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Photoluminescence Upconversion with the Fluorolog-QM

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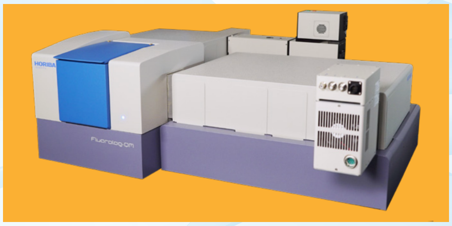
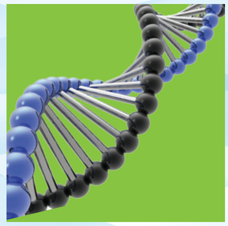
FLUORESCENCE
GRATINGS & OEM SPECTROMETERS
OPTICAL COMPONENTS
FORENSICS
PARTICLE CHARACTERIZATION
RAMAN
SPECTROSCOPIC ELLIPSOMETRY
SPR IMAGING





Modularity, advanced software and a universal interface facilitate the study of multiple aspects of upconversion

Introduction

Upconversion is a very hot topic in fluorescence spectroscopy, with many exciting new applications, particularly for rare earth sciences. Upconverting materials exhibit a unique fluorescence anti-Stokes shift, which enables them to convert NIR wavelength excitation absorbance into visible shorter wavelength emissions (NIR to UV-VIS). The upconversion process involves the sequential absorption of two photons and subsequent emission of a photon of a higher energy. The most efficient upconverters are trivalent lanthanide ions due to their well-shielded 4f and 5f electronic orbitals with reduced electron-phonon coupling, which minimizes multi-phonon relaxation processes and increases the probability of upconversion involving their long-lived metastable states. The research effort to design and characterize upconverting materials has been rapidly growing as numerous applications have emerged. These include designing efficient and inexpensive UV-VIS lasers, increasing solar cell efficiencies, biomedical imaging, drug delivery, optoelectronics et al. The new Fluorolog-QM spectrofluorometers, due to their modularity and advanced software and a universal interface, are an ideal choice for studying multiple aspects of upconversion. This technical note illustrates the use of Fluorolog-QM-75-21 for spectral and time-resolved characterization of these materials.

Instrumentation

The instrument used was the Fluorolog-QM-75-21 PL system equipped with an optional 980 nm DPSS cw laser with variable power (0-2 W) and a modulation option. Other lasers are available at different wavelengths. The laser can be operated either in a continuous mode to generate steady state upconversion spectra or it can be pulsed directly via Felix FL software with the available TTL output from the standard computer interface in order to measure upconversion decays. In the pulsed operation the software controls the repetition rate and the duration of the laser pulses. The detector used was the standard R928 PMT in the standard Fluorolog-QM multi-mode cooled PMT housing. The detector electronics allows for four different detection modes of operation, software switchable: single photon counting for steady state, analog for steady state, Single Shot Transient Digitizer (SSTD) for phosphorescence decays and Time-Correlated Single Photon Counting (TCSPC)/Multi-Channel Scaling (MCS). Steady state and SSTD detection require no additional electronics modules, while TCSPC and MCS require the appropriate optional electronics modules.

980 nm DPSS laser mounted to the front of the Fluorolog-QM sample compartment.

Results

The upconverting samples were continuously excited using a DPSS 980 nm laser in CW mode with user adjustable power from 0 to 2 Watts. The laser was mounted to the front of the Fluorolog-QM sample compartment and focused on a sample in either powder or solid sample holder.

Steady State Upconversion

Figure 1 shows steady-state upconversion emission spectra of 3 powders exhibiting prominent emission spectral peaks at 520, 546 and 658 nm.

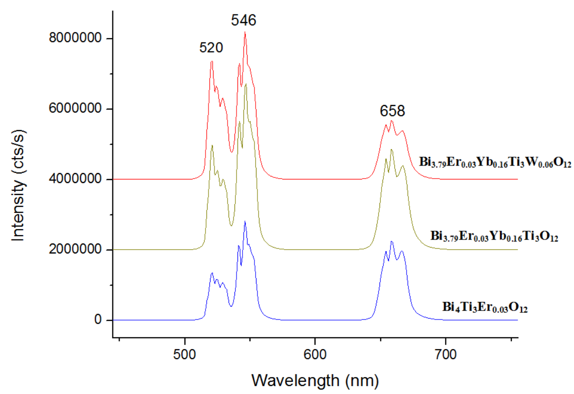


Figure 1: Corrected PL upconversion spectra of three Er^{3+}-containing powders with varying composition of Yb and W excited with 980 nm laser operated at 287 mW.

The results illustrate the effect of Yb and W on the efficiency of Er^{3+} upconversion at different wavelengths. The relative contribution of the 520 nm band increases in the presence of Yb and is further enhanced upon addition of W, while the intensity of the red emission diminishes accordingly.

Upconversion Phosphorescence Lifetimes with 980 nm Laser and standard SSTD Detection

The same 980-nm laser was used for measuring upconversion phosphorescence decays with the standard SSTD detection mode included with the Fluorolog-QM. The laser was triggered by TTL pulses with the repetition rate set at 300 Hz and the pulse width set to 10 µs resulting in 980 nm laser pulses of FWHM ≈ 10 µs. The upconversion emission phosphorescence decays were measured with the R928 PMT operating in the SSTD mode. Each decay trace following the excitation pulse was captured and digitized by the 1MHz interface board operating in the SSTD mode. The SSTD function of the board ensures the most rapid and efficient collection and averaging of decays in the µs-ms range.

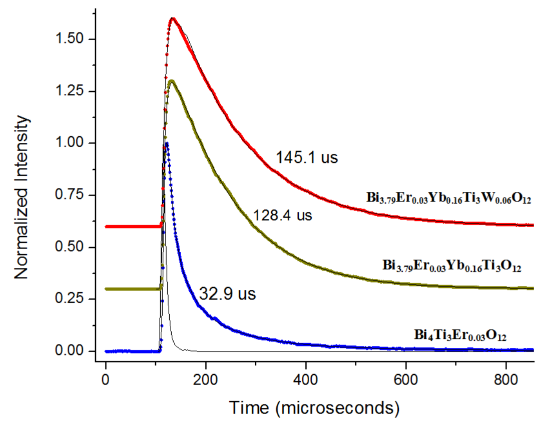


Figure 2: PL upconversion decays of three Er^{3+}-containing powders with varying composition of Yb and W excited with 980 nm laser operating in the pulsed mode. The decays were measured at the 546 nm emission peak. The total number of laser pulses was 10,000 and the total decay acquisition time for these samples was 30 seconds.

Figure 2 shows the PL upconversion decays of the 3 powders measured at the 546 nm emission band. The underlying lifetimes are strongly dependent on the material composition. The decay of $Bi_4Ti_3Er_{0.03}O_{12}$ is non-single exponential with an average lifetime of about 33 µs. Upon addition of Yb to the composition, the average lifetime increases 4-fold to 128 µs and becomes nearly single-exponential. The addition of W further increases the lifetime to 145 µs and the decay remains exponential. These results illustrate the importance of time-resolved measurements in assessing the effects of material composition on the stability of the excited states involved in the upconversion.

Upconversion Phosphorescence Lifetimes with 980 nm laser and optional DeltaHUB module and preamplifier (CFD-2G-C) for MCS detection. Controlling the Fluorolog-QM-LAS-980 upconversion accessory for MCS mode also requires the purchase of the AC-21 cable (LEMO to BNC).

By adding the DeltaHub TCSPC option and constant fraction discriminator (CFD) preamplifier, the Fluorolog-QM becomes capable of measuring PL upconversion lifetimes using the MCS function built into the DeltaHub electronics. While this option is slower than the Fluorolog-QM's standard SSTD technique and adds an extra cost to the instrument, the decays measured with the MCS technique are governed by the Poisson statistics, inherent to the single photon counting. Poisson statistics aids the data analysis by providing accurate estimates of experimental uncertainties making fitting results more reliable, especially for multi-exponential decays. Figure 3 demonstrates the use of the DeltaHub MCS mode with the Fluorolog-QM to measure the PL upconversion decay of erbium-doped fluoride glass.

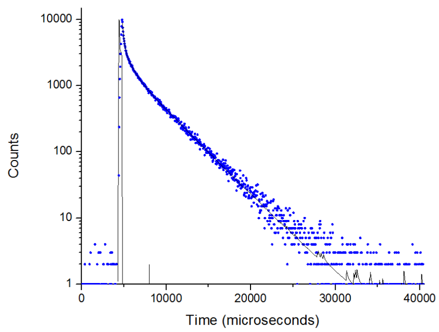


Figure 3: PL upconversion decay of Er^{3+}-doped fluoride glass excited with 980 nm laser operating in the pulsed mode measured with MCS electronics. The decay is 3-exponential with lifetimes 213.3 (74%), 1000.3 (12.5%) and 3412 µs (13.5%). MCS acquisition was set for a total of 10,000 counts per peak channel and the decay acquisition time for these samples was 25 minutes (compared to 30 seconds for the SSTD data collected in figure 2).

Please note that this MCS detection functionality is available with any Fluorolog-QM equipped with HORIBA TCSPC electronics. All that is required is to add the AC-21 cable to interface the DPSS laser to the DeltaHUB. Having a steady state and TCSPC equipped Fluorolog-QM gives you all possible tools for advanced upconversion analysis with the best quality of data and precision.

However, adding MCS to a Fluorolog-QM strictly to add MCS phosphorescence when the standard Fluorolog-QM can measure SSTD phosphorescence should be considered carefully. Adding MCS phosphorescence with the Fluorolog-QM-LAS-980 laser accessory also requires the purchase of the DeltaHUB, the CFD-2G-C constant fraction discriminator and the AC-21 cable. Such an enhancement can be quite expensive and so a customer should carefully consider the added benefit that Poisson statistics provides, weighed against the additional expense and slower speed of MCS compared to the standard SSTD mode available directly with the standard Fluorolog-QM detection and electronics.

Conclusion

The Fluorolog-QM series platform is well-suited for a complete characterization of the steady-state and time-resolved photoluminescence of upconverting materials. The Felix FL software and the universal ASOC interface can control pulsing and pulse duration of a DPSS cw laser thus allowing the use of the same laser source for the steady-state and lifetime measurements. The SSTD mode of the ASOC interface digitizes a complete PL upconversion decay after each laser flash providing the fastest method of lifetime measurements in the µs-ms range. No extra hardware/electronics is required for the SSTD operation.

With the DeltaHub TCSPC option, the Fluorolog-QM can also measure PL upconversion decay using the MCS mode. This well established technique can be beneficial whenever a higher precision is required, especially for complex, multi-component decays. Both the MCS and SSTD techniques operate under the Felix FL software control.

Available Lasers

- 460 nm
- 532 nm
- 660 nm
- 808 nm
- 852 nm
- 980 nm

Safety Notification

The FL-QM-LAS-980 is a Class 4 laser accessory and includes the requisite safety interlocks and features required for such a laser.

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