

# Preparation and Optical Characterisation of $\text{Eu}^{3+}$ Doped $\text{MGdSiO}_4$ ( $M = \text{Li}, \text{Na}$ ) Ortho-Silicates

## Introduction

Since invention of Light Emitting Diodes (LEDs) in 1963, their value increases every year in with respect to variety of application areas. An important breakthrough was in 1997 when the white phosphor converted LED was invented. The main advantages of the application of LEDs for lighting purposes are their long lifetime, flexibility, and high energy efficiency. These pcLEDs have been widely utilized f.e. for automotive lighting, display backlighting, and traffic signals. First white pcLED generation have a cold colour temperature.

To obtain warm white pcLED an additional red phosphor is required. The development of warm white pcLEDs for solid state lighting have attracted much attention in recent years.

Most important selection criteria for alternative red phosphors in warm-white LEDs are a strong absorption at the emission maximum of the LED die, a high quantum efficiency (>90%), a high stability against  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ .

Rare-earth doped materials are of high importance for the phosphor industry as they show high efficiency and stability.

In the lattices  $\text{MGdSiO}_4$  ( $M = \text{Li}, \text{Na}$ ) the trivalent Europium can easily replace the gadolinium ion, because their ion radii are very similar to each other. Alkaline gadolinium ortho-silicates are of interest as host materials for  $\text{Eu}^{3+}$  due to the strong absorption in the near UV range.

The aim of this research was the synthesis and optical characterization of two types of ortho-silicates (sodium gadolinium silicate and lithium gadolinium silicate), doped by different concentration of  $\text{Eu}^{3+}$ . All samples were prepared by a solid state reaction at 1000 - 1200°C in ambient atmosphere.

## $\text{NaGdSiO}_4$

Crystal system: Orthorhombic

Space group: P21nb

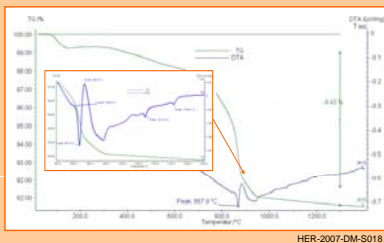


Fig. 1 DTA/TG curves of a blend of starting materials to obtain  $\text{NaGdSiO}_4$

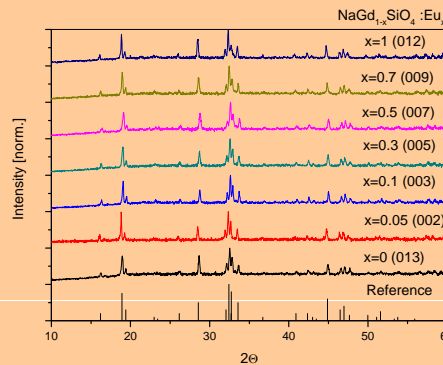


Fig. 2 XRD patterns of as synthesized  $\text{NaGdSiO}_4$  samples

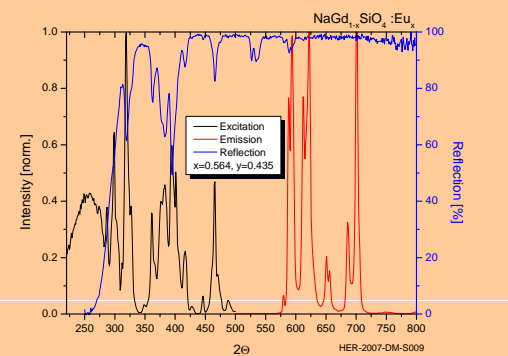


Fig. 3 Excitation-, emission-, and reflection spectra of  $\text{NaGdSiO}_4$

## $\text{LiGdSiO}_4$

Crystal system: Hexagonal

Space group: P63/m

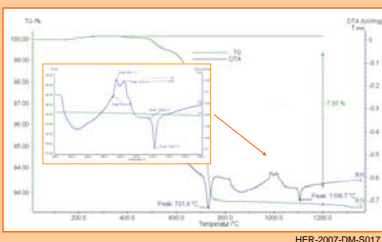


Fig. 4 DTA/TG curves of a blend of starting materials to obtain  $\text{LiGdSiO}_4$

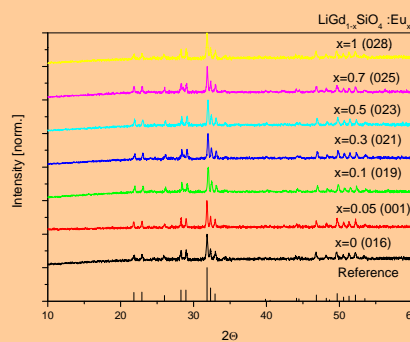


Fig. 5 XRD patterns of as synthesized  $\text{LiGdSiO}_4$  samples

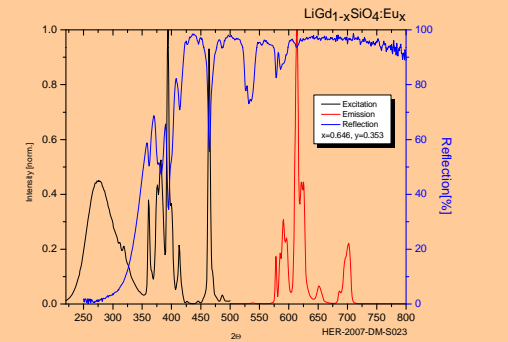


Fig. 6 Excitation-, emission-, and reflection spectra of  $\text{LiGdSiO}_4$

## Relative Integral Intensity

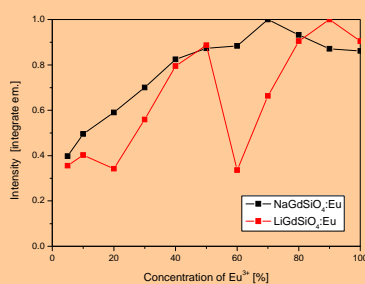


Fig. 7 Influence of the Europium concentration upon 319 nm excitation for  $\text{NaGdSiO}_4:\text{Eu}^{3+}$  and upon 394 nm excitation for  $\text{LiGdSiO}_4:\text{Eu}^{3+}$  on the integral intensity

## Conclusions

Fig. 2 and 5 show the powder diffraction patterns of all prepared samples, which demonstrate that the substitution of  $\text{Gd}^{3+}$  by  $\text{Eu}^{3+}$  does not result in any phase transition. The samples of  $\text{NaGdSiO}_4$  are of single phase. In the ternary system  $\text{Li}_2\text{O}-\text{Gd}_2\text{O}_3-\text{SiO}_2$  two phases, viz.  $\text{LiGdSiO}_4$  and  $\text{LiGd}_3(\text{SiO}_4)_6\text{O}_2$  exist. In Fig. 4 the DTA curve presents two endothermic peaks which can be explained by the coexistence of two phases.

All samples (Fig. 3 and 6) show strong  $4f^6-4f^6$  transitions at 395 nm and 465 nm, as proven by the reflection and excitation spectra.

The presented results show that sodium gadolinium silicates might be interesting red phosphors as colour converters in solid state light sources, in particular based on near UV emitting  $\text{AlInGaIn}$  dies.

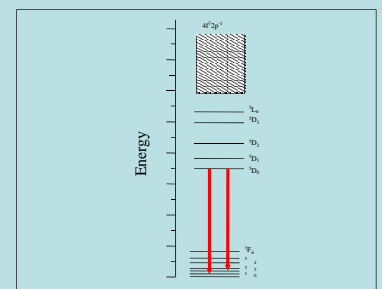


Fig. 8 Simplified energy level diagram of  $\text{Eu}^{3+}$

## References:

- [1] Shanshan Yao, Donghua Chen; Central European Journal of Physic; Luminescent properties of  $\text{Li}_2(\text{Ca}_{0.99}\text{Eu}_{0.01})\text{SiO}_4$ ; B<sup>3+</sup> particles as a potential bluish green phosphor for UV LEDs
- [2] Takeshi Hiray; Chemical Physics Letters 446(2007) 138-141
- [3] Shannon R.D.; Gier T.E.; Foris C.M.; Nelen J.A.; Appleman D.E.; Crystal Data for some sodium rare earth silicates; Phys. Chem. Minerals 5, 245-253 (1980)
- [4] Nakayama, S., Sakamoto, M., J. Ceram. Soc. Jpn. Inter. Ed., 100, (1992), 858