

# On the Temperature-Dependent External Photoluminescence Quantum Yield of $\text{Mg}_{14}\text{Ge}_5\text{O}_{24}:\text{Mn}^{4+}$ by Employing an Integrating Sphere

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## Background

Manganese-activated magnesium germanate (MGM) is a candidate for the conversion of blue to red light in the rapidly expanding market of warm white light emitting pcLEDs [1]. The luminescence quenching temperature is an important parameter especially in high-power LEDs, since the chip temperature can rise up to 200 °C or higher. Thus, for LED phosphors the external quantum yield as a function of the operation temperature is an important figure of merit.

In literature some procedures for the determination of quantum yield are stated, such as a calorimetric, an absolute and a relative reference-based method [2]. All those techniques can also be applied for temperature-dependent measurements but require rather sophisticated equipment. In order to conduct measurements according to the absolute method we have designed an integrating sphere with a sample holder that can be heated up to 500 K. To the best of our knowledge up to now published temperature-dependent external quantum yields are limited to emission values as function of temperature only. Thus, changes in absorption with increasing temperature have been neglected to this point. In this work we present the determination of the absolute external quantum yields of MGM as function of temperature using a heatable integrating sphere and compare the findings to results gained by the relative method.

## Determination of the External Quantum Yield as Function of Temperature

### Absolute method by using a heatable integrating sphere ( $\text{Mg}_{14}\text{Ge}_5\text{O}_{24}:\text{Mn}^{4+}$ )

#### Idea

- Incident photons from the excitation source are either absorbed or reflected
- Only absorbed photons can be converted and contribute to the emission integral of the sample
- External Quantum Yield is unity if all absorbed photons are converted
- Not only emission values are temperature-dependent, but absorption as well

#### Requirements

- Highly reflective coating which covers a wide spectral range
- Low spectral overlap between excitation and emission of the sample to avoid reabsorption
- Thin sample layer to minimize temperature gradients

#### Procedure

- Determination of excitation (fixed wavelength) and emission values at different temperatures
- eQY as f(T) can be calculated by Eq. 1:

$$eQY(T) = \frac{\int_{\lambda_{em}}^{\lambda_{em} + \Delta\lambda} \frac{1}{\lambda_{em}} (I_x(\lambda_{em}) - I_b(\lambda_{em})) \lambda_{em} d\lambda_{em}}{\int_{\lambda_{ex} - \Delta\lambda}^{\lambda_{ex} + \Delta\lambda} \frac{1}{\lambda_{ex}} (I_b(\lambda_{ex}) - I_x(\lambda_{ex})) \lambda_{ex} d\lambda_{ex}} = \frac{N_{em}}{N_{abs}} \quad (1)$$

$\lambda_{ex}$ : excitation wavelength;  $\lambda_{em}$ : emission wavelength;  $I_x$ : measured emission spectrum of sample x;  $I_b$ : measured emission spectrum of blank b

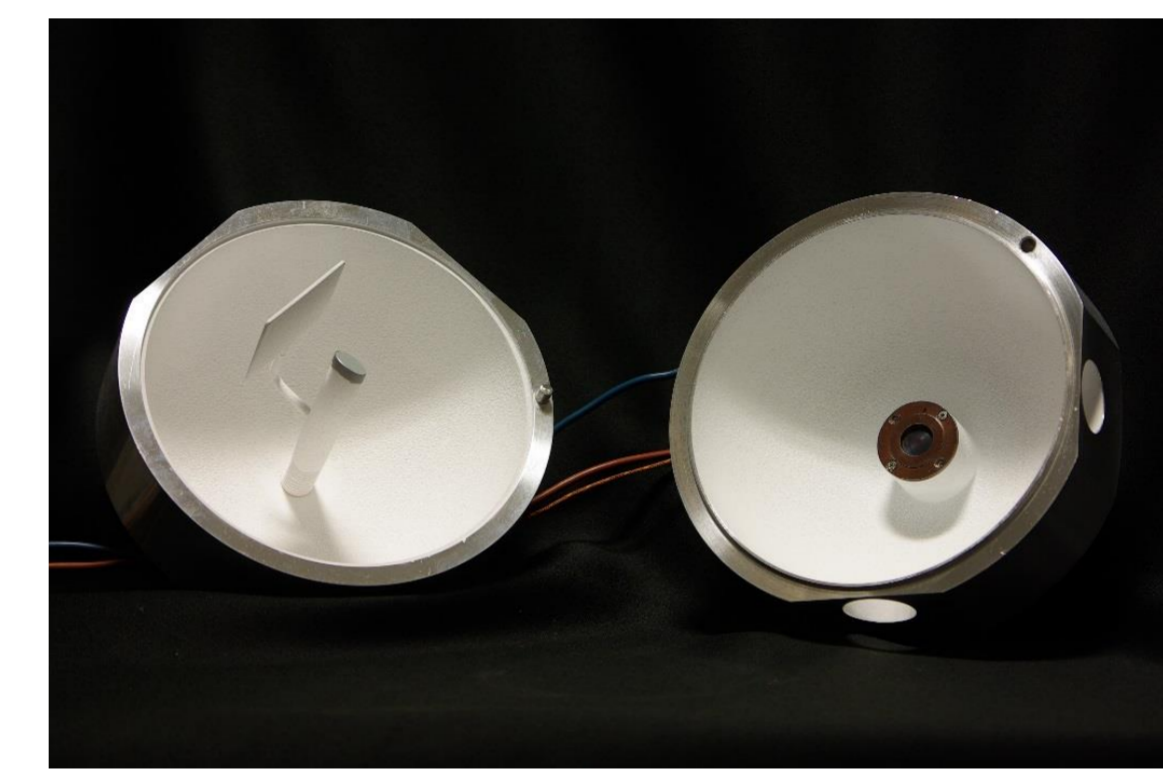


Fig. 1. Heatable integrating sphere with copper sample holder and a  $\text{BaSO}_4$  coating as diffuse reflecting layer.

## Results

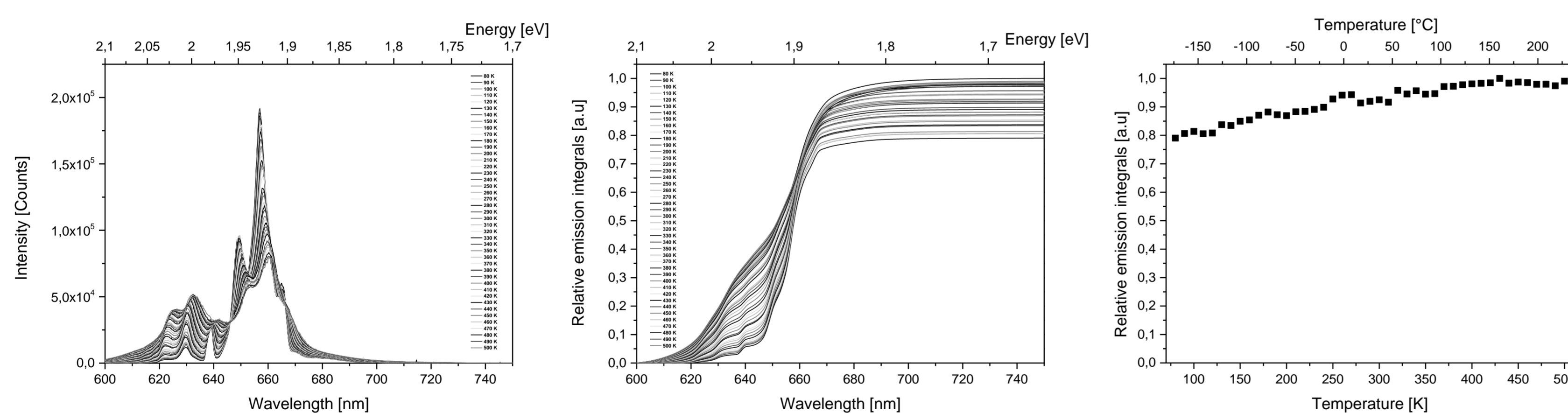


Fig. 1. Emission spectra and integrals as function of temperature in the red spectral range for the phosphor  $\text{Mg}_{14}\text{Ge}_5\text{O}_{24}:\text{Mn}^{4+}$ , a well known luminescent material.

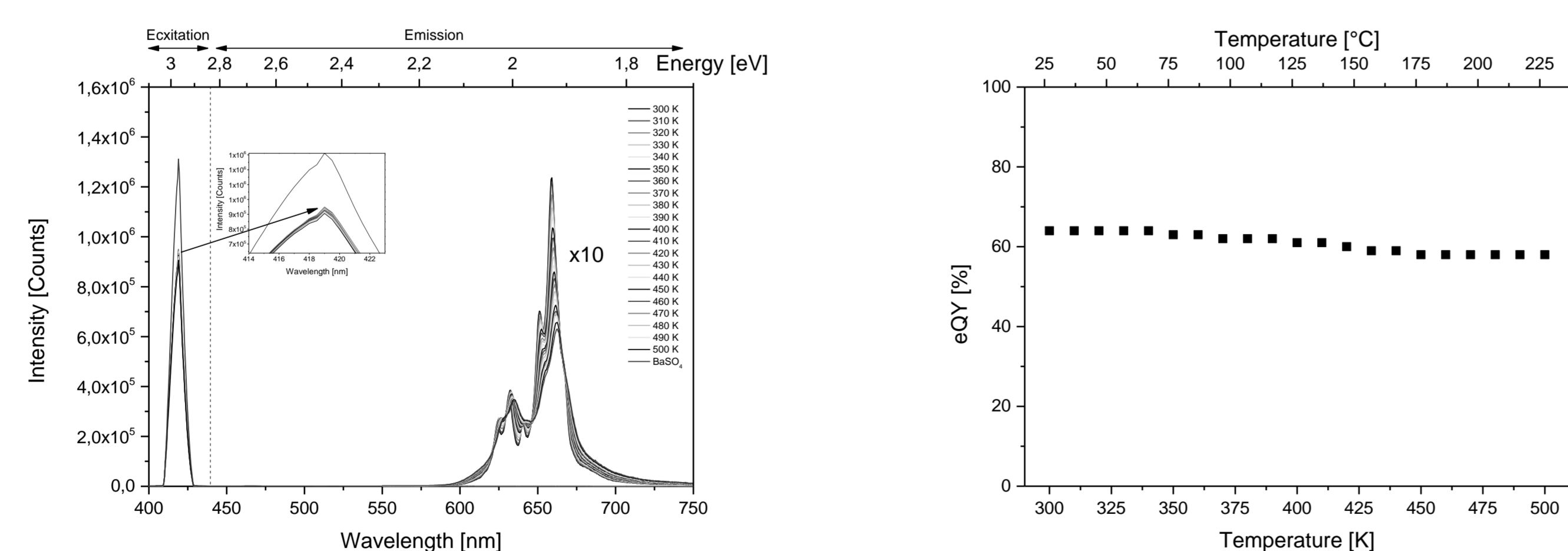


Fig. 2. T-dependent signals of integrating sphere measurement for the sample and the reference ( $\text{BaSO}_4$  99.999% Aldrich). The position between excitation and emission is separated by a dashed vertical line.

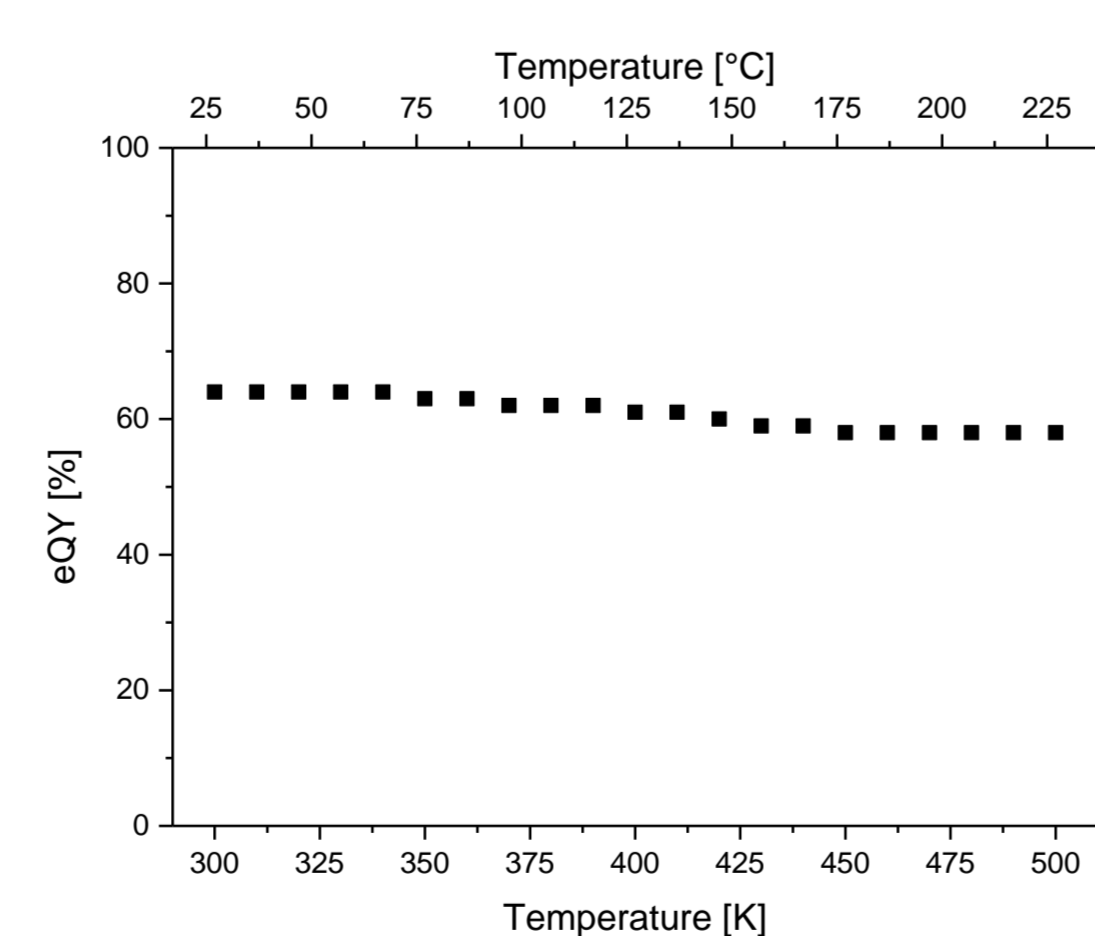


Fig. 3. Absolute external Quantum Yields as function of temperature.

- Emission spectra as function of temperature (Fig. 1) were recorded for  $\lambda_{exc} = 420$  nm, which corresponds to the spin-allowed transition of  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  of  $\text{Mn}^{4+}$  in  $\text{Mg}_{14}\text{Ge}_5\text{O}_{24}$ . Emission originates from the transition  ${}^2E_g \rightarrow {}^4A_{2g}$ . With increasing temperature a decrease of the peak intensity can be observed, which is compensated by spectral broadening. Due to the effect of spectral broadening emission integrals even increase
- Fig. 2 shows that with increasing temperature absorption values increase slightly. However, for calculation of the external Quantum Yield changes in absorption can not be neglected
- In Fig. 3 the progress of eQY from 300 to 500 K can be observed. Compared with the curve shape of the emission integrals gained by the relative method there is a significant difference. Due to the effect of absorption increase the eQY drops slightly, while the emission integrals steady increase
- In consequence for the construction of pcLEDs it is of high importance to measure not only relative emission integrals as function of temperature, but one should also take the temperature-dependency of the absorption spectrum into account

#### References

- [1] L. Thorington, J. Opt. Soc. Am. 40 (1950) 579.
- [2] U. Resch-Genger, Standardization and quality assurance in fluorescence measurements: 1: Techniques, Springer, Berlin, London, 2008.

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