

Yellow Persistent Luminescence of the $\text{Sr}_3\text{SiO}_5:\text{Eu}^{2+}, \text{R}^{3+}$ Materials

Jorma Hölsä^{1,2,3}, Aleksei Kotlov⁴, Taneli Laamanen^{1,2}, Mika Lastusaari^{1,2}, Mikael Lindström¹,
Marja Malkamäki^{1,5}

¹ University of Turku, Department of Chemistry, FI-20014 Turku, Finland

² Turku University Centre for Materials and Surfaces (MatSurf), Turku, Finland

³ Universidade de São Paulo, Instituto de Química, São Paulo-SP, Brazil

⁴ Deutsches Elektronen-Synchrotron, a Research Centre of the Helmholtz Association, Hamburg, Germany

⁵ National Doctoral Programme in Nanoscience (NGS-Nano), Jyväskylä, Finland

Efficient persistent luminescence – emission after the removal of the irradiation source – has been observed from many Eu^{2+} doped alkaline earth silicates and aluminates (*e.g.* $\text{Sr}_2\text{MgSi}_2\text{O}_7$ and SrAl_2O_4) without R^{3+} (R: rare earth) co-doping [1,2]. In some cases, as $\text{Sr}_3\text{SiO}_5:\text{Eu}^{2+}$, persistent luminescence is not observed without the introduction of the R^{3+} co-dopant [3]. The electronic structure of such hosts including the band gap energy and the rare earth energy levels need to be explored to solve the details of the mechanism of the persistent luminescence from these materials.

In this work, the excitation spectra of $\text{Sr}_3\text{SiO}_5:\text{Eu}^{2+}$ were measured with synchrotron radiation (SR) using the beamline I (SUPERLUMI) at HASYLAB (DESY, Hamburg, Germany). The spectra were measured using a 2 m McPherson type primary monochromator (3.7-40 eV) and the emission was detected with a Hamamatsu R6358P photomultiplier. The spectra were corrected for the sensitivity of the experimental setup. Conventional photoluminescence measurements on the R^{3+} co-doped materials were also carried out.

The excitation from the top of the valence (VB) to the bottom of the conduction band (CB) was observed at 202 nm (6.14 eV) in the VUV-UV SR excitation spectrum of $\text{Sr}_3\text{SiO}_5:\text{Eu}^{2+}$ at 10 K (Fig. 1). This corresponds approximately to the band gap energy (E_g). This energy decreases from 6.14 to 5.96 eV when the temperature is increased from 10 to 300 K, respectively. The broad bands between 220 (5.6) and 330 nm (3.9 eV) were assigned to the $4f^7(^8\text{S}_{7/2}) \rightarrow 4f^65d^1(^2\text{D})$ transitions of the Eu^{2+} ion. The excitation to the $4f^65d^1$ ground level is probably above 330 nm, the experimental limit of the setup. The charge transfer energy of 3.2 eV observed in the excitation spectrum of Eu^{3+} , is used to position the $\text{Eu}^{2+} 4f^7(^8\text{S}_{7/2})$ ground level above the valence band in the band structure of Sr_3SiO_5 .

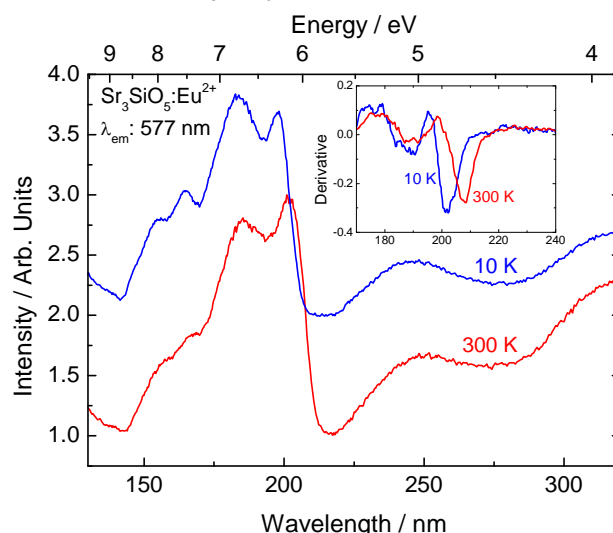


Figure 1: The synchrotron radiation VUV-UV excitation spectra of $\text{Sr}_3\text{SiO}_5:\text{Eu}^{2+}$ at 10 and 300 K.

The $\text{Sr}_3\text{SiO}_5:\text{Eu}^{2+}, \text{R}^{3+}$ (R: Y, La-Nd, Sm, Gd-Lu) materials show yellow emission at 577 nm (λ_{exc} : 320 nm) due to the $4f^65d^1(^2\text{D}) \rightarrow 4f^7(^8\text{S}_{7/2})$ transition of Eu^{2+} . A weaker band is also observed at *ca.* 480 nm. The relative intensity of the weaker band increases with increasing dopant and co-dopant concentration, while the intensity of the 577 nm emission decreases with co-doping. The yellow persistent luminescence at *ca.* 575 nm was observed only from some of the R^{3+} (R: La-Nd, Gd, Dy, and Tm) co-doped materials. The

strongest persistent luminescence was obtained with the $x_{\text{Eu}}/x_{\text{R}}$ ratios of 0.01/0.01 and 0.001/0.01 for the Nd^{3+} and Dy^{3+} co-doped materials, respectively.

The persistent luminescence process in $\text{Sr}_3\text{SiO}_5:\text{Eu}^{2+},\text{R}^{3+}$ begins with the excitation of an electron from the $4f^7(^8\text{S}_{7/2})$ ground level to the excited $4f^65d^1(^2\text{D})$ levels of Eu^{2+} (Fig. 2). The $4f^65d^1$ levels partially overlap with CB and the electrons can easily escape from these levels to CB directly or aided by thermal energy. The electrons moving freely in the host's CB are then trapped by defects below CB. The reverse process takes place by the release of electrons from the traps with thermal energy followed by the migration (or retrapping) back to the luminescent centre, relaxation within the $4f^65d^1$ levels and emission of visible light. However, the energies of the processes are based on data consisting of broad band emission, excitation and absorption resulting in the estimated accuracy of the order of 0.5 eV. The trap depths (1.0-1.5 eV) were obtained from thermoluminescence (TL) measurements (not shown here).

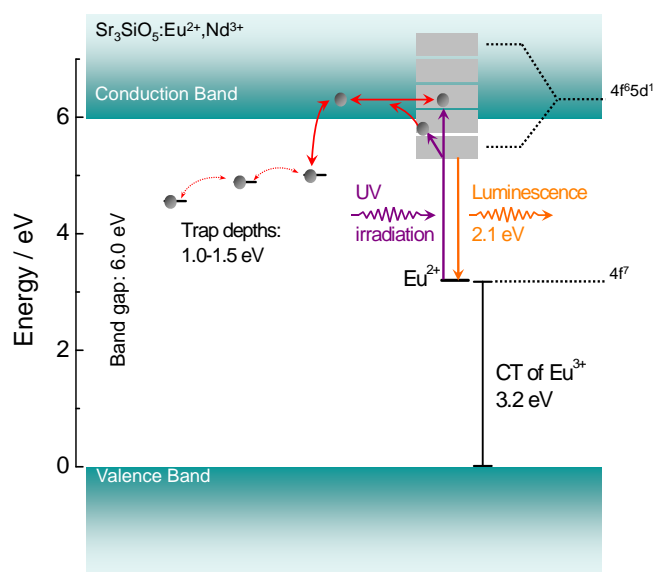


Figure 2: The mechanism of persistent luminescence in $\text{Sr}_3\text{SiO}_5:\text{Eu}^{2+},\text{Nd}^{3+}$.

The details of the energy storage and release processes including *e.g.* retrapping have to be clarified further employing the VUV-UV spectroscopy, photoluminescence and TL methods. In addition, in situ XANES measurements will be employed to probe the $\text{Eu}^{2+/3+}$ and $\text{R}^{3+/IV}$ species in Sr_3SiO_5 and preliminary studies have already been carried out. The local structure around the Eu^{2+} and R^{3+} ions will also be studied using EXAFS calculations. Other research topics studied at the SUPERLUMI beamline included the VUV excited luminescence properties of several potential persistent luminescence materials (with *e.g.* Eu^{3+} and Ti^{3+} as the luminescent centre). Studies on the excitonic features in the VUV excitation spectra were carried out, too. The results will be published promptly in appropriate international journals.

Acknowledgements

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 226716. Financial support from the Turku University Foundation, Jenny and Antti Wihuri Foundation and the Academy of Finland through contracts 117057 (2000), 123976 (2006) and 134459 (2009) as well as 137333 (2010) containing the joint project with the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Brazil, is gratefully acknowledged. Prof. Kari O. Eskola and Prof. Högne Jungner (University of Helsinki, Helsinki, Finland) are acknowledged for the thermoluminescence measurements.

References

- [1] J. Hölsä, *Electrochem. Soc. Interface* **18**(4), 42 (2009).
- [2] A.A. Setlur, A.M. Srivastava, H.L. Pham, M.E. Hannah, and U. Happek, *J. Appl. Phys.* **103** 053513 (2008).
- [3] J. Hölsä, A. Kotlov, T. Laamanen, M. Lastusaari, M. Malkamäki, and E. Welter, *Proc. Exc. States Trans. Elem. 2010 (ESTE2010)*, Piechowice, Poland, Sept. 4-9, 2010. P49.