Absolute quantum yield of UV- to NIR-emitting samples

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**Introduction**

The photoluminescence quantum yield (QY) or quantum efficiency $\eta$ is one of the core parameters in the characterisation of luminescent materials\textsuperscript{1,2}. The absolute QY, defined as the ratio of the photons emitted by the material over the absorbed photons, has widely replaced the relative QY method, requiring a fluorescent standard of known QY. It also constitutes a simpler method relying on minimum alignment and calibration compared to thermal lens/beam deflection and photoacoustic methods\textsuperscript{3}. Instead, a fluorescence spectrometer equipped with an integrating sphere is employed in the absolute method.

**Methods & Materials**

Liquid and solid materials were measured spanning excitation and emission wavelengths from the UV to the NIR. LED phosphor powders and thin films doped with lanthanides such as Cerium (Ce$^{3+}$), Terbium (Tb$^{3+}$) and Europium (Eu$^{2+}$) were measured in standard PTFE trays. In the NIR range, semiconductor nanocrystal lead sulfide (PbS) quantum dots (QD-NIR-1V, Ocean Optics) in toluene were dispensed into 10 mm path-length quartz cuvettes.

Excitation and emission spectra were measured in a fluorescence spectrometer FS5-NIR equipped with an integrating sphere module (SC-30) and a single photon PMT detector (Hamamatsu, R2658P) extending the emission detection range to 1010nm. For liquid samples a measurement over the scattering $L_{sam}$ and emission $E_{sam}$ of the sample, followed by a measurement of the solvent, also called reference or blank, $L_{ref}$ and $E_{ref}$, as:

$$QY = \frac{E_{sam} - E_{ref}}{L_{ref} - L_{sam}}$$

For solid powder and thin film samples three measurements were performed for the calculation of the quantum yield: i) A measurement of the scattering without the sample, $L_{ref}$, ii) a measurement of the emission of the sample under direct excitation, $E_{samdir}$, and iii) a measurement of the scattering with the sample under indirect excitation, $E_{samind}$, as$^4$:

$$QY = E_{samdir} \times \left[ 1 - \frac{1 - (E_{samdir} / E_{samind})}{1 - (L_{samdir} / L_{samind})} \right] / L_{ref} \times \left[ 1 - \frac{1 - (E_{samdir} / E_{samind})}{1 - (L_{samdir} / L_{samind})} \right]$$

The calculation of the QY was performed in the wizard of the instrument's operating software, Fluoracle.

**Results – Discussion**

Figures 1 and 2 display the scattering and emission spectra of Ce$^{3+}$ and Ce$^{3+}$/Tb$^{3+}$-doped phosphor, respectively.
In addition to the intense green emission, the QY increases from 85.1\% for the Ce$^{3+}$-doped phosphor to 92\% for Ce$^{3+}$/Tb$^{3+}$-doped phosphor$^{5,6}$.

Figure 1: Scattering and emission spectra of LaPO$_4$-Ce$^{3+}$ phosphor. The measurement conditions were: $\Delta \lambda_{\text{exc}}=10$nm, $\Delta \lambda_{\text{em}}=1$nm, step=0.5nm, dwell=0.2s.

Figure 2: Scattering and emission spectra of Ce$^{3+}$/Tb$^{3+}$-doped phosphor. The measurement conditions were: $\Delta \lambda_{\text{exc}}=10$nm, $\Delta \lambda_{\text{em}}=0.5$nm, step=0.25nm, dwell=0.1s.
Scattering, direct and indirect excitation emission spectra of a Eu\(^{2+}\)-doped thin film and PbS quantum dots can be seen in Figure 3 and 4, respectively. Note the considerable emission measured under indirect excitation of the thin film in the integrating sphere.

**Figure 3**: Eu\(^{2+}\)-doped thin film under (a) direct and (b) indirect excitation. The samples were excited at 480nm with excitation and emission bandwidths \(\Delta\lambda_{\text{exc}}=3\)nm and \(\Delta\lambda_{\text{em}}=0.2\)nm, respectively, with a step of 0.25nm and integration time of 0.1s.

**Figure 4**: Scattering and emission spectra of PbS quantum dots. Conditions were: \(\Delta\lambda_{\text{exc}}=5\)nm, \(\Delta\lambda_{\text{em}}=2\)nm, step=1nm, dwell=0.5s.
References

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