Photoluminescence of Eu^{2+} Doped Silicates

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Introduction

This work deals with an Eu^{2+} doped silicate, viz. $BaMg_2Al_6Si_9O_{30}:Eu^{2+}$, which was prepared by a two-step high temperature solid state synthesis, and the characterization of its optical properties. From the XRD patterns it was assumed that all prepared samples were of single phase. The structure, as depicted in Fig. 2, is a cyclosilicate, consisting of layers of six-membered double-rings with the bigger cations located between the silicon layers.

Fig. 4 exhibits that the emission spectrum of a typical $BaMg_2Al_6Si_9O_{30}:Eu^{2+}$ sample is unusually broad, i.e. it consists of at least two overlapping bands. This implies that the Eu^{2+} ions occupy more than one site in the crystal structure of $BaMg_2Al_6Si_9O_{30}$, since the 4f5d luminescence of Eu^{2+} can solely cause one emission band. However, according to Winter et al. there is only one crystallographic site for divalent barium in undoped $BaMg_2Al_6Si_9O_{30}$.[1] The nature of the luminescence and the number of emitting sites will be discussed in the framework of the Eu^{2+} concentration and the presence of impurity phases.

Crystal Structure and XRD

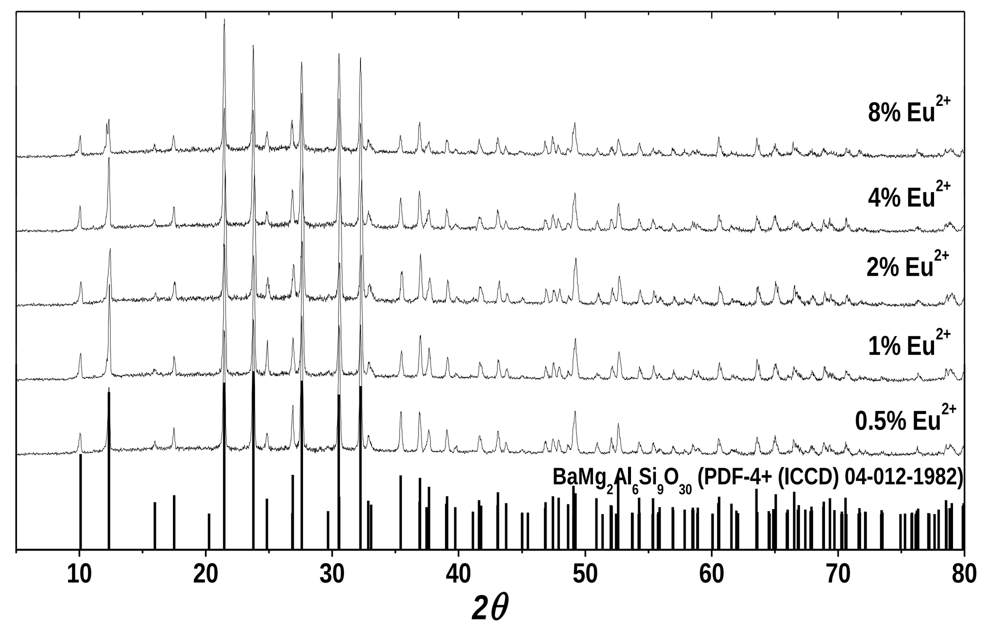


Fig. 1. XRD of $BaMg_2Al_6Si_9O_{30}$ doped with various amounts of Eu^{2+}.

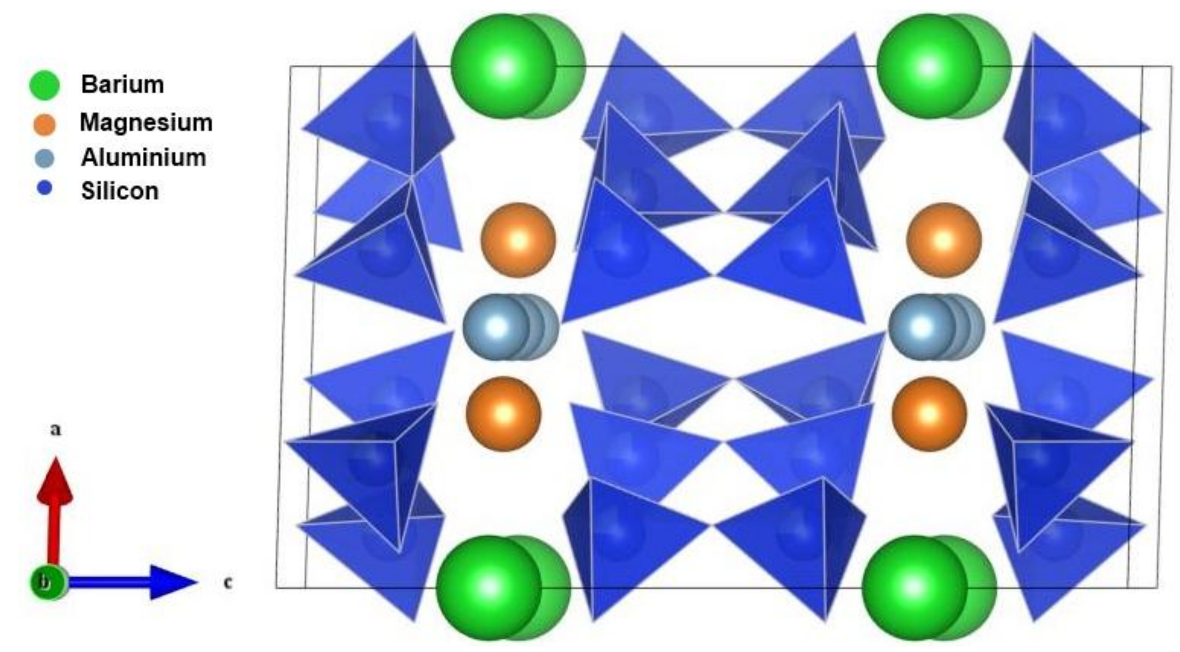


Fig. 2. Crystal structure of $BaMg_2Al_6Si_9O_{30}$.

Results

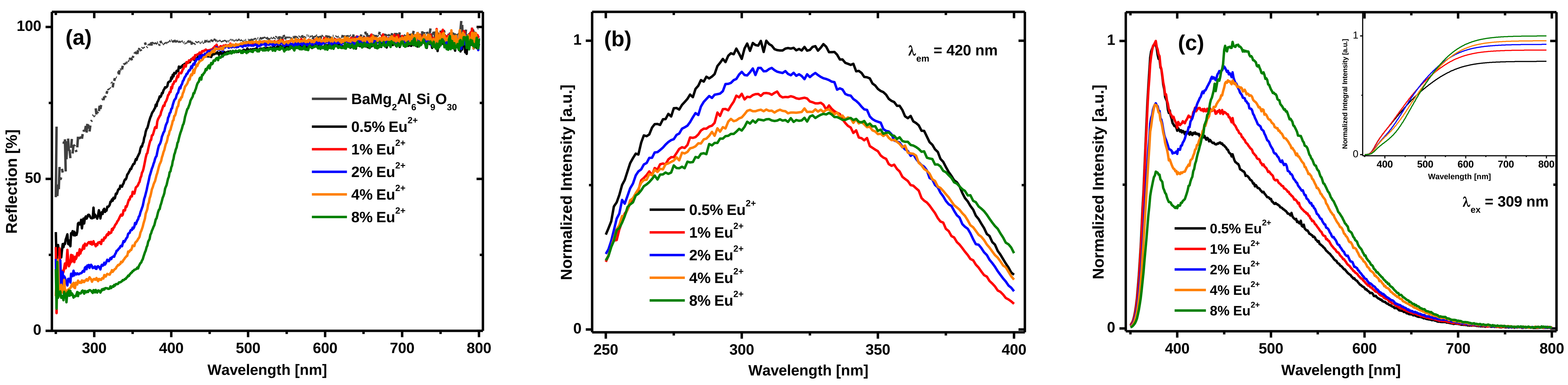


Fig. 3. (a) Reflection spectra, (b) excitation spectra and (c) emission spectra of $BaMg_2Al_6Si_9O_{30}$ with different Eu^{2+} concentrations. Inset: Integrated emission intensity.

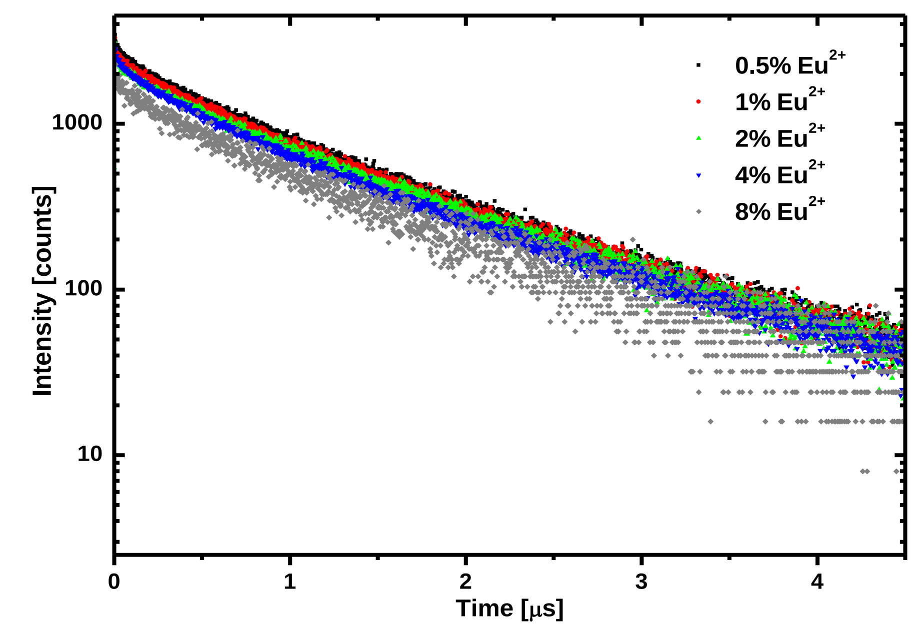


Fig. 5. Fluorescence decay curves of $BaMg_2Al_6Si_9O_{30}$ with different Eu^{2+} concentrations measured at 460 nm.

Table 1. Decay times and Luminous Efficacies (LE).

Conc. Eu^{2+}	Decay [µs]		LE [lm/W]
	377 nm	450 nm	
	τ [µs]	τ [µs]	
0.5%	0.86	1.013	155
1%	0.74	1.102	162
2%	0.71	1.115	175
4%	0.63	1.080	203
8%	0.58	1.088	211

Sample with 0.5% Eu^{2+}

Temp. [K]	τ [µs]	τ [µs]	
100	0197	1.00	185
150	0.206	1.02	178
200	0.232	1.04	168
250	0.247	1.01	158
300	0.355	1.04	148
350	0.302	1.04	140
400	0.257	1.01	133
450	0.310	0.890	125
500	0.305	0.867	119

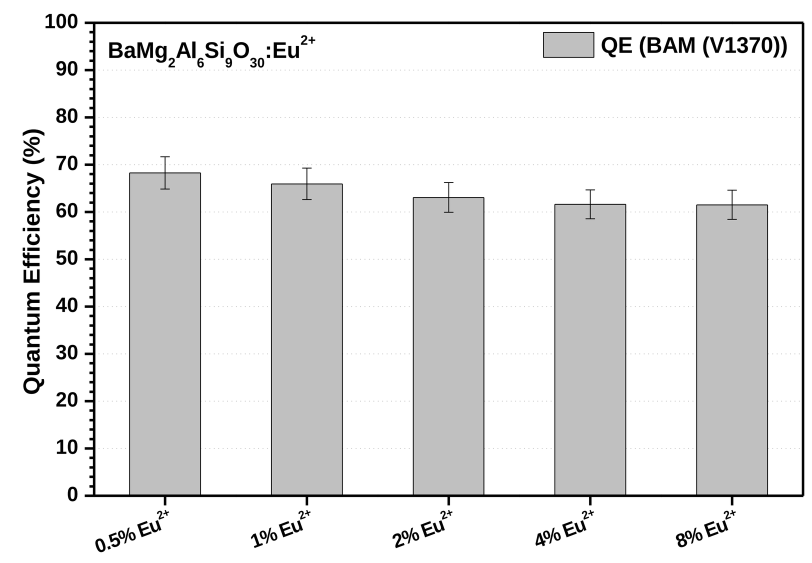


Fig 6. Quantum Efficiencies (QE) of $BaMg_2Al_6Si_9O_{30}:Eu^{2+}$.

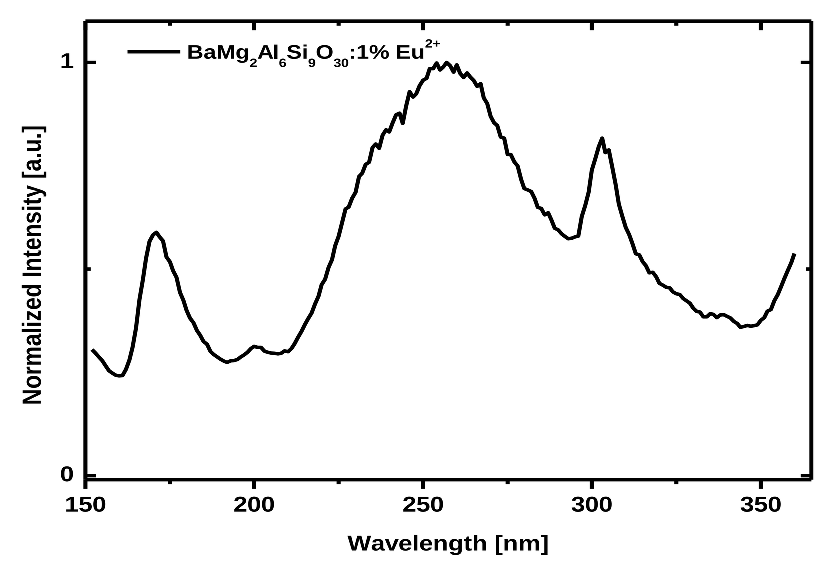
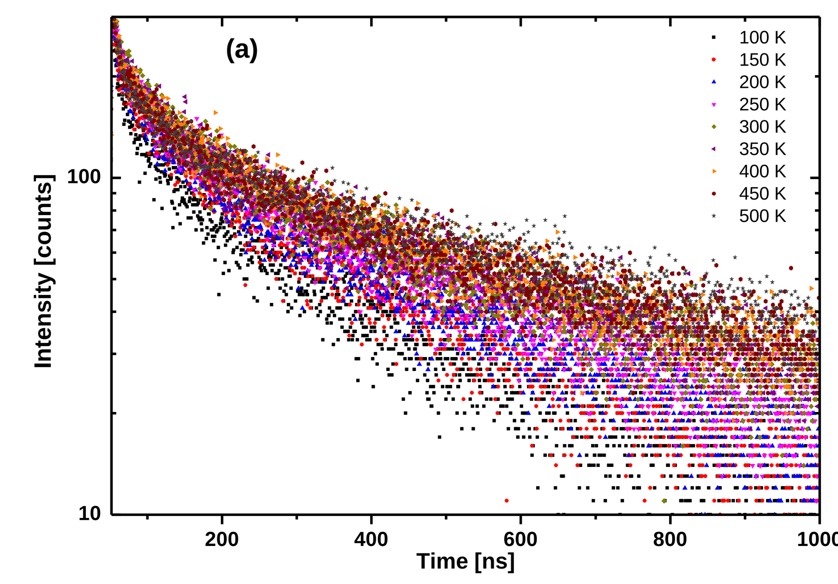


Fig 8. VUV excitation spectrum of $BaMg_2Al_6Si_9O_{30}$:1%Eu^{2+}.



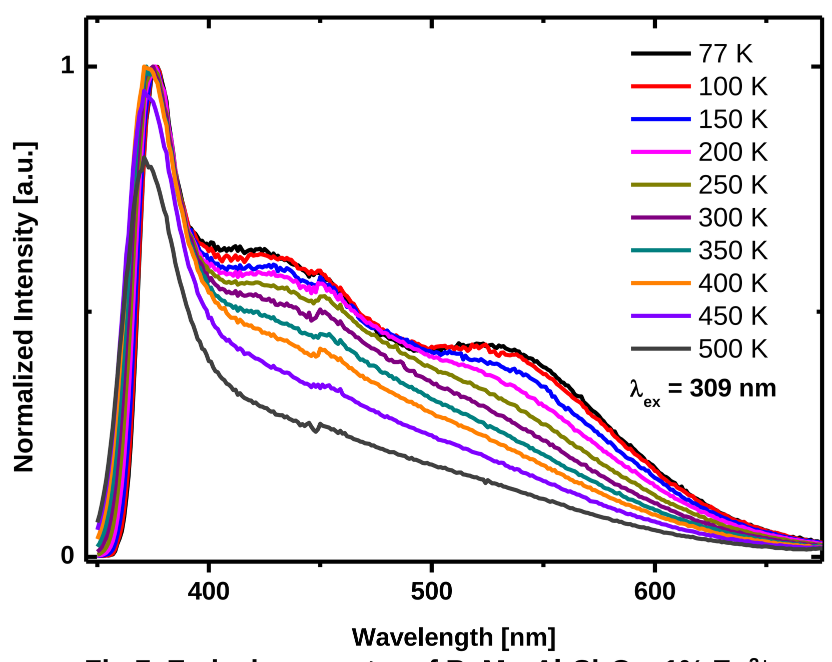


Fig 7. Emission spectra of $BaMg_2Al_6Si_9O_{30}$:1% Eu^{2+}. recorded at different temperatures

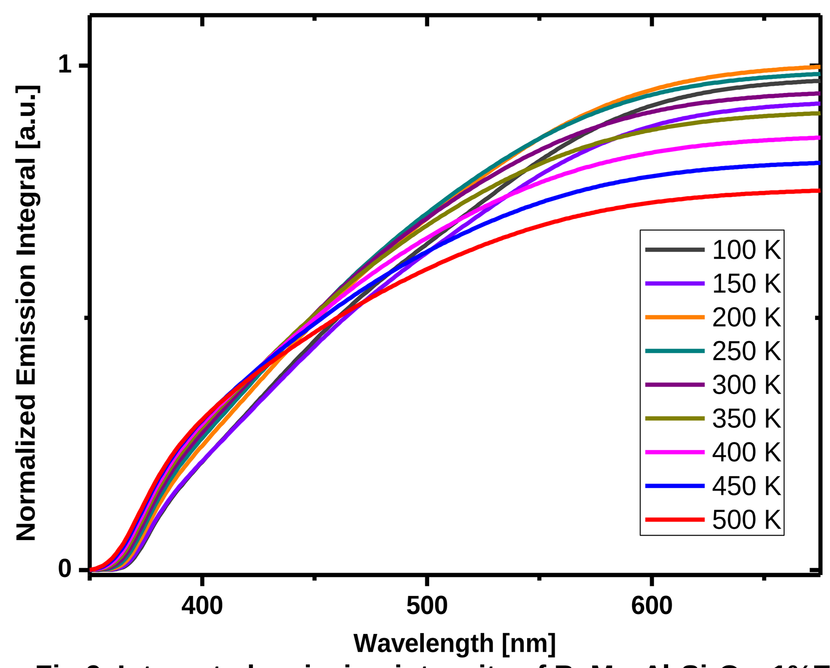


Fig 9. Integrated emission intensity of $BaMg_2Al_6Si_9O_{30}$:1%Eu^{2+}. recorded at different temperatures

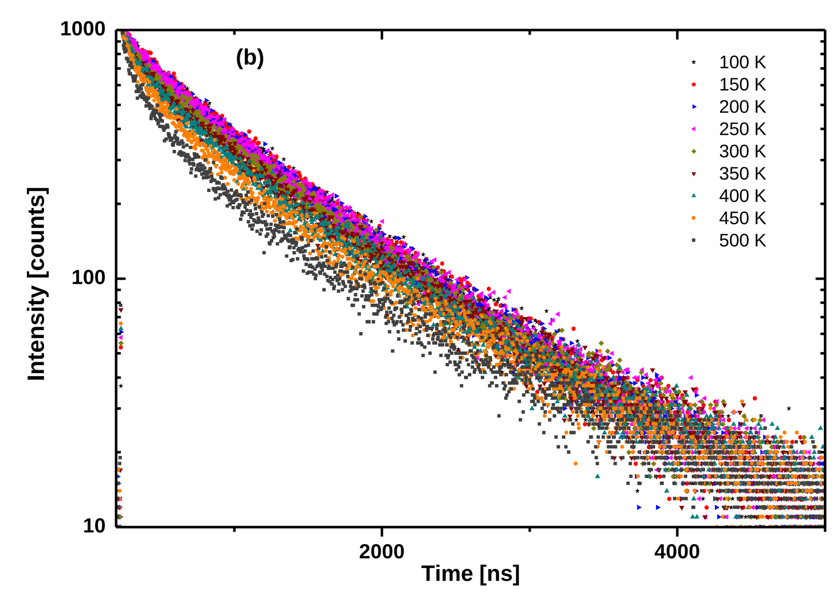


Fig. 10. Fluorescence decay curves of $BaMg_2Al_6Si_9O_{30}$:4%Eu^{2+} measured at different temperatures at (a) 390 nm and (b) 460 nm.

Conclusions

- Single phase target materials can be prepared by calcining stoichiometric amounts of the respective oxides or carbonates at 700 °C for 2 h and then annealing at 1300 °C for 10 h in CO. At activator concentrations > 0.5% the material did melt during annealing. Lower temperatures were not sufficient to obtain single phase material.
- The optical band gap of $BaMg_2Al_6Si_9O_{30}$ is about 250 nm (≈ 5.0 eV). The phosphor can be efficiently excited in the UV-B and UV-A spectral regions.
- The unusual emission spectrum can be explained by assuming two distinct crystallographic Eu^{2+} sites, substituting Ba^{2+} or Mg^{2+} in the host structure.[2] The higher energy UV-A emission could stem from Eu^{2+} located at Ba^{2+} sites, while the lower energy blue emission could stem from Eu^{2+} located at Mg^{2+} due to a difference in crystal field strength.
- With increasing Eu^{2+} concentration the high energy emission decreases, while the lower energy emission increases in intensity. This might indicate a potential energy transfer between the two sites. This assumption agrees well with the decreasing decay time of the 376 nm emission and the constant decay time of the 450 nm emission (Fig. 5, Table 1).
- The change in the emission spectra is reflected in a change in color point and luminous efficacy (LE). High activator concentrations result in increased LE and a red-shift of the CP. This property of the material allows for a fine-tuning of the CP, making the phosphor an interesting choice for emissive displays.
- The quantum efficiency (QE) remains constant with increasing Eu^{2+} concentration up to 8%.

- The author would like to thank A. Katelnikovas for his valuable assistance in spectroscopy and discussion.

[1] Eur. J. Mineral. (1995) 7, 277; [2] J. Alloys Compd. (2012) 513, 430