

Persistent Luminescence and Energy Transfer in $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+},\text{Dy}^{3+}$

Danuta Dutczak^{1,2}, Arturas Katelnikovas¹, Cees Ronda^{2,4}, Adrie J.J. Bos³, Andries Meijerink², and Thomas Jüstel¹

¹ Department of Chemical Engineering, Münster University of Applied Sciences, Steinfurt, Germany

² Debye Institute for NanoMaterials Science, Utrecht University, Utrecht, The Netherlands

³ Faculty of Applied Sciences, Delft University of Technology, Delft, The Netherlands

⁴ Philips Research Laboratories, Eindhoven, The Netherlands

Introduction

During the last decade, afterglow phosphors have attracted considerable attention due to their potential applications in various fields, including emergency lighting, road signs, special light sources or optical data storage. One of the most efficient afterglow materials is $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+},\text{Dy}^{3+}$, which yields strong luminescence due to the interconfigurational $[\text{Xe}]4f^65d^1 - [\text{Xe}]4f^7$ transition of Eu^{2+} . It shows persistent luminescence even without co-doping. The afterglow can be prolonged by co-doping additional ions like Dy^{3+} or Nd^{3+} . Although extensive studies have been performed on afterglow phosphors, the mechanisms underlying the persistent luminescence phenomenon in this phosphor still remain unclear.

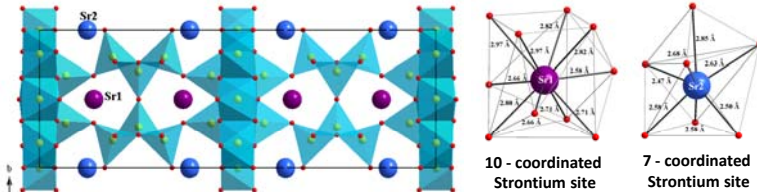
Aim

This contribution deals with Eu^{2+} doped $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ and aims at understanding the mechanism of the luminescence and persistent luminescence of this phosphor. New insights are reported on the nature of the higher energy emission band, which shows a blue-shift upon heating.

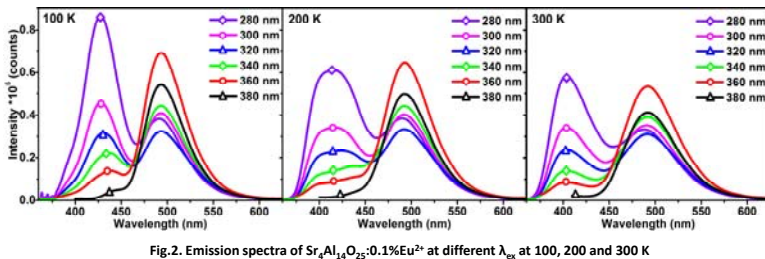
The PL and TL of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+},\text{Dy}^{3+}$ were studied and compared with $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}$ in order to elucidate the role of Dy^{3+} in the physical process leading to afterglow.

Results

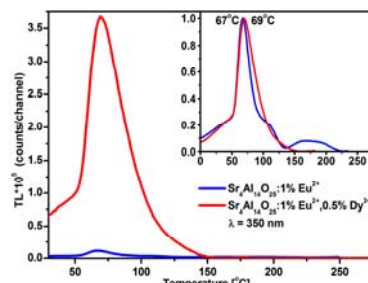
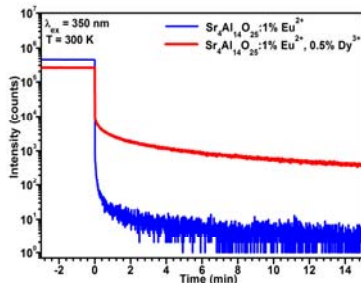
1 Two different crystallographic strontium sites with coordination numbers 10 and 7 exist in the $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$.



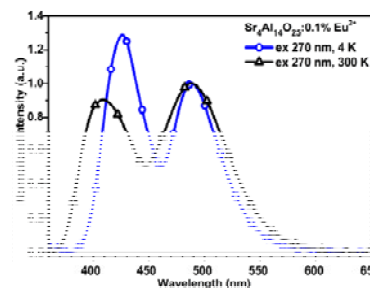
3 A close inspection of emission spectra of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}$ reveals the existence of three emission bands peaking at 400, 425, and 490 nm.



5 Persistent luminescence of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}$ can be amplified by co-doping with Dy^{3+} ions. The intensity of the TL glow peaks of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+},\text{Dy}^{3+}$ are much stronger than for $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}$, but the position does almost not vary.



2 Upon decreasing temperature the 425 nm emission band apparently shifts to 400 nm.



Emission band	Decay Time [μs]	
	100 K	300 K
400 nm	-	0.24
425 nm	0.52	-
490 nm	0.94	0.83

The decay times of emission bands at 400 and 425 nm are much shorter than characteristic decay time for the $4f^65d^1 - 4f^7$ transition of Eu^{2+} (1 μs).

4 Three emission bands:
400 nm - 5d-4f emission of Eu^{2+} in 10 - fold coordination (HT)
425 nm - Eu^{2+} Trapped Exciton Emission (LT)
490 nm - 5d-4f emission of Eu^{2+} in 7 - fold coordination

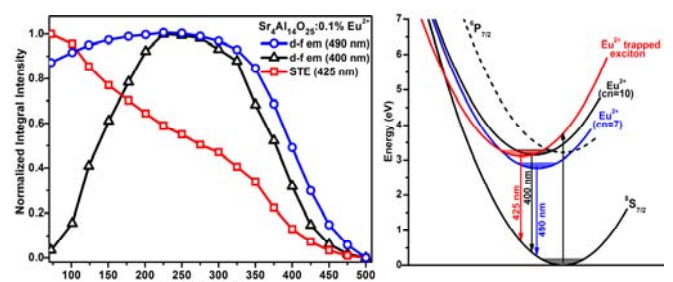


Fig. 4. Simplified configurational coordinate diagram of Eu^{2+} luminescence in $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$

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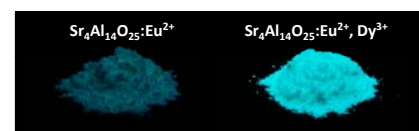


Fig. 7. Photographs of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}$ and $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+},\text{Dy}^{3+}$ 1 s after removal of excitation source

Conclusions

✓ We have reported, for the first time, the Eu^{2+} trapped exciton emission in $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}$. Now, the peculiar behavior of the emission of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}$ as function of temperature can be explained by a temperature induced transition between Eu^{2+} exciton states and crystal-field states of Eu^{2+} . The Eu^{2+} trapped exciton emission at 425 nm is observed only at low temperatures. At higher temperatures, the higher phonon levels are occupied and the crossing point with the Eu^{2+} parabol in the excited state is reached (Fig. 4). The Eu^{2+} trapped exciton emission is quenched and 5d-4f Eu^{2+} emission at 400 nm is observed.

✓ It was also demonstrated, that both $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}$ and $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+},\text{Dy}^{3+}$ show persistent luminescence. The persistent luminescence of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}$ is rather weak and lasts for solely a few minutes, while the same material co-doped with Dy^{3+} shows long, i.e. a few hours, and strong afterglow.

✓ The results from TL measurements suggest, that Dy^{3+} causes a trapping centre with a trap depth almost the same as the depth of the trapping centre responsible for the afterglow in the not co-doped material or that the nature of the electron traps is the same with and without Dy^{3+} present. In this case, an ionised oxygen vacancy is the electron trap. As the intensity of the afterglow is much higher in case of Dy^{3+} containing samples, we assume that the Dy^{3+} ions induce oxygen vacancies.