Luminescence and Energy Transfer in Eu^{3+} Activated $Li_3Ba_2Tb_3(MoO_4)_8$

David Böhnisch, Florian Baur, and Thomas Jüstel

Münster University of Applied Sciences, Department of Chemical Engineering

Stegerwaldstrasse 39, 48565 Steinfurt, Germany

Corresponding authors: *boehnisch.david@fh-muenster.de ; tj@fh-muenster.de*

Rare Earth Research Conference 2017, Ames, Iowa, USA

RERC 2017

Background

Light emitting diodes (LEDs) widely replaced conventional light sources like incandescent and fluorescent lamps. This is due to their longer lifetime, higher wall plug efficiency, and high colour rendering index (CRI). Commercially available LEDs comprising a blue emitting LED chip coated with a yellow emitting phosphor such as YAG:Ce exhibit high luminous efficacies. However, due to the weak intensity of red emission, the overall spectrum results in a high correlated colour temperature (CCT) and a low CRI. Therefore, introducing a red emitting phosphor is inevitable to achieve lower CCTs and higher CRIs. Eu^{3+} activated phosphors show great potential use in LEDs, but suffer from low absorption in the blue spectral range. Hence, a sensitizer such as Tb^{3+} has to be used.

Experimental Section

- Preparation via solid state method
- Li_2CO_3, $BaCO_3$, Tb_4O_7, MoO_3 and Eu_2O_3 were ground with acetone in an agate mortar
- Dried mixtures were placed in a porcelain crucible and were fired at 800 °C for 10 h in air
- Tb^{4+} in Tb_4O_7 is reduced to Tb^{3+} during sintering

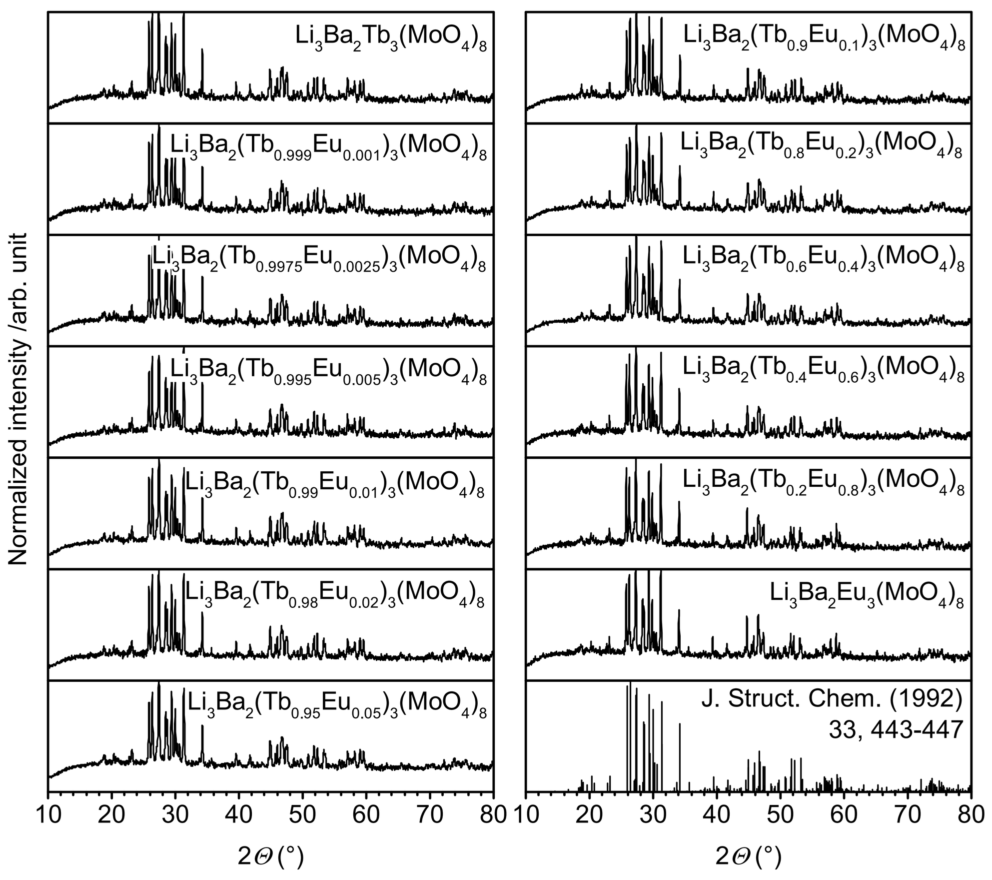
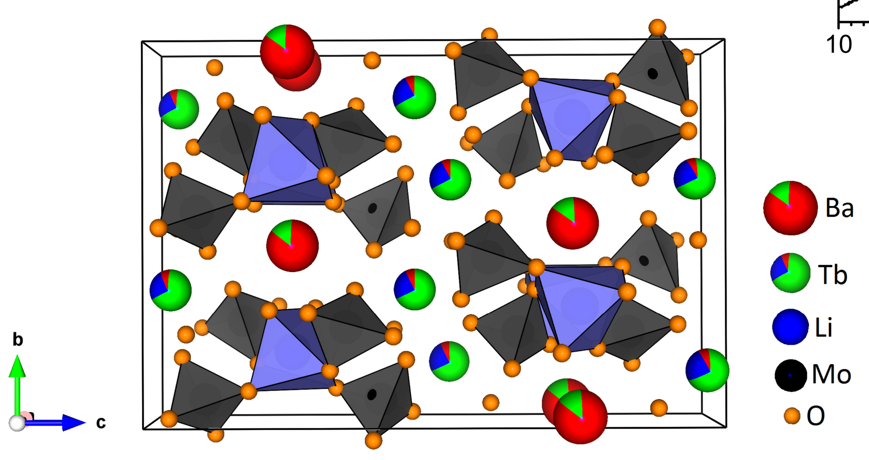


Fig. 1 XRD patterns of synthesized $Li_3Ba_2(Tb_{1-x}Eu_x)_3(MoO_4)_8$ and of $Li_3Ba_2Gd_3(MoO_4)_8$ reference



*C*12/*c*1 (15)	a = 0.52380(5) nm
β = 91.126(8)°	b = 1.2758(2) nm
V = 1.27955 nm³	c = 1.9151(2) nm

Fig. 2 Unit cell of $Li_3Ba_2Tb_3(MoO_4)_8$

Results and Discussion

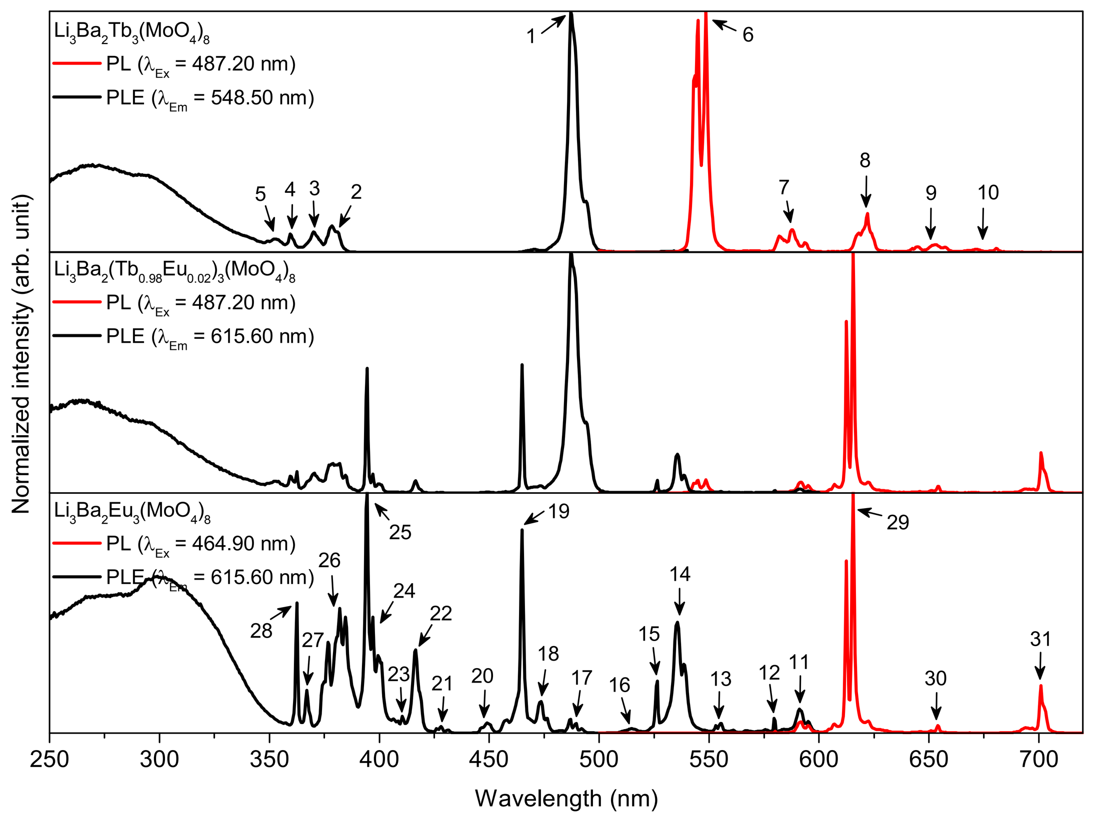


Fig. 3 Excitation and emission spectra of $Li_3Ba_2Tb_3(MoO_4)_8$, $Li_3Ba_2(Tb_{0.98}Eu_{0.02})_3(MoO_4)_8$ and $Li_3Ba_2Eu_3(MoO_4)_8$

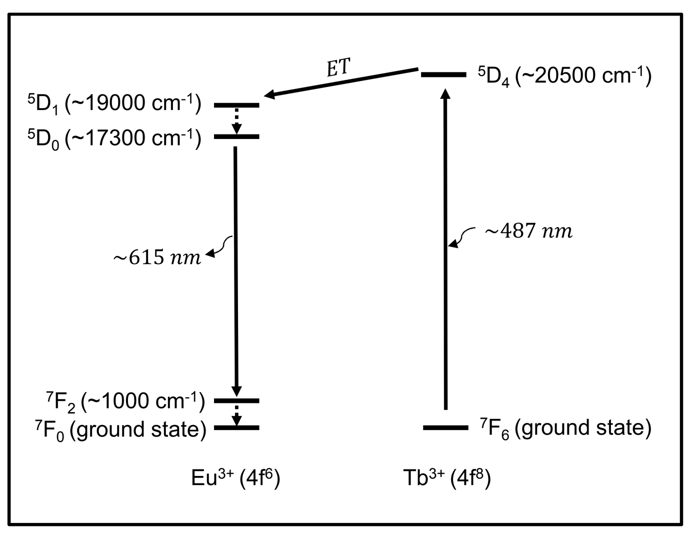


Fig. 4 Schematic drawing of the presumed Tb^{3+} to Eu^{3+} energy transfer mechanism

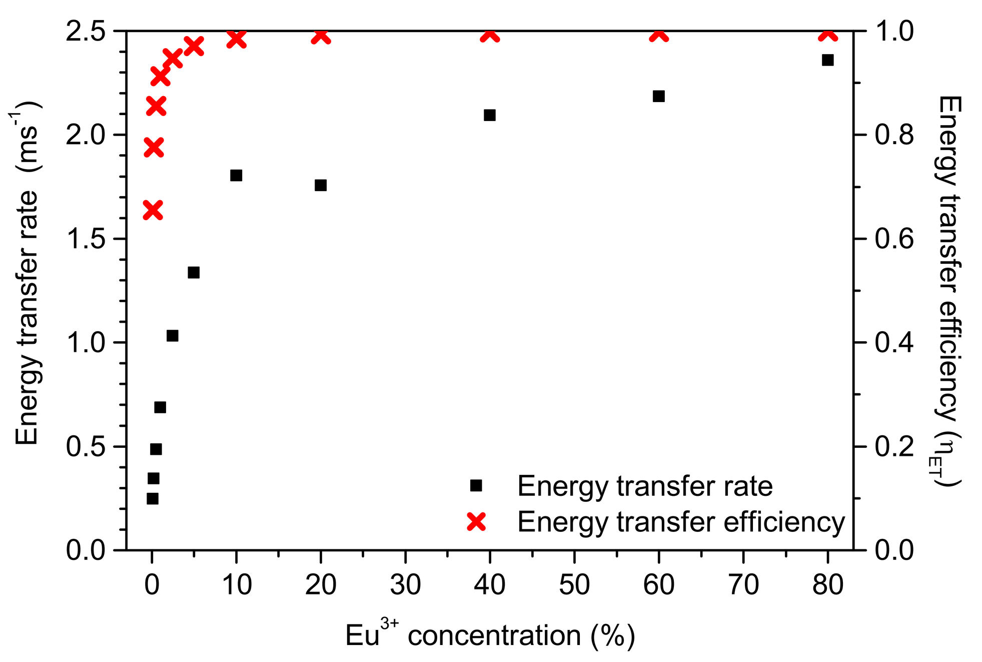


Fig. 5 Energy transfer efficiency and energy transfer rate as function of Eu^{3+} concentration

Table. 1 Tb^{3+} (Excitation: 1-5, Emission: 6-10) and Eu^{3+} (Excitation: 11-28, Emission: 29-31) intraconfigurational transitions with their respective peak wavelengths and allocation numbers

Number	Wavelength (nm)	Transitions
1	487.0	$^7F_6 \rightarrow {}^5D_4$
2	378.5	$^7F_6 \rightarrow {}^5D_3$
3	370.0	$^7F_6 \rightarrow {}^5L_{10}$
4	359.5	$^7F_6 \rightarrow {}^5D_2$
5	353.5-349.0	$^7F_6 \rightarrow {}^5L_{8,} {}^5G_{4,} {}^5L_7$
6	545.0	$^5D_4 \rightarrow {}^7F_5$
7	582.0	$^5D_4 \rightarrow {}^7F_4$
8	618.0	$^5D_4 \rightarrow {}^7F_3$
9	645.0	$^5D_4 \rightarrow {}^7F_2$
10	672.0	$^5D_4 \rightarrow {}^7F_1$
11	591.5	$^7F_1 \rightarrow {}^5D_0$
12	579.5	$^7F_0 \rightarrow {}^5D_0$
13	553.0	$^7F_2 \rightarrow {}^5D_1$
14	535.5	$^7F_1 \rightarrow {}^5D_1$
15	526.5	$^7F_0 \rightarrow {}^5D_1$
16	514.5	$^7F_3 \rightarrow {}^5D_2$
17	487.0	$^7F_2 \rightarrow {}^5D_2$
18	473.5	$^7F_1 \rightarrow {}^5D_2$
19	465.0	$^7F_0 \rightarrow {}^5D_2$
20	448.0	$^7F_3 \rightarrow {}^5D_3$
21	426.0	$^7F_2 \rightarrow {}^5D_3$
22	416.0	$^7F_1 \rightarrow {}^5D_3$
23	410.5	$^7F_0 \rightarrow {}^5D_3$
24	397.0	$^7F_0 \rightarrow {}^5L_6$
25	394.0	$^7F_0 \rightarrow {}^5L_7$
26	376.5	$^7F_0 \rightarrow {}^5L_{8,} {}^5L_{9,} {}^5L_{10}$
27	367.0	$^7F_1 \rightarrow {}^5D_4$
28	362.5	$^7F_0 \rightarrow {}^5D_4$
29	614.8	$^5D_0 \rightarrow {}^7F_2$
30	654.0	$^5D_0 \rightarrow {}^7F_3$
31	701.0	$^5D_0 \rightarrow {}^7F_4$

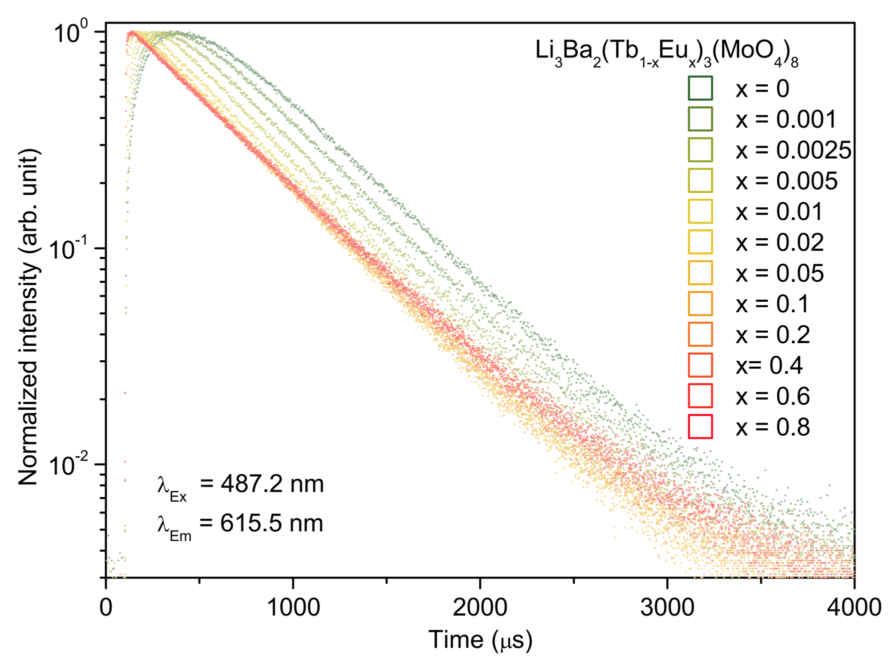


Fig. 6 Decay curves of $Li_3Ba_2(Tb_{1-x}Eu_x)_3(MoO_4)_8$ with x = 0 - 0.8

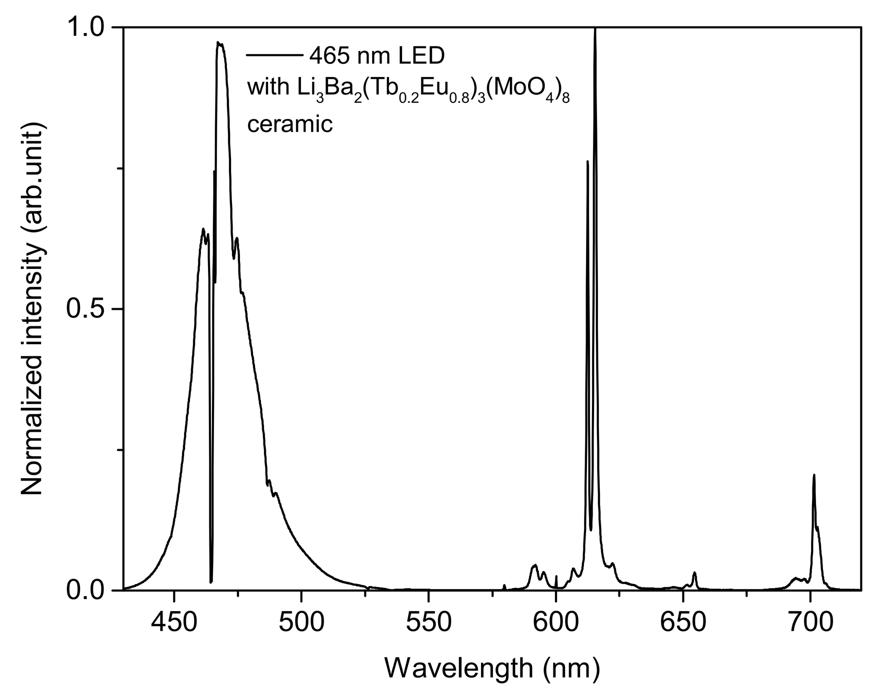
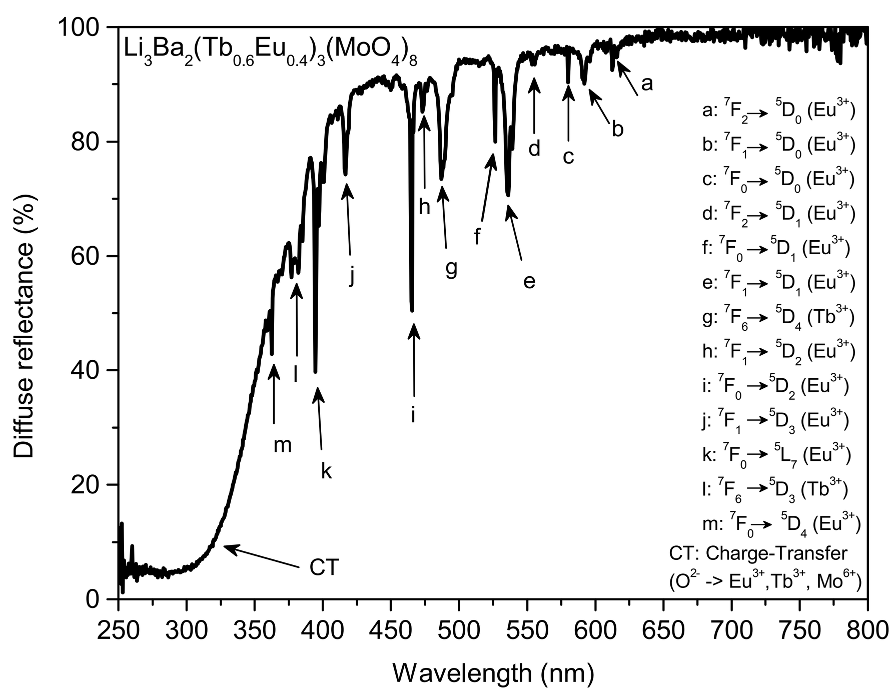


Fig. 7 Emission spectrum of a 465 nm LED behind a $Li_3Ba_2(Tb_{0.2}Eu_{0.8})_3(MoO_4)_8$ ceramic disc.



:trum of $Li_3Ba_2(Tb_{0.6}Eu_{0.4})_3(MoO_4)_8$

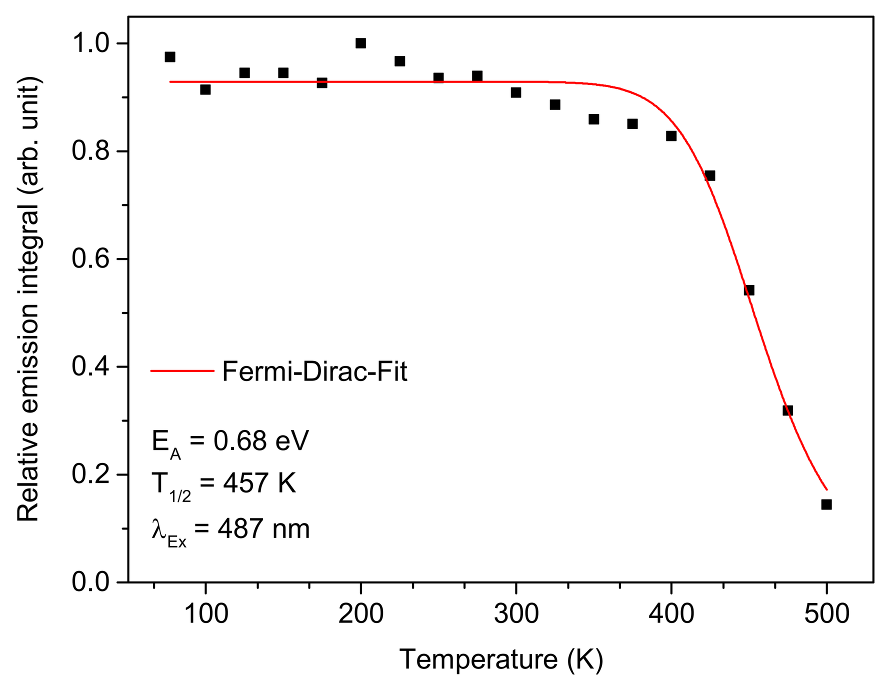


Fig. 9 Emission integrals as a function of temperature

- Efficient energy transfer from Tb^{3+} to Eu^{3+} upon excitation at 487 nm, which results in an emission at 615 nm
- Already at 10% Eu^{3+} concentration an energy transfer efficiency of 100% can be achieved
- Observed rise time decreases with increasing Eu^{3+} concentration which also leads to a higher energy transfer rate
- Diffuse reflectance spectrum reveals a white body colour
- $T_{1/2}$ of co-doped sample was found to be 457 K
- No shift of colour point is observed with increasing temperature
- Phosphor is excitable with a 465 nm LED and leads to efficient red and blue emission