

PLQY in NIR with Fluorolog-QM and K-Sphere



Introduction

Demands for Photoluminescence Quantum Yield (PLQY) applications are growing, and one big area for the growth is in the Near Infrared (NIR) spectral region. NIR emission plays an important role in optical communications (optical signal generation and amplification), biomedical applications, development of efficient laser glasses, such as Nd³⁺ laser systems, solar energy concentrators, optoelectronics and many others. The overwhelming majority of these applications involve lanthanide ions, many of which emit in the NIR. PLQY measurements are critical in assessing optical efficiency and performance of devices based on such materials. This application note illustrates the use of the Fluorolog-QM-75-21 fluorescence system with an integrating sphere option for the determination of PLQY in the NIR spectral region for two different lanthanide-based materials.

All HORIBA spectrofluorometers equipped with integrating spheres are validated with two very specific standard samples, quinine sulfate and rhodamine, which are accepted PLQY reference materials in the scientific community. Instruments must pass the accepted PLQY values for these samples in the final QC process prior to shipment to a customer. The spectral correction curves used for detector wavelength correction and for PLQY are based on the method described below and they encompass the entire spectral range of the specific NIR detector selected with the instrument. Today there is no globally accepted NIR reference material for PLQY qualification, but we demonstrate below that the Fluorolog-QM is indeed an excellent choice for NIR PLQY measurements.

Experimental

PLQY measurements were conducted with the Fluorolog-QM-75-21 fluorescence system equipped with an optional liquid nitrogen cooled InGaAs solid state detector (QM-NIR-IGA(1.9)P) with the spectral sensitivity range of 900-1900 nm. The integrating sphere was the 3.2 inch diameter K-Sphere mounted inside the Fluorolog-QM sample compartment, directly coupled to the excitation and emission optics. The sphere comes with cuvette, powder and slide holders and has a removable top section for easy access and replacement of the samples (Figure 1).

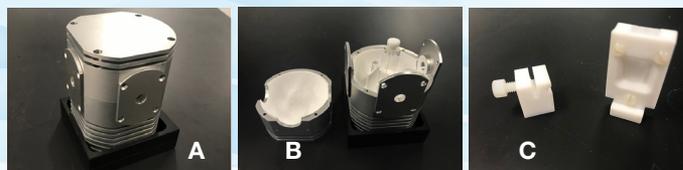


Figure 1: K-Sphere fully assembled (A); with top section removed and cuvette inserted (B); powder and slide holders, which plug into the cuvette holder (C).

The excitation source was either the standard 75 W xenon arc or a 980 nm DPSS laser (2 W, variable power) attached to the front of the Fluorolog-QM sample compartment.



Figure 2: 980 nm DPSS laser mounted to the front of the Fluorolog-QM sample compartment.

Spectral emission corrections were carried out with a HORIBA emission correction kit, which included a calibrated, NIST-traceable tungsten light source, covering a range of 250-2200 nm. For PLQY calculations the corrected emission spectra were expressed in relative quantum units.

Results

Two samples emitting in NIR were used for the PLQY measurements. The first sample was Nd³⁺ doped phosphate glass cut to 12.4 x 12.4 x 40 mm with polished sides (Kigre Inc.). The sample was placed into the cuvette holder of the K-Sphere (Figure 3) and excited with a 75W Xe arc lamp attached to the double excitation monochromator. The Nd-doped glass was excited at 825 nm and the emission scanned from 800 to 1500 nm with a 1-nm step and 0.5 s integration. An identical scan was performed with the empty sphere in order to obtain a blank signal.

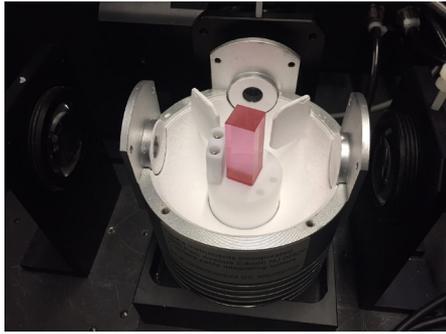


Figure 3: The Nd-doped glass sample inside the K-Sphere with the top part removed.

The PLQY emission scans are presented in Figure 4. The PLQY value was calculated with the Quantum Yield Calculator, which is a standard function of the Fluorolog-QM Felix FL software. The Nd³⁺-doped glass is a strong emitter and exhibits **QY = 0.77 ± 0.01** (based on 5 repeat measurements).

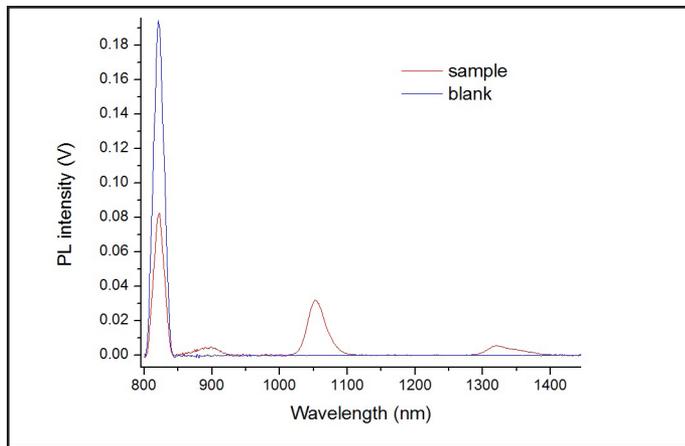


Figure 4: NIR PLQY scans of Nd-doped phosphate glass and a blank using 75W Xe lamp excitation.

The second sample was a composite powder $\text{Bi}_{3.79}\text{Er}_{0.03}\text{Yb}_{0.16}\text{Ti}_3\text{W}_{0.06}\text{O}_{12}$ (sample courtesy of Prof. K. Sreenivas, Delhi University). This sample is a strong upconverter (Figure 4) but also exhibits a weak emission in the NIR. Because of its weak emission the sample was excited with a 980 nm DPSS laser adjusted to 300 mW output power. BaSO₄ powder was used as a blank.

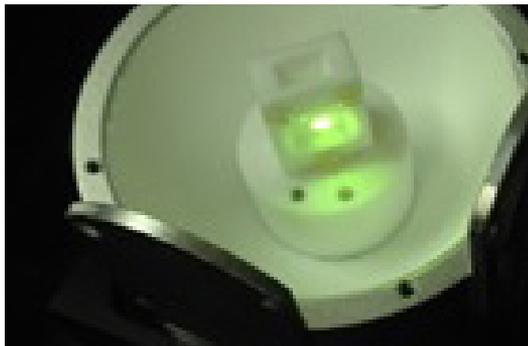


Figure 5: K-Sphere with $\text{Bi}_{3.79}\text{Er}_{0.03}\text{Yb}_{0.16}\text{Ti}_3\text{W}_{0.06}\text{O}_{12}$ powder sample excited with 980 nm laser. The strong green glow is the upconversion emission.

The NIR emission intensity from the powder sample was very low and it was impossible to measure in a single scan the excitation peak and the sample emission spectrum without saturating the detector at the excitation wavelength. Therefore, separate scans were conducted for the sample emission range and the excitation range. For the latter a metallic mesh neutral density filter was used. Since the throughput of the mesh filter is wavelength independent, it was placed on the emission side in order to keep the laser power constant. Keeping the excitation power constant is necessary for an upconverting sample since the excited state kinetics are laser power dependent, which may also affect the QY of the prompt luminescence.

An important factor in QY calculation, especially for weakly emitting samples, is proper background subtraction. At high excitation intensities and low signal levels, there is often some background emission from the sphere, which interferes with the sample luminescence. Due to the excitation light absorption by the sample, the background measured with a blank is always higher than the same background measured with the sample in place. Therefore, in order to subtract the background, the blank signal should be re-scaled properly. The scaling factor can be calculated as the ratio of integrated excitation peaks for the sample and the blank (Figure 6A). For this experiment, the scaling factor was determined to be 0.467 and the raw and adjusted background curves are shown in Figure 7.

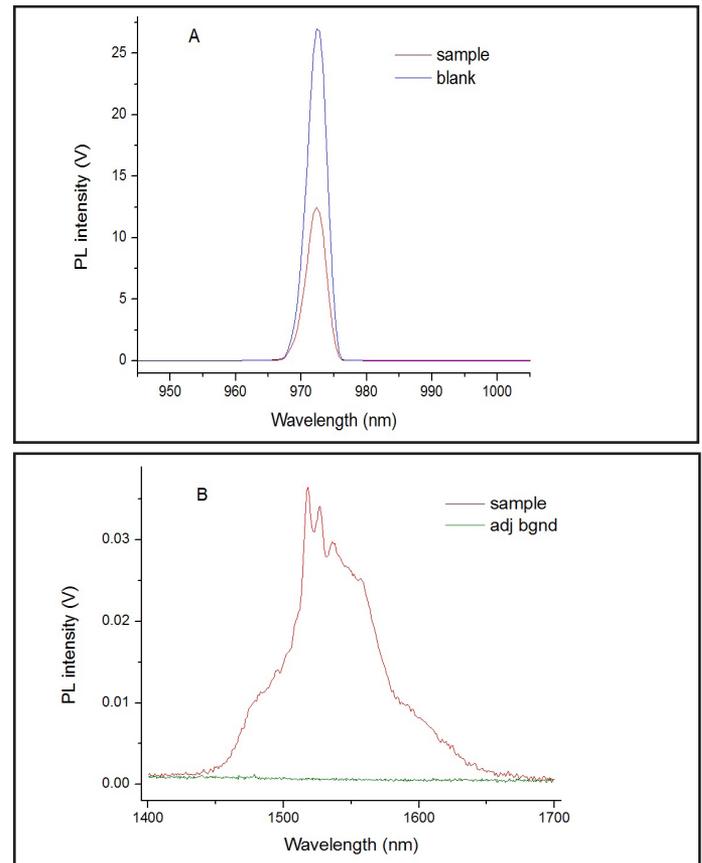


Figure 6: (A) Emission scan across the excitation peak for $\text{Bi}_{3.79}\text{Er}_{0.03}\text{Yb}_{0.16}\text{Ti}_3\text{W}_{0.06}\text{O}_{12}$ powder sample and BaSO₄ blank with ND metal mesh filter (5-fold attenuation) placed on the emission side. (B) Sample emission with background from BaSO₄ blank adjusted for sample transmittance.

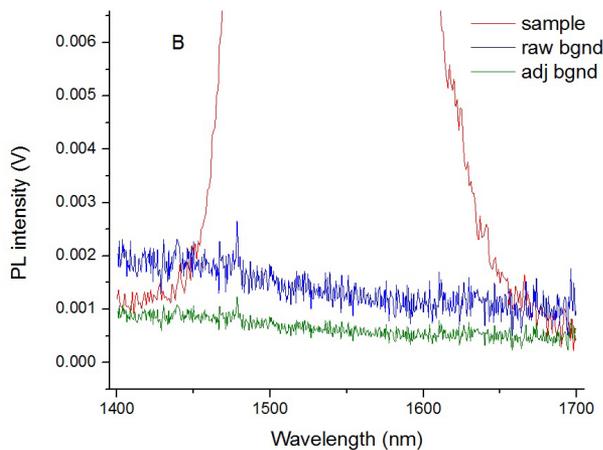


Figure 7: Expanded sample emission graph with the blank background raw (blue) and adjusted for sample transmittance (green).

It has also been observed that the background signal can even be higher than the sample signal for weak emitters, so in this case the background subtraction is even more critical.

The calculated PLQY value for NIR emission of $\text{Bi}_{3.79}\text{Er}_{0.03}\text{Yb}_{0.16}\text{Ti}_3\text{W}_{0.06}\text{O}_{12}$ is very low: $\text{QY} = 0.0094 \pm 0.0006$ (based on 5 repeats). The experiment demonstrates that $\text{PLQY} < 1\%$ can be determined reliably with a good precision using the Fluorolog-QM 8075 with the K-Sphere accessory and a high power laser source.

Conclusion

The Fluorolog-QM fluorescence spectrometer with an integrating sphere option is an excellent choice for PLQY measurements in NIR. The K-Sphere is very convenient and easy to use, as it couples directly to the sample compartment optics and allows a use of external light sources, such as DPSS lasers, which can be attached to the front of the sample compartment. The sphere has holders for cuvettes, slides and powders that can be easily interchanged. The results demonstrate very good reproducibility and precision for NIR PLQY measurements spanning almost two orders of magnitude. Based on multiple measurements, the demonstrated PLQY standard deviations range from 1.3% for high QY value (77%) to 6.4% for the QY below 1%.

