

## Revealing charge transfer by x-ray absorption and radioluminescence in SrAl<sub>2</sub>O<sub>4</sub>:Eu,Dy

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Persistent luminescent materials can emit light for several hours after they are excited. The best known of these is SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup>, introduced by Matsuzawa *et al.* in 1996. Since then, several new persistent phosphors have been discovered, almost all based on Eu<sup>2+</sup> as the emission center and codoped with trivalent rare earth ions [1]. Despite considerable efforts and the use of advanced analytical techniques, a fundamental understanding of the working principle of persistent phosphors is still lacking.

Crucial unknowns are the exact valence states of the dopant and codopant and possible charge transfer between them. Recently, paramagnetic resonance (EPR) and x-ray absorption spectroscopy (EXAFS, XANES) have been introduced in the study of persistent phosphors. Contrary to the former, the latter technique has the advantage of being able to detect all possible valence states of an element. In contrast, it is sometimes more invasive. Using XANES, Hölsä *et al.* observed a constant Eu<sup>2+</sup>/Eu<sup>3+</sup> ratio in CaAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>,Nd<sup>3+</sup> as a function of temperature [2], although an ionization of the Eu<sup>2+</sup> during the charging is usually assumed.

We have studied the temperature dependence of the x-ray absorption in SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup>, combined with in situ monitoring of the radioluminescence and afterglow behaviour of the x-ray irradiated phosphor. Based on the light output of thermally annealed SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup> at low temperature (i.e. with empty traps) upon exposure to the x-ray beam, it was concluded that after a few minutes the phosphor is fully charged by the beam. Therefore, short measurement cycles were necessary to probe the valence state of europium with XANES.

In line with earlier reports, we found that part of the europium ions are incorporated in the phosphor material in their trivalent state. During the charging of the persistent luminescent material, an increase in the Eu<sup>3+</sup>/Eu<sup>2+</sup> ratio was observed, suggesting the ionization of Eu<sup>2+</sup> while charging. By thermal recycling, the effect was reproducible and thus an irreversible oxidation induced by the x-ray beam could be ruled out. Regarding the valence state of the co-dopant, divalent dysprosium could not be detected with XANES, irrespective of measurement temperature. Hence, it seems that the Dy<sup>3+</sup> ions do not act as electron trap centers.

[1] K. Van den Eeckhout, P.F. Smet, D. Poelman, *Materials* **3** (2010) 2536-2566.

[2] J. Hölsä, T. Laamanen, M. Lastusaari, M. Malkamäki, E. Welter, D.A. Zajac, *Spectrochim. Acta Part B* **65** (2010) 301-305.