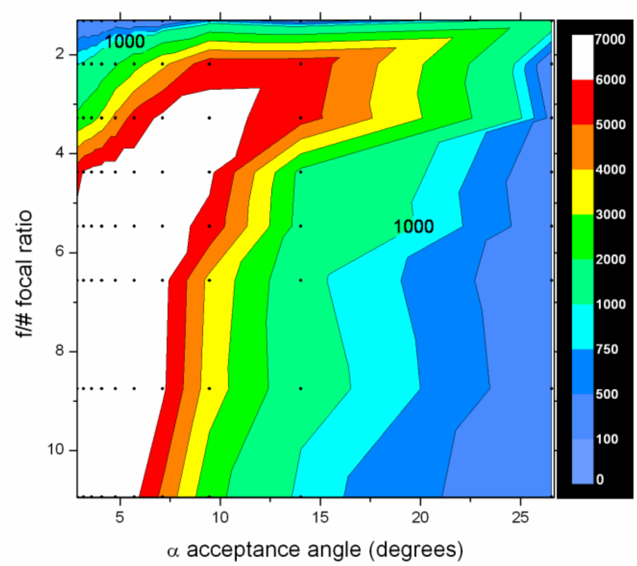

Figure 3: Solar concentration of the system as a function of acceptance angle α of the taper and focal ratio *f*/# of the lens. The solar concentration at 1000 X is indicated as a standard margin for CPV systems

We modeled the optical system to determine the geometrical concentration (C_{geo}) at the end of the taper and consequently at the β-NaYF$_4$:Er^{3+} sample. C_{geo} is defined as the ratio of entrance to exit aperture. As shown in Figure 3, C_{geo} can effectively reach values above 6000 X for acceptance angles below 10^{o} and *f*/# above 3 [11]. It should be noted that the transmission of the solar cell is not included in these simulations. Assuming a constant C_{geo} per wavelength, this corresponds to a power density of approximately 1500 W/m^2 under the AM1.5D spectrum at 1500 nm. This power density is three orders of magnitude higher than the one used to determine the iPLQY. Since this power density falls in the linear regime on the log-log plots of iPLQY vs power density, where only energy transfer upconversion (ETU) takes place [12], this would effectively result in a higher iPLQY applied on the described optical system.

5. References

[1] W. Shockley and H. J. Queisser, "Detailed Balance Limit of Efficiency of p-n Junction Solar Cells",J. Appl. Phys. **32**, 510 (1961)

[2] T. Trupke, M. A. Green, and P. Wurfel, "Improving solar cell efficiencies by up-conversion of sub-band-gap light", J. Appl. Phys. **92**, 4117 (2002)

[3] A. Shalav, B.S. Richards, M.A. Green, "Luminescent layers for enhanced silicon solar cell performance - Up-conversion", Solar Energy Materials & Solar Cells **91,** 829–842 (2007)

[4] C. Strumpel *et al.*, "Modifying the solar spectrum to enhance silicon solar cell efficiency - An overview of available materials", Solar Energy Materials & Solar Cells **91**, 238–249 (2007)

[5] B.S. Richards and A. Shalav, "Enhancing the near-infrared spectral response of silicon optoelectronic devices via up-conversion" Electron Devices, IEEE Transactions on **54**.10 (2007): 2679-2684

[6] S. Fischer, J. C. Goldschmidt, P. Loper, G. H. Bauer, R. Bruggemann, K. Kramer, D. Biner, M. Hermle, and S. W. Glunz, "Enhancement of silicon solar cell efficiency by upconversion: Optical and electrical characterization", J. Appl. Phys. **108**, 044912 (2010)

[7] S. Ivanova, and F. Pellé. "Strong 1.53 μm to NIR-VIS-UV upconversion in Er-doped fluoride glass for high-efficiency solar cells" JOSA B **26**.10 (2009): 1930-1938.

[8] Handy, J., & Peterson, T., "Concentrating PV survey: an unbiased overview", in SPIE Solar Energy+ Technology, International Society for Optics and Photonics, (2011), pp. 810808-810808

[9] A. Ivaturi *et al.*, "Optimizing infrared to near infrared upconversion quantum yield of b-NaYF4-Er^{3+} in fluoropolymer matrix for photovoltaic devices", J. Appl. Phys. **114**, 013505 (2013)

[10] K.W. Krämer, *et al*. "Hexagonal sodium yttrium fluoride based green and blue emitting upconversion phosphors" Chemistry of Materials **16**.7, 1244-1251 (2004)

[11] G.E. Arnaoutakis, *et al*. "Coupling of sunlight into optical fibres and spectral dependence for solar energy applications" Solar Energy **93**, 235-243 (2013)

[12] S.K.W. MacDougall, *et al*. "Ultra-high photoluminescent quantum yield of β-NaYF4: 10% Er3+ via broadband excitation of upconversion for photovoltaic devices." Optics express **20**.23 (2012): A879-87.