

ON THE INFLUENCE OF SAMPLE PREPARATION ON THE RE-ABSORPTION IN ABSOLUTE QUANTUM YIELD MEASUREMENTS BY INTEGRATING SPHERES

XVI International Symposium on Luminescence Spectrometry
Rhodes Island, Greece, September 2014

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Background: Quantum yield (QY) determination is presently done by different techniques, i.e. by relative or absolute methods. A widely applied procedure to measure the absolute quantum yield of organic solid state compounds by an integrating sphere (Ulbricht sphere) were firstly described by Y. Kawamura [1]. However, for this method the effect of re-absorption has to be considered if the luminescent material shows spectral overlap between the respective excitation and emission band. Due to the measuring principle of an integration sphere, emitted

photons can partially be reabsorbed by the phosphor and subsequently re-emitted with a probability determined by the quantum yield of the phosphor. This effect leads to a lowered measured QY. We investigated the QY of YAG:Ce and the influence of the re-absorption on the QY correlated with the phosphor concentration. Furthermore, we applied a correction algorithm to the measured QY as described by Ahn et al.[2] and reveal novel challenges in this context.

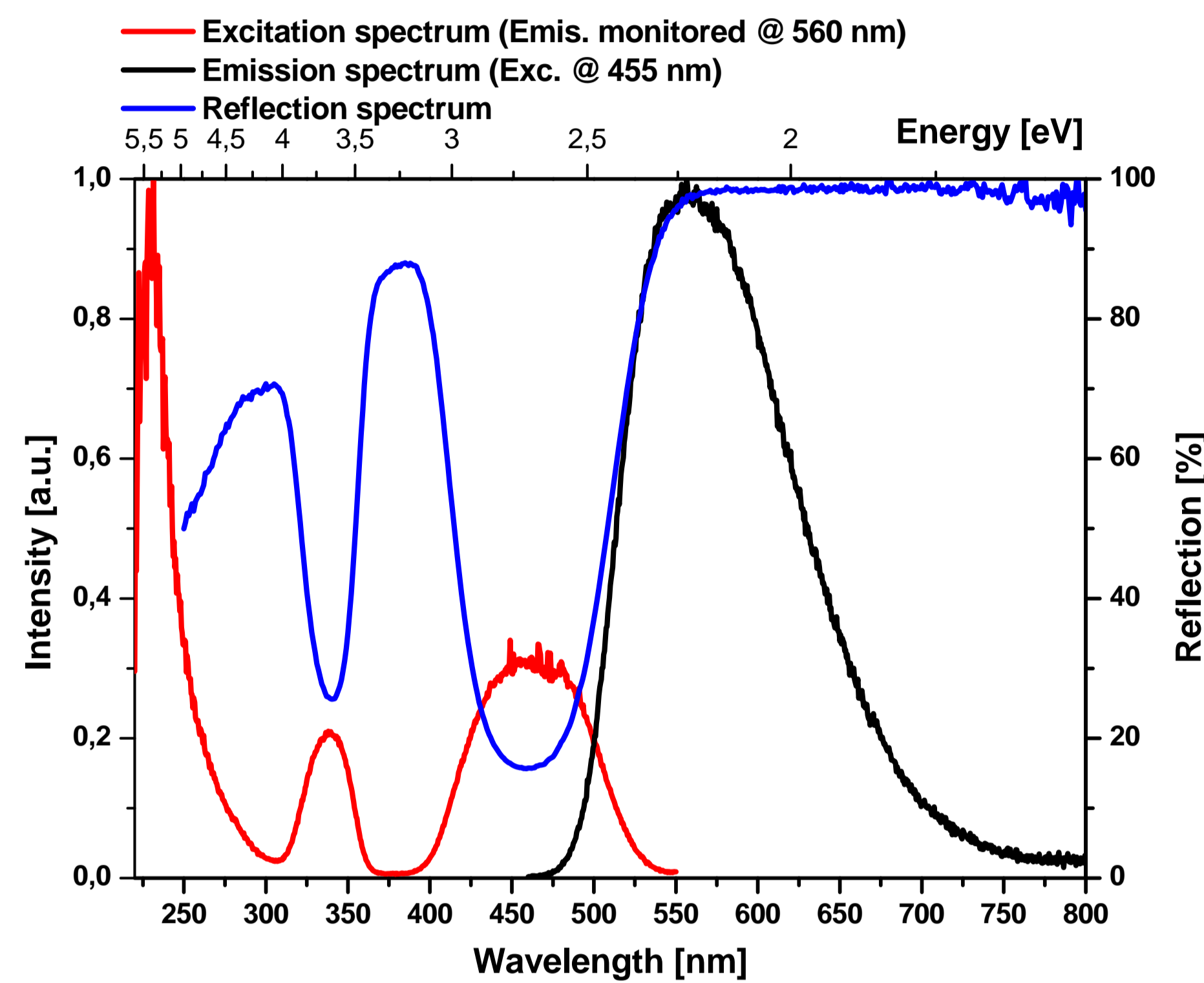


Fig. 1: Reflection spectra, normalised excitation- and emission spectra of YAG:Ce

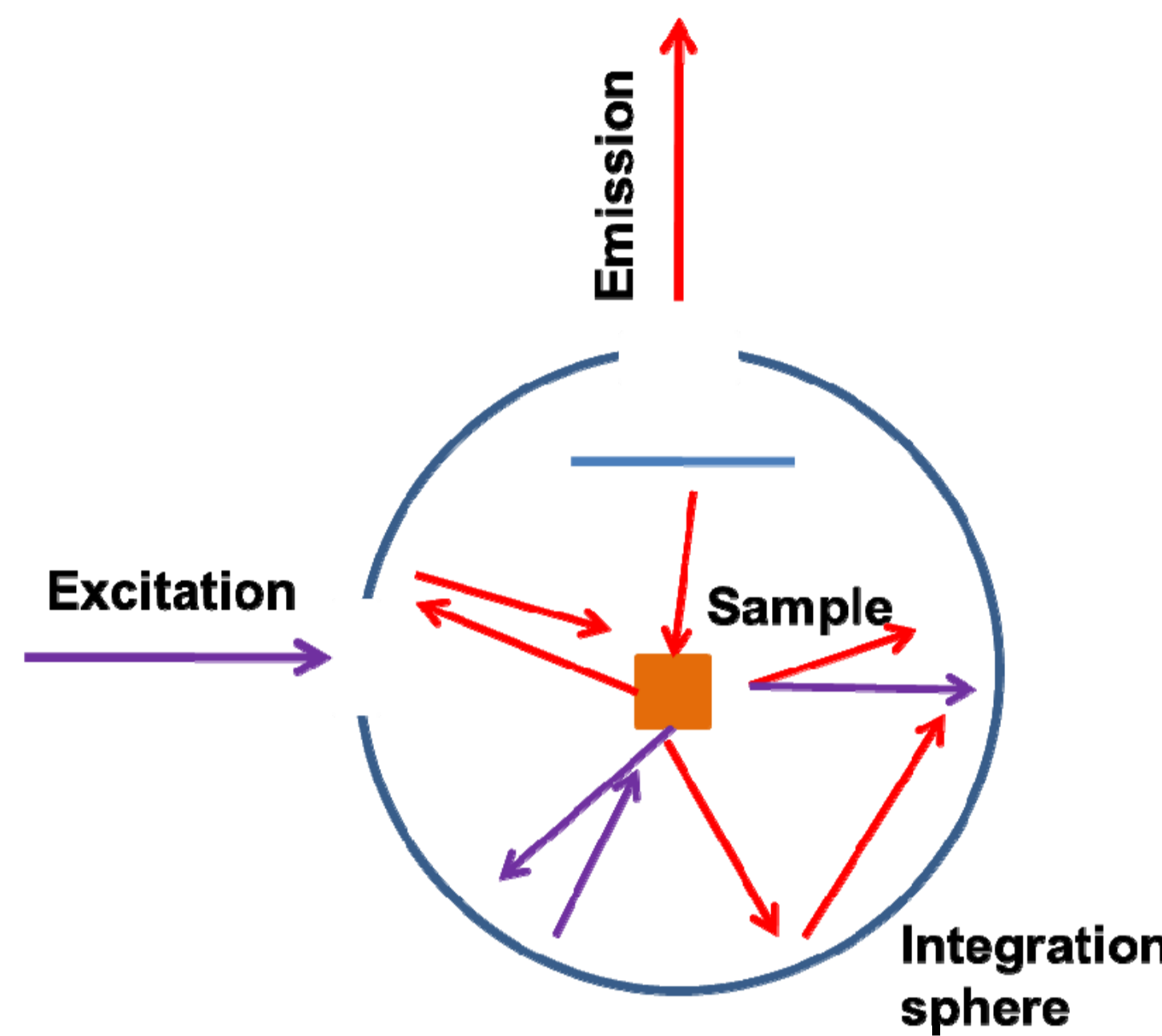


Fig. 2: Measuring scheme of the integration sphere for recording emission and reflection spectra

$$\phi_f = \frac{N(em)}{N(abs)} = \frac{\int \frac{\lambda}{hc} [I_{em}^{sample}(\lambda) - I_{em}^{reference}(\lambda)] d\lambda}{\int \frac{\lambda}{hc} [I_{ex}^{reference}(\lambda) - I_{ex}^{sample}(\lambda)] d\lambda} \quad (1)$$

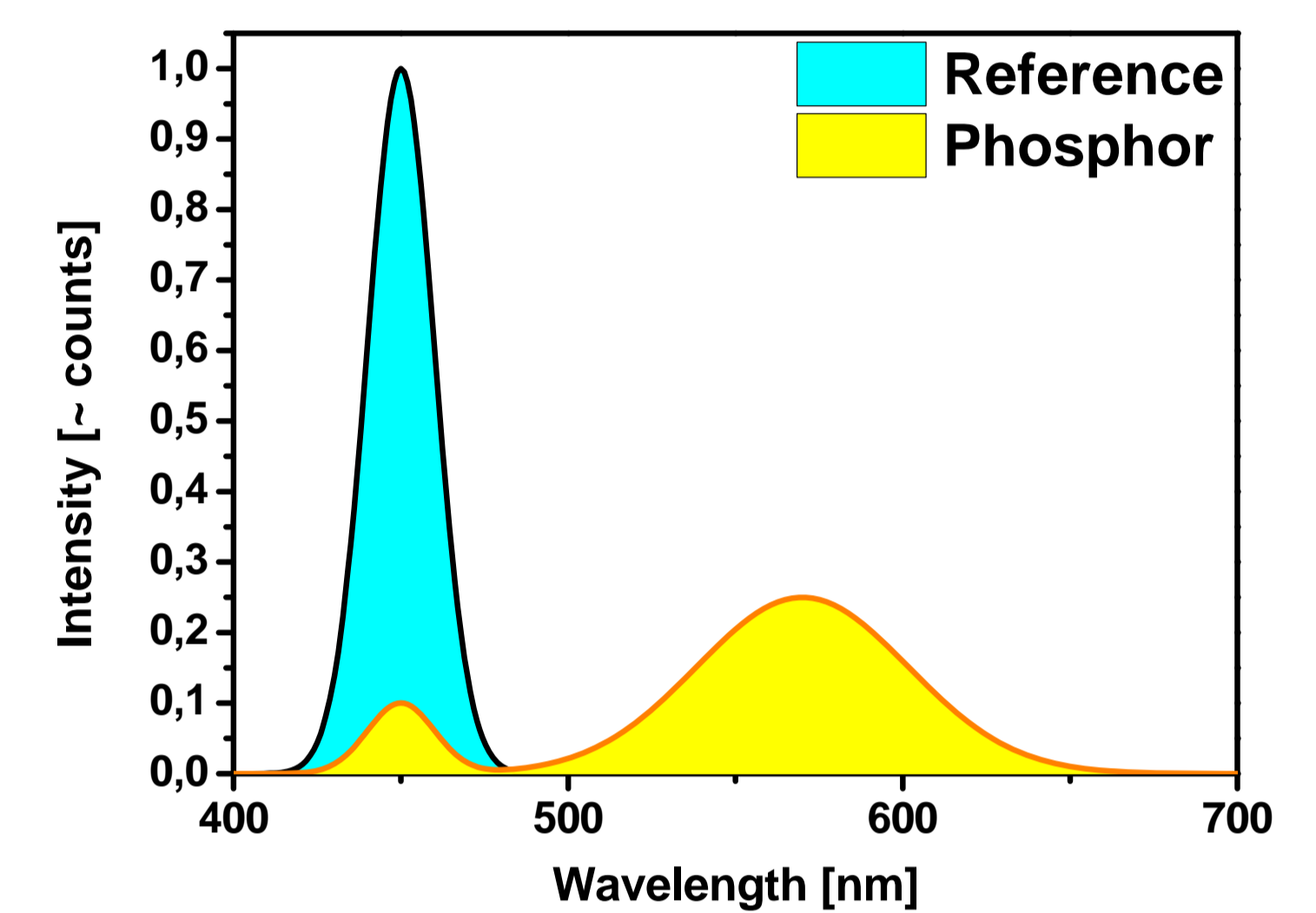


Fig. 3: Equation for QY calculation and schematic depiction of the measurement

Principle: A concentration series of YAG:Ce (Philips U819) was prepared (Fig. 4). To this end, the phosphor was mixed with the reference white standard ($BaSO_4$) in 1 %, 2 %, 5 %, 10 %, 20 %, 40 %, 60 % and 80 % by mass. The emission spectra (including the excitation band) (Fig. 5) were recorded with an Edinburgh Instruments FS 920 spectrometer using a Spectralon integration sphere. The measuring scheme is presented in Fig. 2. To calculate the observed QY, equation 1 (Fig. 3) was used.

For the correction of the observed quantum yields using the approach of Ahn et al. (eq. 3) the re-absorption parameter a is necessary. Re-absorption parameter a is computed according to eq. 2. To determine the absorption the reflection spectra of the concentration sequence was recorded (Fig. 6) using the same spectrometer with integrating sphere as described above.



Fig. 4: Sample holder with YAG:Ce (U819)/ $BaSO_4$ - concentration series. Increasing YAG:Ce content 1 % (left, bottom), 2 %, 5 %, 10 %, 20 %, 40 %, 60 %, 80 % (right, bottom)

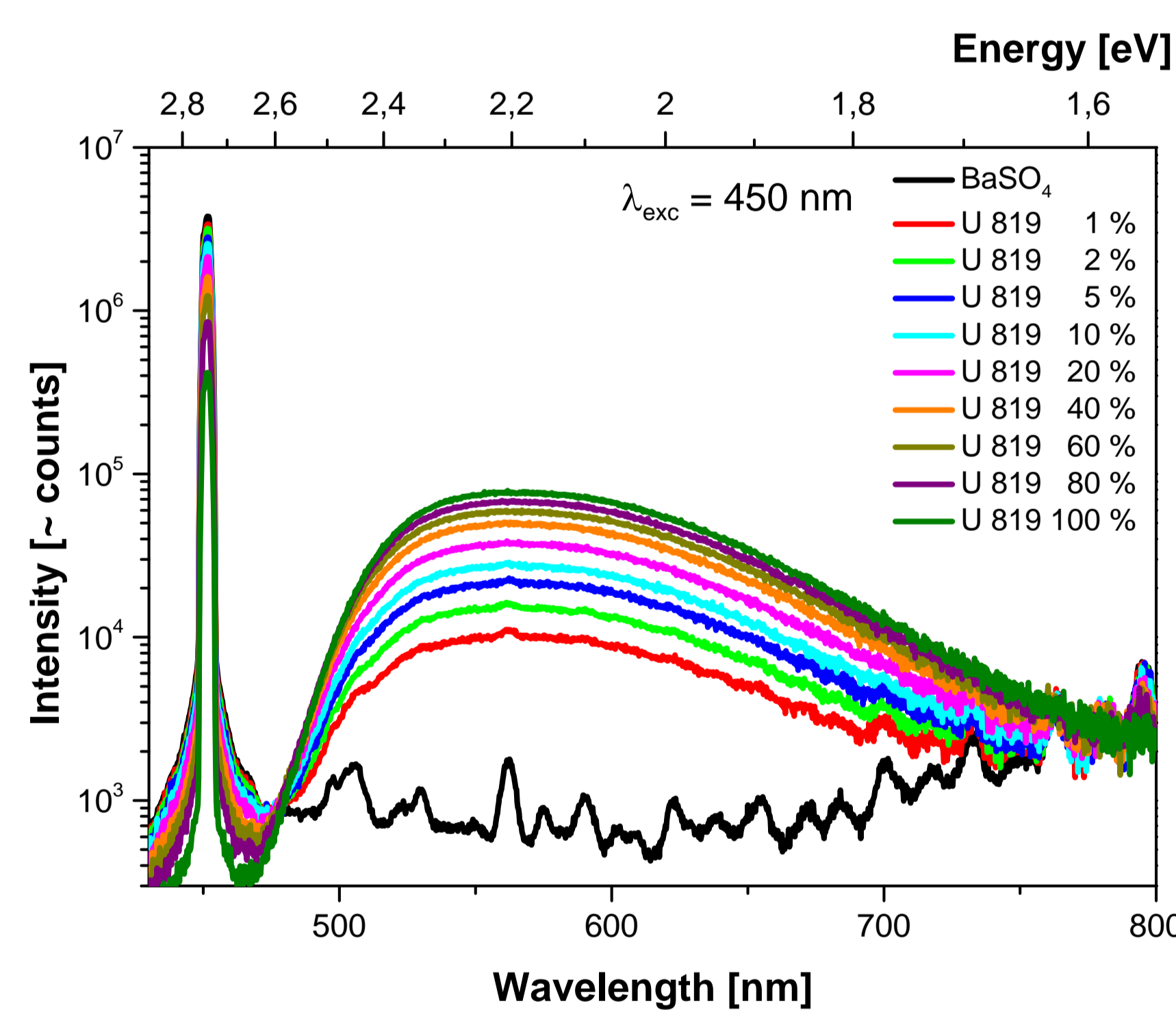


Fig. 5: Emission spectra of the YAG:Ce (U819)/ $BaSO_4$ concentration sequence (with excitation band at 450 nm)

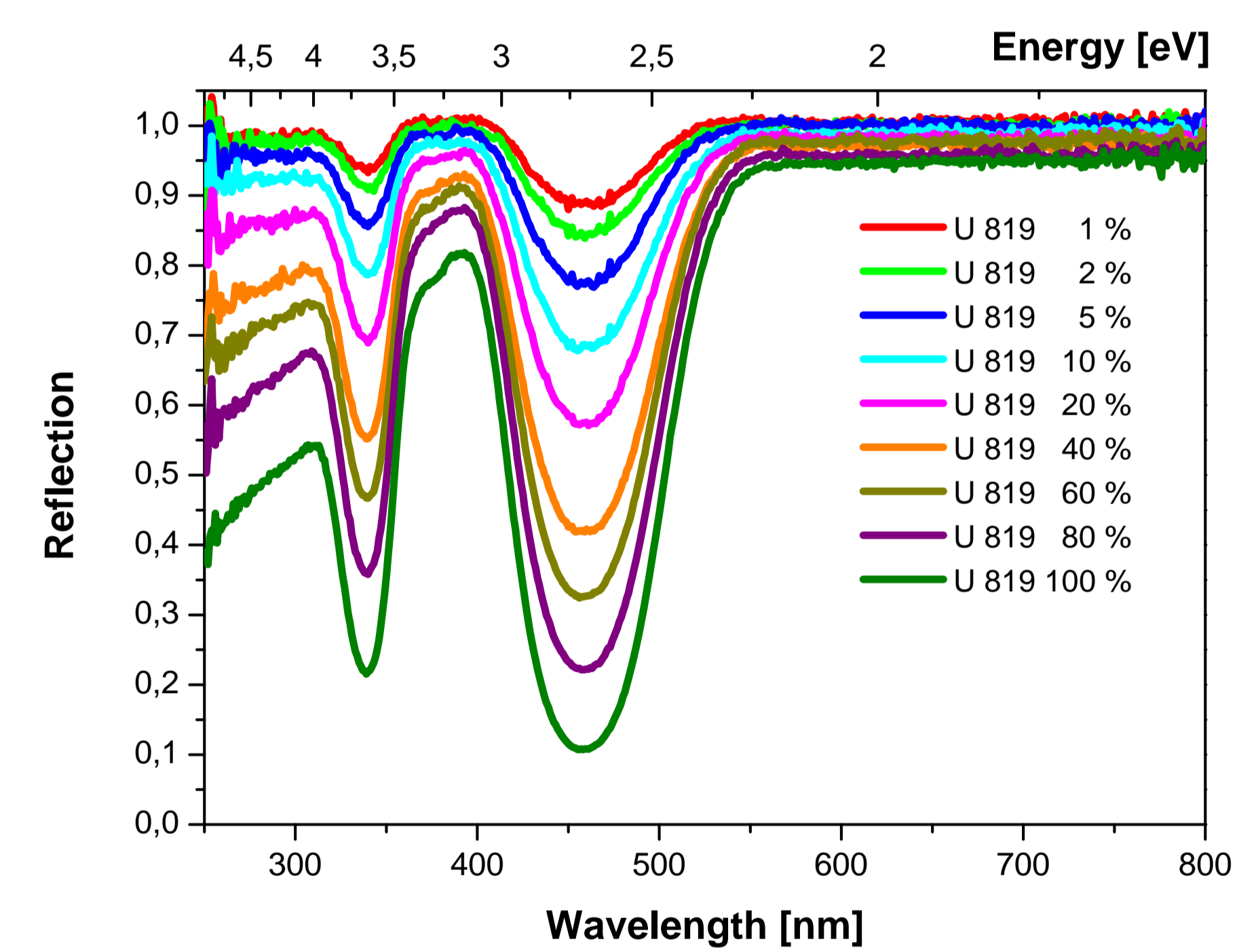


Fig. 6: Reflection spectra of the YAG:Ce (U819)/ $BaSO_4$ concentration sequence

$$a = \int (emission_{\lambda} * absorption_{\lambda}) d\lambda \quad (2)$$

$$\phi_{corr} = \frac{\phi_{obs}}{1 - a * \phi_{obs}} \quad (3)$$

Results and Discussion: It turned out that a strong influence of the phosphor concentration on the QY exist. We observed an increase of the QY for a decrease of the YAG:Ce (U819) concentration (Tab. 1, Fig. 7). This phenomenon can be explained with a reduced re-absorption effect for low phosphor concentrations.

The correction of the measured QY values is more essential for high YAG:Ce concentrations which can be explained with a higher re-absorption due to the high phosphor concentration. However, the corrected values should show a constant value for all concentrations. The problem here is the correct determination of the absolute absorbed photons. Due to scattering effects, the re-absorption of powder samples can not be so easily determined as in non-scattering samples.

Tab. 1: Measured QY and corrected QY by approach of Ahn et al. [2]

Sample	QY obs.	Re-Absorption	QY corr.
U 819 1 %	98	0,02	98
U 819 2 %	99	0,01	99
U 819 5 %	97	0,02	97
U 819 10 %	96	0,10	96
U 819 20 %	94	0,14	95
U 819 40 %	93	0,23	95
U 819 60 %	94	0,22	95
U 819 80 %	93	0,33	95
U 819 100 %	92	0,43	95

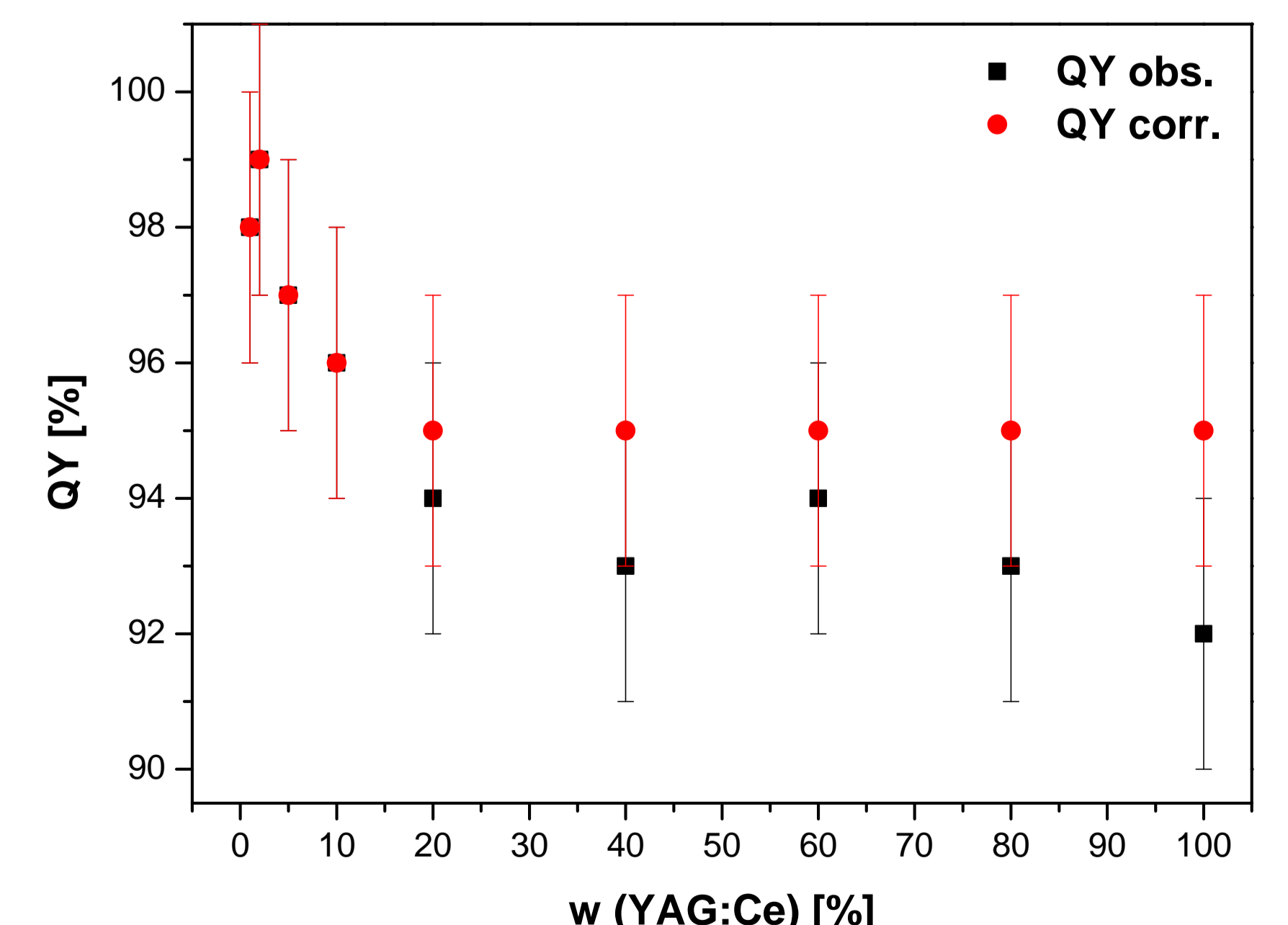


Fig. 7: Measured QY and corrected QY by the approach of Ahn et al. [2]

Conclusions: The effect of the phosphor concentration on the re-absorption and therefore on the QY is shown when using an integrating sphere. Furthermore, the lack of optimised correction of the values is shown due to the lack of a correct determination of the absolute absorbed photons. By determination the QY using an integrating sphere several parameters with respect to the re-absorption has to be considered. Not only the concentration of the phosphor but also the sample area and size of the Ulbricht sphere are crucial for QY measurements.