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Determination of Quantum Yields for Luminescent Materials Emitting in the Near-Infrared Range

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Introduction

This work was part of the BMBF project CoMaMed – Converter Materials for Laser Diodes in Medical Applications. The main objective was the development of novel optical materials which main emission is peaking within the optical window of (human) tissue from 700 to 1300 nm (Fig. 1). The main focus was directed towards activators emitting in the NIR and their sensitization by suitable co-dopants with a large absorption cross-section in the blue spectral range as well as appropriate energy levels for an efficient energy transfer to the activators. To evaluate the prepared samples it was necessary to develop a reliable method for obtaining the external quantum yield (eQY) in the near infrared by optical spectroscopy.

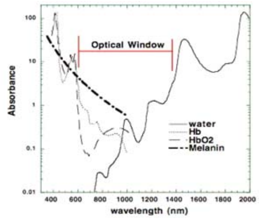

Fig. 1: Absorbance over wavelength in the visible and near infrared for components of human tissue. (www.photobiology.info/Hamblin.html (March 12th, 2009))

Background of External Quantum Yield Determination

The eQY of a luminescent material gives the ratio of emitted to absorbed photons and is thus a measure for the efficacy of the phosphor. In general to methods can be used:

Absolute Method Conducted in an Integrating Sphere

Idea:
- Incident photons from the excitations source are either absorbed or reflected (transmission is considered to be zero)
- Only absorbed photons can be converted and contribute to the emission integral of the sample
- eQY is 100 % if all absorbed photons are converted and thus the quotient of the emission integrals with and without sample including the excitation is unity

Requirements:
- Integrating sphere with a highly reflective coating for a wide spectral range covering excitation and emission band(s) of the sample
- Excitation source with constant radiant power

Procedure:
- Step 1: Emission scan without sample for $\lambda_1 \leq \lambda_{Excitation} \leq \lambda_2 \leq \lambda_{Emission} \leq \lambda_3$
- Step 2: Emission scan with sample for $\lambda_1 \leq \lambda_{Excitation} \leq \lambda_2 \leq \lambda_{Emission} \leq \lambda_3$
- Step 3: Calculation (see eq. (1))

$$eQY = \frac{\int_{\lambda_2}^{\lambda_3} I_{Sample} d\lambda - \int_{\lambda_2}^{\lambda_3} I_{noSample} d\lambda}{\int_{\lambda_1}^{\lambda_2} I_{noSample} d\lambda - \int_{\lambda_1}^{\lambda_2} I_{Sample} d\lambda} \qquad (1)$$

Advantages:
- No reference needed

Relative Method by using a Reference Material with known eQY

Idea:
- Ratio of the number of emitted photons N_{em} to the number of absorbed photons N_{abs} multiplied with the conversion efficiency η is unity for all samples

$$\frac{N_{em}}{N_{abs} \cdot \eta} = 1 \qquad (2)$$

- Absorption can be derived from reflectance measurements (sum of absorption and reflection is unity if transmission is considered to be zero)
- Emission integral is direct proportional to the number of emitted photons

Requirements:
- Reference sample with known η which is called eQY for luminescent materials
- Similar luminescent properties of sample and reference because all data has to be acquired under identical conditions

Procedure:
- Determination of reflectance at excitation wavelength and measurement of emission spectra for reference and sample
- Eq. (2) gives

$$eQY_{Sample} = eQY_{Reference} \cdot \frac{\int_{\lambda_1}^{\lambda_2} I_{Sample} d\lambda}{\int_{\lambda_1}^{\lambda_2} I_{Reference} d\lambda} \cdot \frac{1 - \mathrm{Refl}_{Reference}^{\lambda(Exc)}}{1 - \mathrm{Refl}_{Sample}^{\lambda(Exc)}} \qquad (3)$$

Advantages:
- Reference material enhances reliability (intrinsic correction)

Determination of the External Quantum Yield for Near-Infrared Phosphors

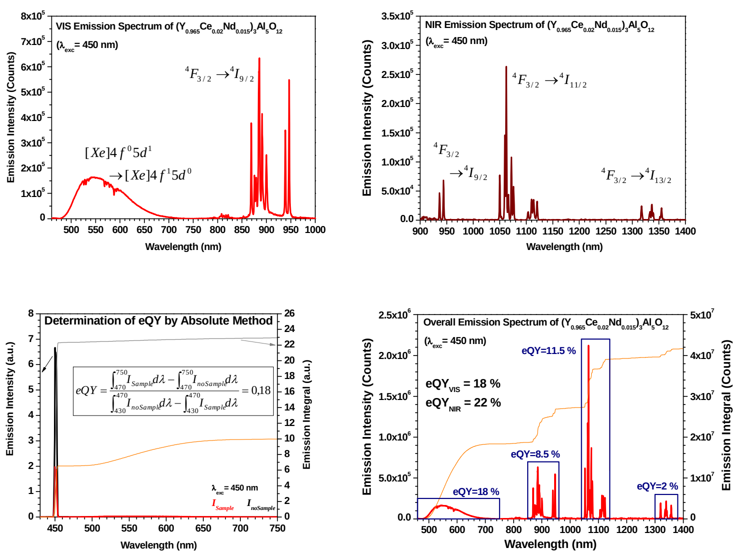

Fig.2. Procedure of the determination of the external quantum yield in the visible and near-infrared spectral range for the phosphor $(Y_{0.965}Nd_{0.02}Ce_{0.015})_3Al_5O_{12}$, a well known garnet type luminescent material.

Problem:
- So far no applicable method for determining the eQY for NIR-emitting samples
- Necessity to develop a procedure feasible with given spectroscopic equipment, especially with available detectors:
  - cooled single-photon counting photomultiplier (Hamamatsu R2658P) for 400 nm $\leq \lambda \leq$ 1,000 nm
  - two-stage thermoelectrically cooled InGaAs photodiode (Hamamatsu G8605-23) for 900 nm $\leq \lambda \leq$ 1,650 nm

Idea:
- Utilisation of the direct proportionality of the emission integral of a sample to the eQY (see eq. (1) and (3))
- Application of one of the established methods to determine the eQY of a sample in the visible range
- Calculation of the overall eQY, i.e. in the visible and NIR, by using said proportionality

Requirements:
- Sample needs to emit in the visible range of the spectrum and within the overlap of the detection ranges of the two detectors, otherwise no combination possible

Procedure:
- Step 1: Emission scan of the sample in the visible range
- Step 2: Determination of eQY for emission in the visible range by either method
- Step 3: Emission scan of the sample in the NIR range
- Step 4: Appending the NIR spectra to the VIS spectra using a suitable method for data scaling (in case of Nd^{3+}: absolute peak intensity, branching ratios)

Limitations:
- Both detectors posses low sensitivity in the spectral overlap range
- Method restricted to samples emitting in visible and overlap range

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