Energy Transfer and Unusual Decay Behaviour of $BaCa_2Si_3O_9:Eu^{2+},Mn^{2+}$ Phosphor

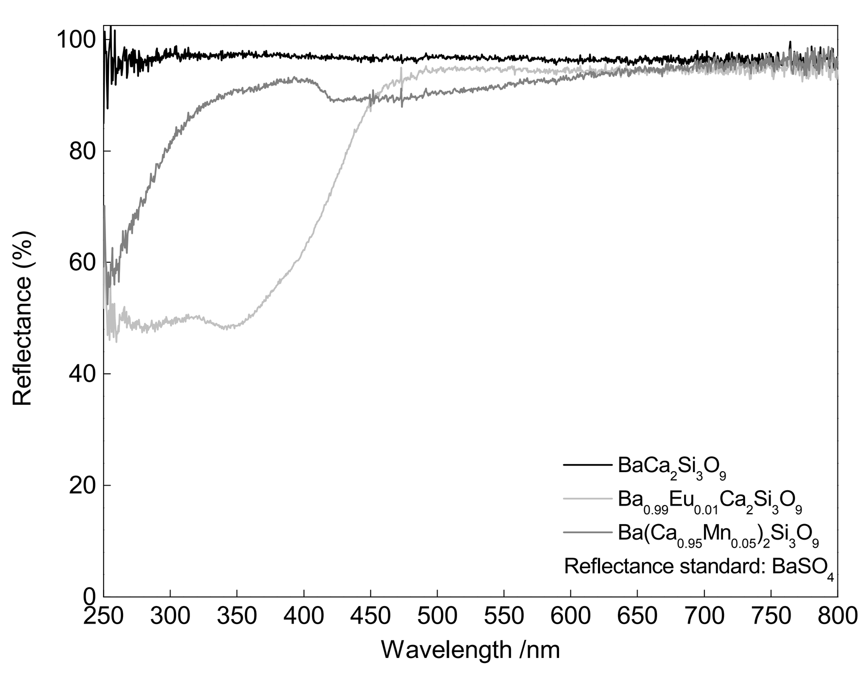
Matthias Müller and Thomas Jüstel

Münster University of Applied Sciences, Stegerwaldstraße 39, D-48565 Steinfurt, Germany

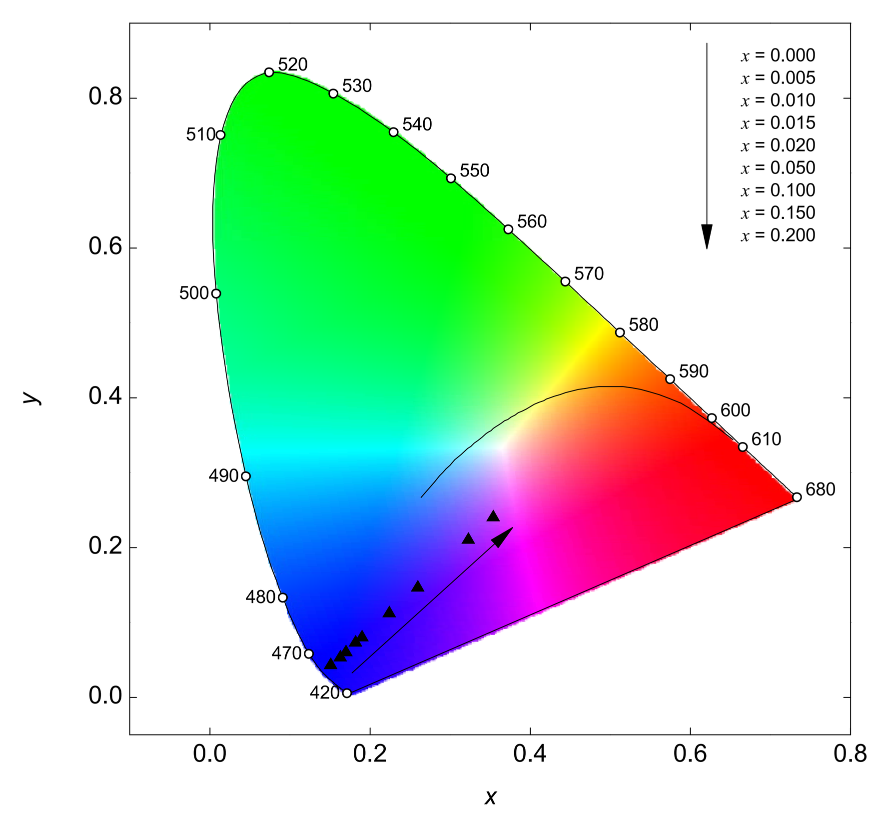
Conclusions

- Co-doped $Ba_{0.99}Eu_{0.01}(Ca_{1-x}Mn_x)_2Si_3O_9$ exhibits two emission bands under UV excitation, located at 445 and 590 nm.
- The highest photoluminescence intensity was found for a Mn^{2+} concentration of $x = 0.15$.
- It was demonstrated that energy transfer from Eu^{2+} to Mn^{2+} is of resonant type and occurs *via* dipole-quadrupole interaction.
- PL of $Ba_{0.99}Eu_{0.01}(Ca_{1-x}Mn_x)_2Si_3O_9$ possesses a „double-sigmoidal" temperature behaviour due to photoluminescence from crystallographically distinct sites of Eu^{2+}. $T_{1/2,a}$ and $T_{1/2,b}$ values for $Ba_{0.99}Eu_{0.01}(Ca_{0.90}Mn_{0.10})_2Si_3O_9$ were calculated to be 242 and 666 K, respectively.
- Temperature dependent luminescence lifetime measurements revealed that thermal quenching in $Ba_{0.99}Eu_{0.01}(Ca_{1-x}Mn_x)_2Si_3O_9$ is mainly caused by the Mn^{2+} ions.
- Luminescence lifetimes of Eu^{2+} show an unusual increase with increasing temperature in $Ba_{0.99}Eu_{0.01}(Ca_{1-x}Mn_x)_2Si_3O_9$.
- The colour point of the emission of $Ba_{0.99}Eu_{0.01}(Ca_{1-x}Mn_x)_2Si_3O_9$ can be tuned from blue to magenta colour range by increasing the Mn^{2+} concentration.

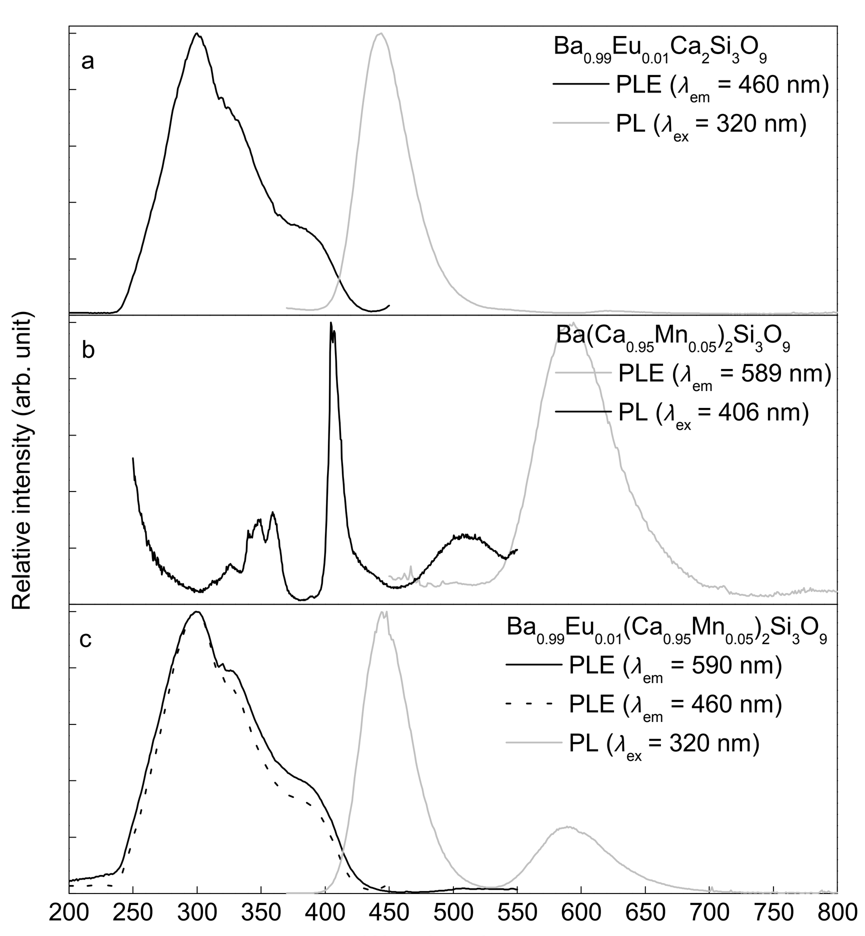
Results



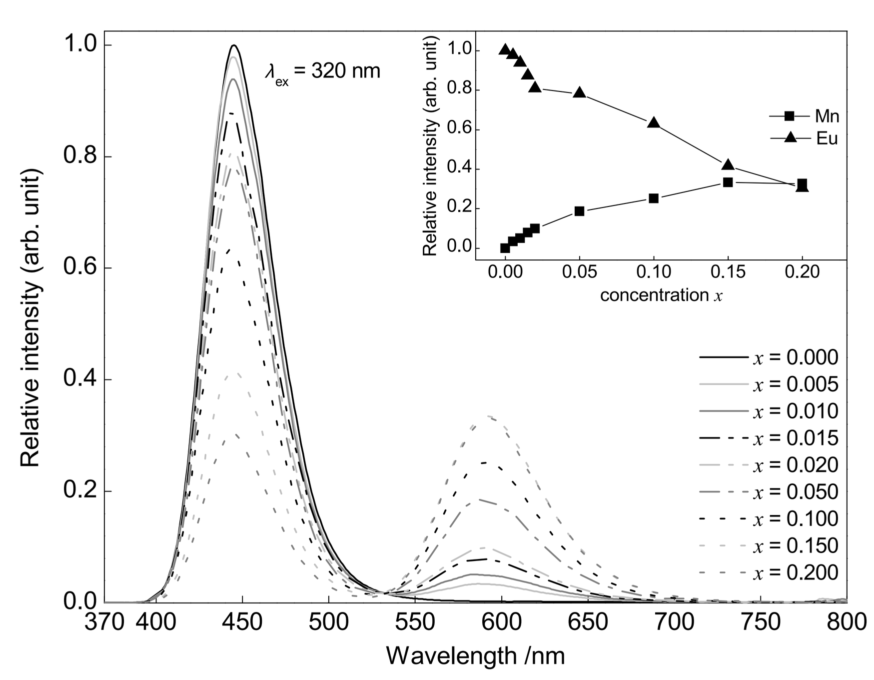
Diffuse reflectance spectra of selected samples.



Colour point can be tunend from blue to magenta colour range.



Excitation and emission spectra of selected samples.



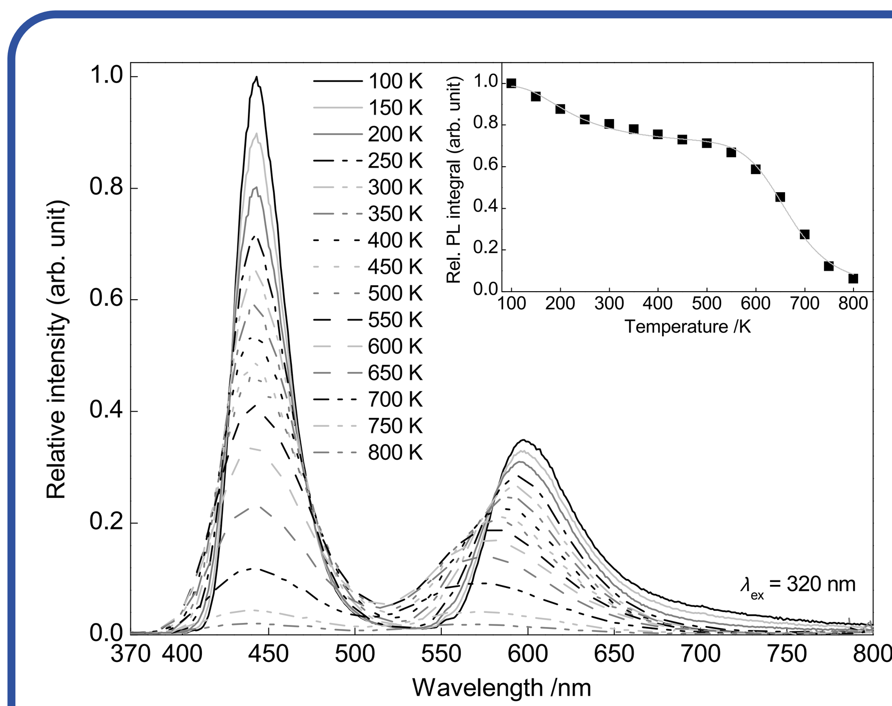
Highest photoluminescence intensity of $Ba_{0.99}Eu_{0.01}(Ca_{1-x}Mn_x)_2Si_3O_9$ was found for $x = 0.15$.

Acknowledgement

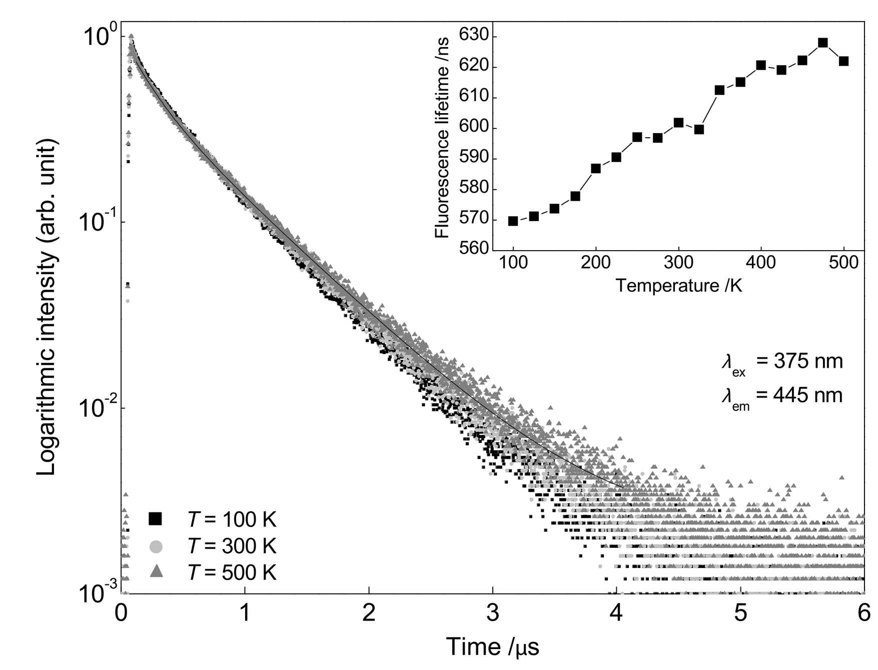
The authors are grateful to Merck KGaA Darmstadt, Germany for generous financial support.

Experimental Section

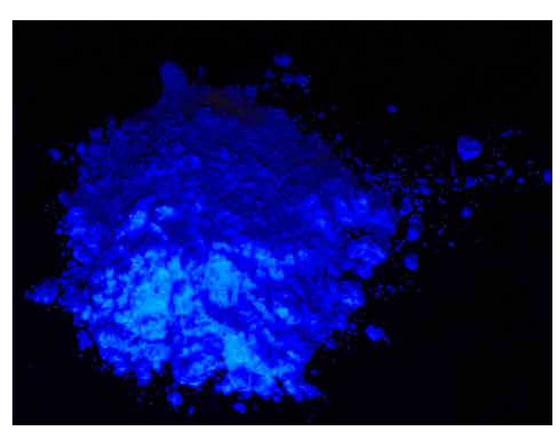
- $Ba_{0.99}Eu_{0.01}(Ca_{1-x}Mn_x)_2Si_3O_9$ samples were synthesized by a high temperature solid state reaction.
- The samples were primarily annealed at 1000 °C for 2 h in air and finally sintered in alumina boats at 1200 °C for 12 h in reducing forming gas atmosphere.
- Phase purity was investigated using x-ray powder diffractometry.
- Optical properties were investigated by recording photoluminescence spectra as well as by performing luminescence lifetime measurements at different temperatures. Furthermore, diffuse reflectance measurements were executed (reflectance standard: $BaSO_4$).



Photoluminescence of $Ba_{0.99}Eu_{0.01}(Ca_{0.90}Mn_{0.10})_2Si_3O_9$ shows a „double sigmoidal" temperature behaviour.



Luminescence lifetimes of Eu^{2+} show an unusual increase with increasing temperature.



$Ba_{0.99}Eu_{0.01}Ca_2Si_3O_9$

$Ba_{0.99}Eu_{0.01}(Ca_{0.95}Mn_{0.05})_2Si_3O_9$

$Ba_{0.99}Eu_{0.01}(Ca_{0.80}Mn_{0.20})_2Si_3O_9$

Background

- Nowadays, most of the commercially available white light emitting pcLEDs comprise a blue emitting (In,Ga)N chip pumping a green-yellow emitting phosphor, e.g. $(Y,Gd)_3Al_5O_{12}:Ce^{3+}$.
- Unfortunately, these light sources are unpopular for domestic lighting due to high colour temperature and low colour rendering index (CRI)
- One approach to obtain reasonable CRIs, is to use a phosphor blend comprising a blue, green, and red phosphor, which is excited by an ultraviolet emitting LED.
- However, these packages underlie a loss in blue emission due to re-absorption by the green and red phosphors.
- Alternatively, the ion couple Eu^{2+} and Mn^{2+} can be used. The broad emission bands in the blue and red spectral range of Eu^{2+} and Mn^{2+} in many host materials complement each other to white light due to additive colour mixing.
- Eu^{2+} usually exhibits a broad excitation band in the UV range and is well appropriated for pumping by UV LEDs. Additionally, the blue emission band of Eu^{2+} is also suitable to sensitize the spin and parity forbidden $[Ar]3d^5$-$[Ar]3d^5$ excitation transitions of Mn^{2+} *via* energy transfer.

Münster University of Applied Sciences

Matthias Müller
Department of Chemical Engineering
Inorganic Chemistry and Material Science
Research Group Prof. Dr. Thomas Jüstel
Phone +49 2551 9-62851
e-mail: matthias_mueller@fh-muenster.de, tj@fh-muenster.de

TOM Tailored Optical Materials