

# Charging mechanisms in persistent phosphors

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## Abstract

The development of novel persistent phosphors is currently hampered by a limited understanding of the charging mechanism. Using x-ray absorption and thermoluminescence spectroscopy we evaluate the validity of recently proposed models for the charging mechanism.

## 1. Introduction

Despite fifteen years of intensive research since the introduction of SrAl<sub>2</sub>O<sub>4</sub>:Eu,Dy as a bright afterglow phosphor with night-long decay, the mechanism behind the persistent luminescence phenomenon is not yet fully resolved [1]. Most authors agree on the concept that charge carriers are created inside the material upon exposure to short-wavelength radiation, which subsequently get captured at long-lived trap states inside the band gap of the host crystal. However, the nature of these traps and the type and origin of the trapped carriers remains subject of debate. Many of the models that were developed in recent years predict the formation of electrons by ionization of photo-excited Eu<sup>2+</sup>-ions to Eu<sup>3+</sup>. The hereby created electrons are then supposedly trapped by the rare earth codopants [2], neighboring crystal vacancies [3] or both [4].

## 2. Experimental details

Several types of samples were investigated, such as the established, green-emitting SrAl<sub>2</sub>O<sub>4</sub>:Eu,Dy and novel persistent phosphors such as M<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu,(RE), where M stands for the alkaline earth elements Ca or Ba, and the co-dopant RE comprises a number of rare earth elements. X-ray absorption measurements, combined with in-situ radioluminescence, were measured at the ESRF synchrotron (Grenoble, France). The influence of temperature and excitation wavelength on the charging efficiency was studied using a spectroscopic thermoluminescence setup.

## 3. Results and discussion

### 3.1. Valence state changes

X-ray absorption studies were conducted on thermally emptied persistent phosphors (SrAl<sub>2</sub>O<sub>4</sub>:Eu,Dy) at low temperature (120K) and in dark conditions (avoiding light-induced charging). Exposure to x-rays leads to radioluminescence, in combination with charging of the phosphor (Fig. 1). The intensity of the x-ray beam was sufficiently low not to cause irreversible degradation of the phosphor material. Using XANES (x-ray absorption near edge spectroscopy) we were able to determine the ratio between the trivalent and divalent europium ions in the phosphor. As can be seen from Fig. 1, the charging of the phosphor is accompanied by an ionization of a fraction of the divalent europium ions on the same time scale. Meanwhile, the simultaneous reduction of Dy<sup>3+</sup> to Dy<sup>2+</sup>, as predicted by several models, could not be observed.

### 3.2. Temperature and wavelength dependency

The application area of persistent phosphors is largely determined by the wavelength range which can efficiently induce afterglow. Therefore we determined the excitation spectrum of the persistent luminescence for several (oxy)nitride phosphors. This was done by

recording thermoluminescent glow curves (which can be related to the afterglow intensity) as a function of the excitation wavelength. It appeared that charging via excitation into the 5d levels of europium is the dominant mechanism. However, the relative intensity between excitation into the lower and higher crystal-field split 5d levels is different from the one for the steady state photoluminescent excitation. We were able to explain this by evaluating the influence of the temperature during charging. For several persistent phosphors, excitation via the lower  $\text{Eu}^{2+}$  5d levels strongly depends on the charging temperature, with increased trapping occurring at higher temperature. Hence, at room temperature a thermal barrier is present for charge trapping when exciting via the lower 5d band, but not via the higher 5d levels. The release mechanism (leading to afterglow) of the trapped charges is independent of the charging wavelength, showing that the same traps are responsible.

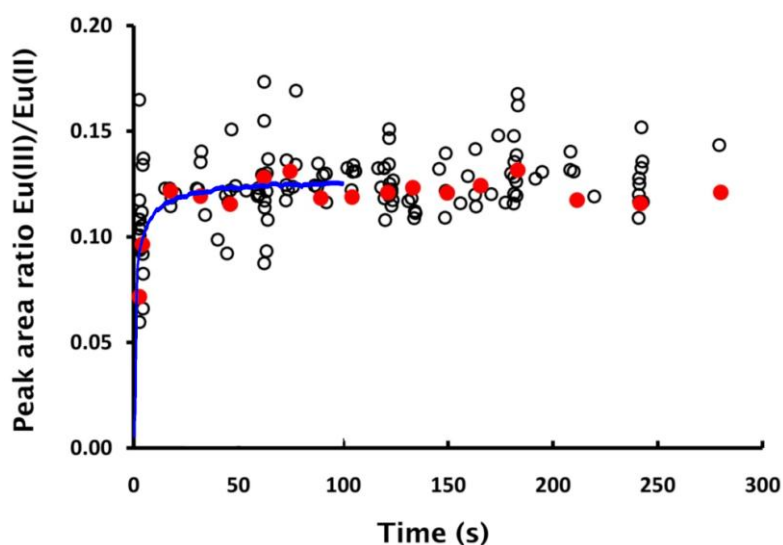


Figure 1. XANES peak area ratio between  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  as a function of irradiation time. The open circles are single spectrum results. The spectra were merged in time intervals of about 10 seconds, to reduce the noise. The results for the merged spectra are displayed by the solid dots. The solid curve shows the radioluminescence build-up as a function of the exposure time to the x-ray beam.

### 3.3. Towards an improved model for persistent luminescence.

The experimental observations on the valence state changes and on the temperature and wavelength dependency of the charging process are used to evaluate the recently proposed models. A refined, generally applicable model will be presented, with special focus on the role of the co-dopants and on the position of the  $\text{Eu}^{2+}$  energy levels relative to the conduction band.

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