APPLICATION NOTE

CHARACTERISATION OF UP CONVERSION IN RARE EARTH MATERIALS

EDINBURGH INSTRUMENTS

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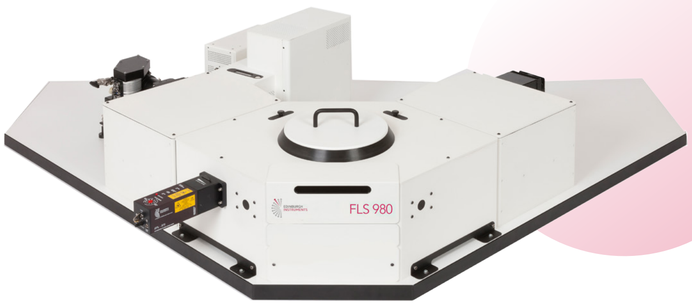
INTRODUCTION

Up conversion finds important applications in biological labels[1] and photodynamic therapy[2], optical sensors[3], laser[4,5], light emitting diodes and solar cells[6,7]. Up conversion involves the addition of photons mainly via sequential absorption and energy transfer between ions in an excited state, with subsequent emission of photons with higher energy. However, this process is not linear with excitation power and the up-converted emission saturates at high powers.



FLS980 Spectrofluorometer

METHODS AND MATERIALS

Excitation spectra were measured using an FLS980 fluorescence spectrometer equipped with a 450 W Xe lamp with double excitation and emission monochromators. For emission and time-resolved spectra, a 976.4 nm diode laser (CNI, MLL-III-980-100mW) with a PM-1 modulator to accommodate continuous and pulsed excitation. Emission was detected with photomultiplier tube (PMT) detectors in the visible (Hamamatsu, R928P) and the NIR (Hamamatsu, R5509-72).

One of the most efficient and extensively studied phosphors for near-infrared to visible up conversion emission is the erbium-ytterbium doped sodium yttrium fluoride ($NaYF_4$:YbEr). For photoluminescence measurements, a thin layer of the up conversion phosphor (Sigma Aldrich 756555-25G, $NaY_{0.77}Yb_{0.20}Er_{0.03}F_4$) was clamped between quartz glass slides and placed in a front-face holder. The widely established method using an integrating sphere[8,9] was used to determine the absolute photoluminescence quantum yield (PLQY).

RESULTS - DISCUSSION

$NaYF_4$:Yb^{3+}+Er^{3+} exhibits intense up conversion emission around 550 nm and 650 nm as shown in the spectrum of Figure 1. The distinctively narrow emissions, owing to the electronic structure of Er^{3+}, can be seen in the emission spectrum measured in a fluorescence spectrometer FLS980 under NIR excitation and variable irradiance. The measurement of this spectrum requires a spectrometer able to resolve the narrow emission lines from partially forbidden transitions occurring in lanthanides[10].

Under the same excitation conditions, emission from the $^4I_{13/2}$ – $^4I_{15/2}$ transition can be seen in Figure 2, measured from 1400 nm to 1650 nm with a liquid nitrogen cooled NIR-PMT. The slope of the integrated intensities were 1.68 for the $^4S_{3/2}$ to $^4I_{15/2}$ and 1.91 for the $^4F_{9/2}$ to $^4I_{15/2}$ transition, agreeing with two-photon up conversion[10].

The absolute quantum yield of the transitions resulting in green and red up conversion emission is listed in Table 1. A PLQY of 3.09% was determined at an irradiance of 20 W/cm^2 [8,11].

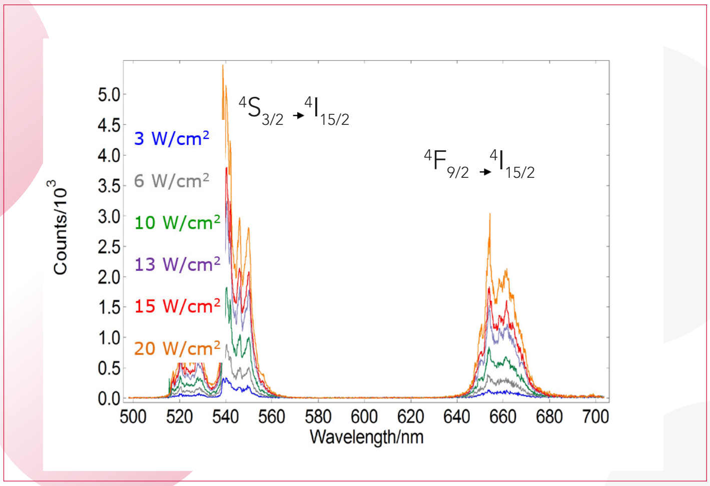


Figure 1: Emission spectra of NaYF: YbEr from the $^4S_{3/2}$ and $^4F_{9/2}$ to $^4I_{152}$ upon 976.4 nm excitation. $\Delta\lambda_{em}$ =0.1 nm, step=0.2 nm

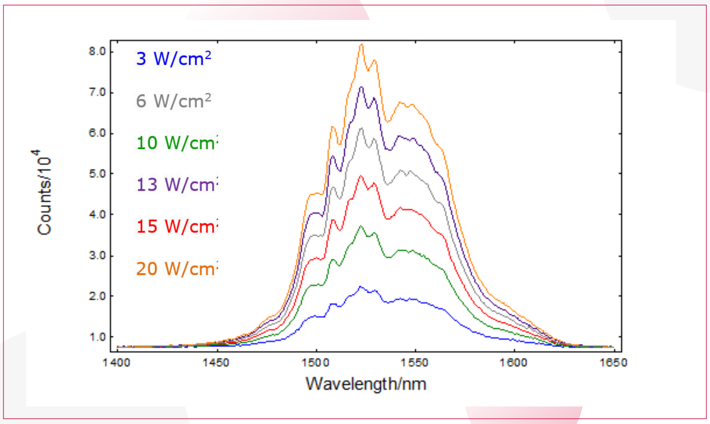


Figure 2: Emission spectra of NaYF:YbEr from the $^4I_{13/2}$ – $4I_{15/2}$ upon 976.4 nm excitation. $\Delta\lambda_{em}$=0.5 nm, step=1 nm

Table 1: Absolute up conversion quantum yield of NaYF^4:Yb^3+Er^3+ measured with an integrating sphere in the FLS980 fluorescence spectrometer.

Irradiance	$^4S_{3/2} > {}^4I_{15/2}$ (green)	$^4F_{9/2} > {}^4I_{15/2}$ (red)
10W/cm^2	1.54%	0.48%
13W/cm^2	2.66%	0.95%
20W/cm^2	3.09%	1.17%

Up conversion can be distinguished from cooperative processes, by the narrow excitation spectra in comparison to the former processes[12]. The narrowing of the excitation spectrum additionally reveals the order of up conversion. The progressively narrow excitation spectrum for higher orders can be seen in the normalized spectra of Figure 3.

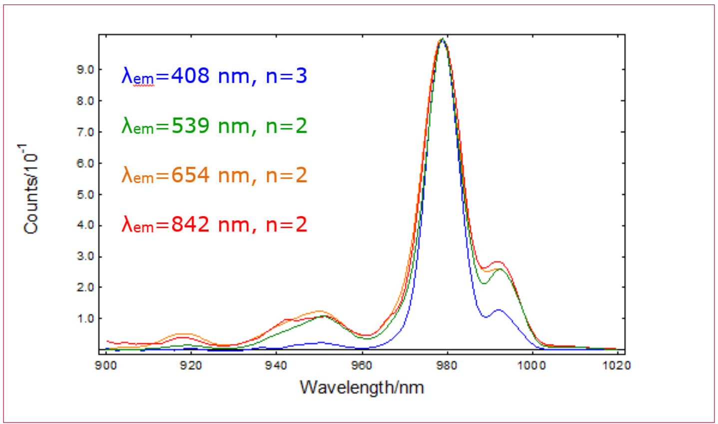


Figure 3: Excitation spectra from 900 nm to 1020 nm at the peak wavelengths of the main emission bands. The experimental conditions were $\Delta\lambda_{exc}$ =15 nm, $\Delta\lambda_{em}$ =5 nm and a step of 1 nm

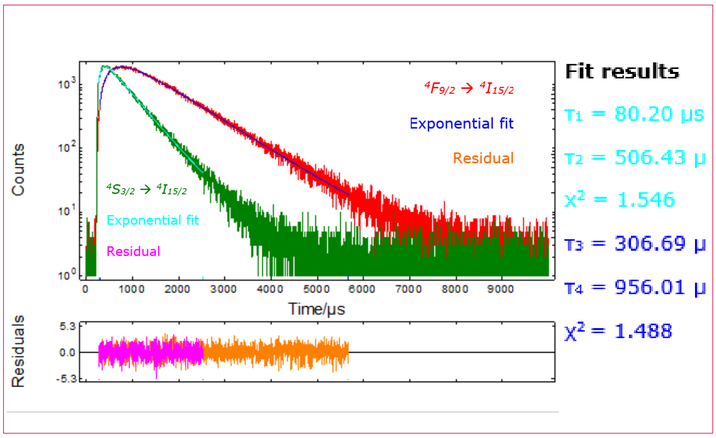


Figure 4: Decay on curves of the $^4S_{3/2}$ and $^4F_{9/2}$ to $^4I_{15/2}$ (green and red, respectively) upon 976.4 nm and 30 μs pulsed excitation.

Another way to distinguish between sequential absorption within a single ion and energy transfer between ions is by recording the temporal evolution of the radiative decays. The energy transfer between Yb^{3+} and Er^{3+} ions can be seen in the time-resolved measurements of Figure 4. The decays are preceded by a faster rise time, characteristic of the energy transfer process[13].

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