Highly Efficient $Tb^{3+} \rightarrow Eu^{3+}$ Energy Transfer in Molybdate Hosts

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Florian Baur, David Böhnisch, and Thomas Jüstel

Münster University of Applied Sciences, Department of Chemical Engineering

Stegerwaldstrasse 39, D-48565 Steinfurt, Germany

Corresponding authors: *florian.baur@fh-muenster.de and tj@fh-muenster.de*

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Background

Eu^{3+} activated red emitting phosphors generally exhibit high LE compared to band emitting Eu^{2+} activated red phosphors, but they suffer from low absorption in the blue spectral range. The use of sensitizers is a suitable method to overcome such shortcomings as for example in the commercial phosphors $BaMgAl_{10}O_{17}$:Eu^{2+},Mn^{2+} or $LaPO_4$:Ce^{3+},Tb^{3+}. However, Eu^{3+} cannot be sensitized by Ce^{3+} as a Ce^{3+}/Eu^{3+} metal-to-metal charge transfer efficiently quenches the luminescence. Energy transfer from Tb^{3+} to Eu^{3+} is well documented in published literature, branding Tb^{3+} as a potential sensitizer for Eu^{3+}. All Tb^{3+} transitions in the visible spectral range are quantum mechanically forbidden and of low absorption intensity. At high Tb^{3+} and Eu^{3+} concentrations though, the combined absorption of both activators is high enough the allow full conversion of a UV-LED via a ceramic phosphor disc.

Results and Discussion

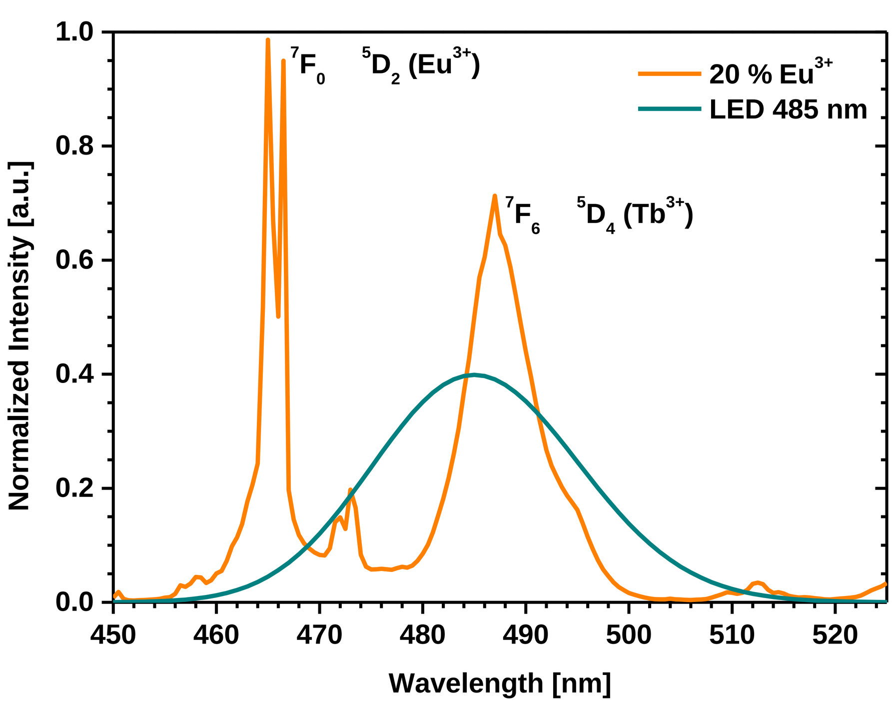

Fig. 3: Detail of the excitation spectrum of $(Tb_{0.8}Eu_{0.2})_2Mo_3O_{12}$ and the emission spectrum of a 485 nm LED.

Fig. 4: $(Tb_{0.8}Eu_{0.2})_2Mo_3O_{12}$ powder irradiated by a smartphone LED

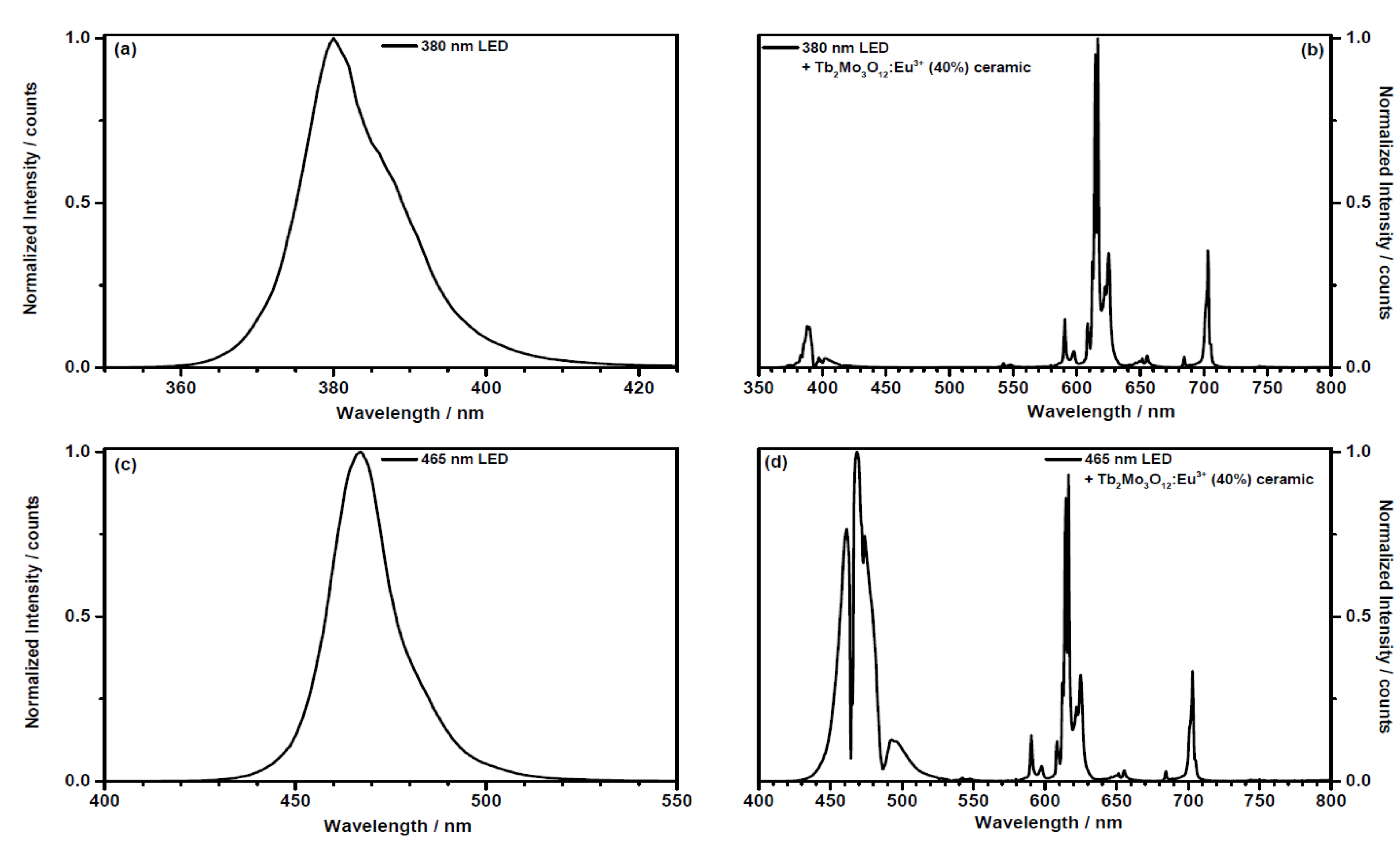

Fig. 5: Emission spectra of a (a) 380 nm LED, (b) 465 nm LED and (c), (d) of the same LEDs with a $(Tb_{0.6}Eu_{0.4})_2Mo_3O_{12}$ ceramic disc placed on the LED

- Efficient energy transfer from Tb^{3+} to Eu^{3+} upon excitation at 487 nm, which results in red emission peaking at 615 nm
- No reductive atmosphere is required to completely reduce Tb from the Tb^{4+}/Tb^{3+} educt Tb_4O_7 to Tb^{3+}
- At a low Eu^{3+} concentration of 10% already an energy transfer efficiency of 100% is achieved in both $Tb_2Mo_3O_{12}$:Eu^{3+} and $Li_3Ba_2Tb_3(MoO_4)_8$:Eu^{3+}

Energy Transfer Rate

- We developed a method to calculate energy transfer rates from decay curves with a rise time component
- Eu^{3+} emission shows a pronounced rise time due to "slow" energy transfer (ET) from Tb^{3+} (Fig. 8 & 9)

$$N_{Eu}(t) = -C\left[e^{-\lambda_{\text{Tb,total}} t} - e^{-\lambda_{\text{Eu}} t}\right]$$

- Fitting the decay curves with this function yields $\lambda_{\text{Tb,total}}$ the total decay rate of Tb^{3+} - which is the sum of the radiative decay rate and the ET rate
- To extract the ET rate from this, the following relation can be used:

$$\frac{I_{\text{Tb}}}{I_{\text{Eu}}} = \frac{\lambda_{Tb}}{\lambda_{\text{ET}}}$$

- As Eu^{3+} is solely excited via ET, the ratio of the emission intensities is equal to the ratio of the radiative decay rate and the ET rate
- From this the ET rate λ_{ET} can be calculated via:

$$\lambda_{\text{ET}} = \frac{\lambda_{\text{Tb,total}}}{1 + \frac{I_{\text{Tb}}}{I_{\text{Eu}}}}$$

- For details, please see: **J. Mater Chem. C 3 (2015) 2054**

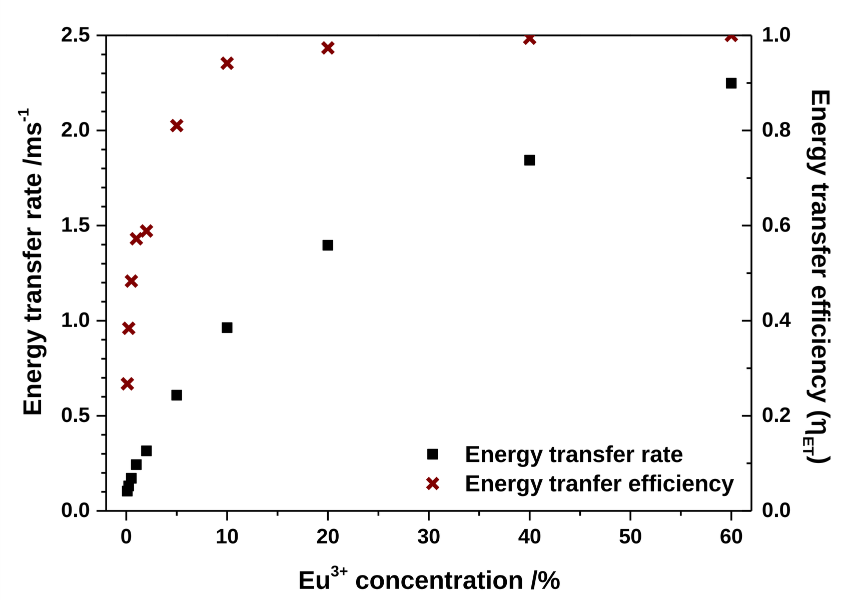

Fig. 1: Energy transfer efficiency and energy transfer rate of $(Tb_{1-x}Eu_x)_2Mo_3O_{12}$ as a function of Eu^{3+} concentration

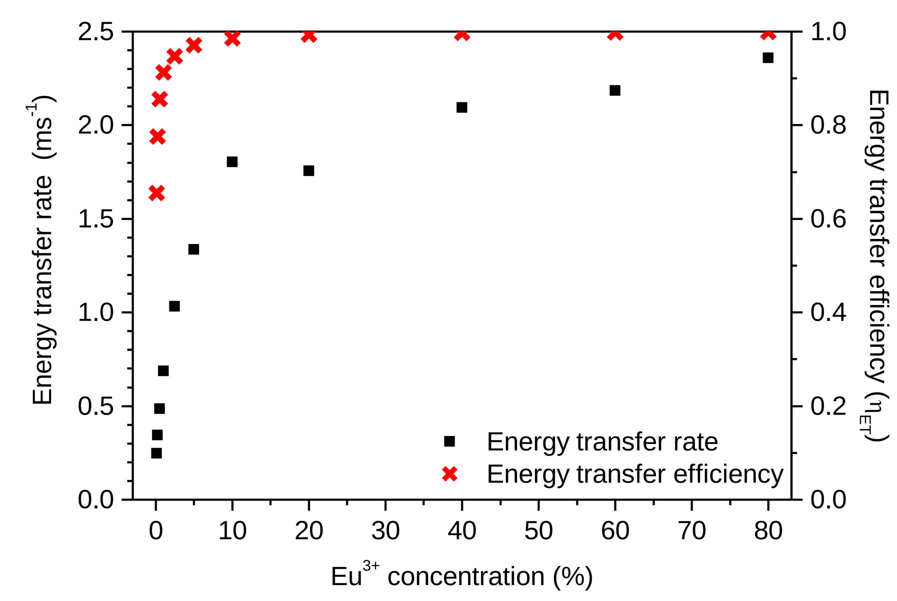

Fig. 2: Energy transfer efficiency and energy transfer rate of $(Tb_{1-x}Eu_x)_2Mo_3O_{12}$ as a function of Eu^{3+} concentration

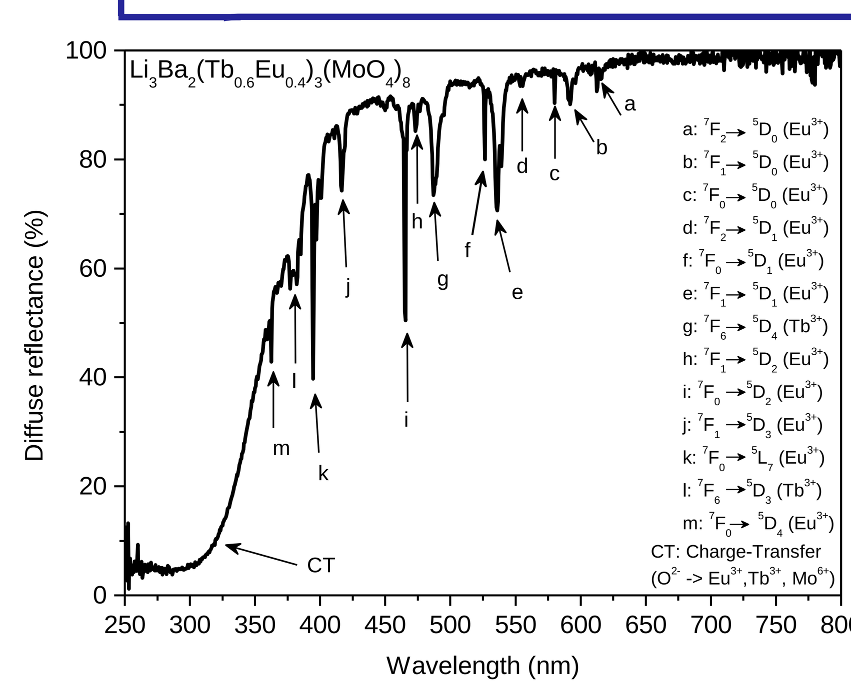

Fig. 6: Reflection spectrum of $Li_3Ba_2(Tb_{0.6}Eu_{0.4})_3(MoO_4)_8$.

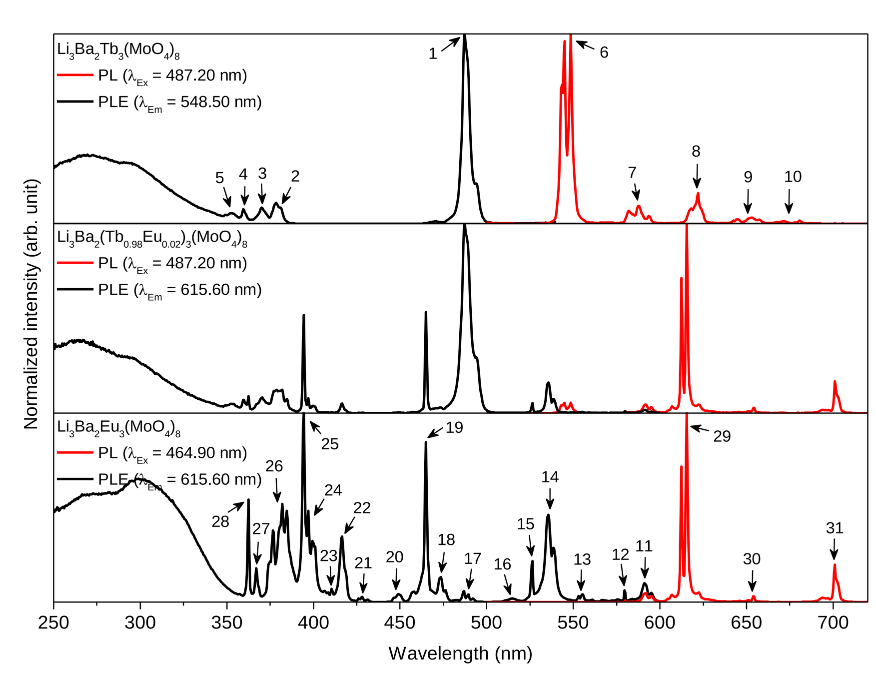

Fig. 7: Excitation and emission spectra of $Li_3Ba_2Tb_3(MoO_4)_8$, $Li_3Ba_2(Tb_{0.98}Eu_{0.02})_3(MoO_4)_8$ and $Li_3Ba_2Eu_3(MoO_4)_8$

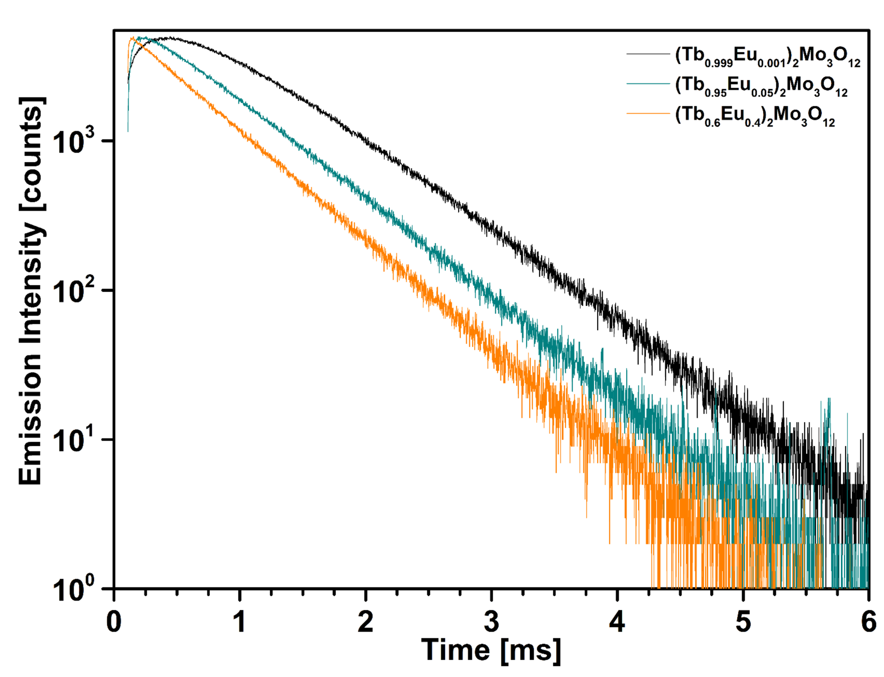

Fig. 8: Decay curves of $(Tb_{1-x}Eu_x)_2Mo_3O_{12}$

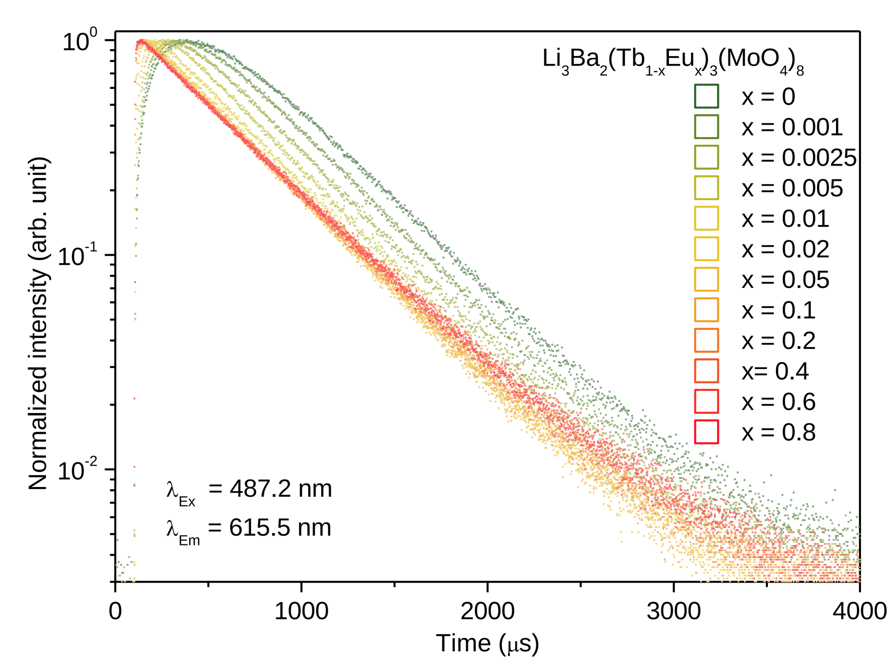

Fig. 8: Decay curves of $Li_3Ba_2(Tb_{1-x}Eu_x)_3(MoO_4)_8$