Persistent Luminescent Materials – From Experiments to Models

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1. Introduction

Persistent luminescent materials, also known as afterglow phosphors or 'glow-in-the-dark' materials, have the ability to continue emitting light for a long time – minutes to hours – after the excitation has ended. They are currently actively under investigation because of their numerous potential applications, from toys, power-less safety signage and road markings to medical imaging [1,2]. In recent years, there has been a lot of progress in the development of new persistent luminescent materials with improved optical properties. Still, the details of the processes governing the persistent luminescence are far from resolved. In particular, the way in which the energy of the optical excitation is stored in traps and the nature of these traps is still debated. We are presenting some advanced experiments trying to shed more light on the number and nature of these traps.

2. Results and discussion

Optical charging behavior of persistent phosphors

In typical experiments and publications on persistent luminescent materials, only the decay of the luminescent intensity with time is studied and reported. However, their charging behavior yields at least as much information: in the present work, the emission intensity was monitored during optical charging, as a function of excitation wavelength and intensity.

During the charging phase, the excitation energy is partly used to fill the traps, and the intensity of the luminescence is thus initially reduced. When more and more traps are filled, the luminescent intensity increases until a steady state situation is achieved, when the filling and (thermal) release of energy from the traps become equal. It is observed that the charging time is – as expected - strongly influenced by the excitation light intensity. Moreover, while the maximum steady state luminescence keeps increasing with excitation intensity, the total afterglow intensity saturates, indicating that from a certain point, all traps are filled and the maximum energy is stored in the material. These experiments allow to estimate the total number of traps available for energy storage in the material.

Valence states of dopants and co-dopants

Several models on persistent luminescence predict a change in the oxidation state of the dopant and the codopant upon charging of the phosphor. For example, in $SrAl_2O_4$:Eu,Dy (one of the best afterglow phosphors known to date), these models predict a change of Eu^{2+} to Eu^{3+} and - in some models - a reduction of the Dy codopant. The latter is then assumed to act as an acceptor and be responsible for storing the excitation energy.

The instability of the valence state of rare earths and the fact that materials are not available as single crystals makes determination of their valence state with common techniques such as XPS (x-ray photoelectron spectroscopy) or ESR (electron spin resonance) difficult to impossible. Time-resolved x-ray absorption spectroscopy (XAS) is a very powerful tool to probe the local environment and valence state of dopant level impurities. Measurements were performed at a synchrotron beam line (European synchrotron radiation facility ESRF, DUBBLE beam line BM26A) in order to measure the valence states of the dopant and co-dopant during in situ filling of the traps. Such experiments are complicated by the fact that the synchrotron x-ray beam is also charging the sample [3] and therefore experimental conditions have to be chosen carefully. For europium we were able to clearly observe the oxidation of Eu^{2+} to Eu^{3+} during the filling of the traps by the x-ray beam [3]. The observed valence state changes in $SrAl_2O_4$:Eu,Dy yield direct experimental input to evaluate the different models of persistent luminescence.

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