ESRF	**Experiment title:** **Unraveling the mechanism of persistent luminescence**	**Experiment number:** **26-01-873**
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Report:

In this experiment we combined in situ luminescence and XAS experiments on the high brightness persistent phosphors $SrAl_2O_4$:Eu,Dy, $CaAl_2O_4$:Eu,Nd and $Sr_2MgSi_2O_7$:Eu,Dy. Persistent luminescent materials (also called afterglow phosphors or glow-in-the-dark materials) have many applications, such as safety signage and emergency lighting. However, the mechanism behind the storage and release of energy in these phosphors is poorly understood, which hampers the development of novel phosphors.

Several models for explaining the storage and release mechanism are available in literature, many of them involving valence state changes of the rare earth dopants. In this experiment we evaluated whether XANES is a useful technique for studying this type of phosphors. In principle, XANES is perfectly suited to determine the valence state of rare earth dopants, which was verified by measuring at the LIII edge for reference materials containing rare earth ions with different valence states. By in-situ monitoring of the radioluminescence (RL) emitted by these persistent phosphors when exposed to the x-ray beam, their 'charging state' could be determined. Given the low dopant concentration and the large self-absorption of the samples, measurements were performed in fluorescence mode.

Fig. 1 shows the experimental setup. RL was monitored using an Ocean Optics QE65000 CCD-based spectrometer. Sample temperature was varied using an Oxford cryostream (low temperature (120K) and room temperature). Prior to exposure to the x-ray beam, samples were heated until the thermoluminescent glow peak occurred and then stored in the dark. Also in the hutch, the sample was shielded from external light.

Then the XANES experiment was started. It turned out that 1) the persistent phosphors are emitting strong RL emission, 2) the RL intensity of the phosphors initially increases as a function of x-ray exposure time and then saturates, which is consistent with the trap centers filling, 3) when closing the x-ray shutter, the samples emit afterglow and/or show strong thermoluminescent emission. The time evolution of the RL intensity build-up was studied, and it appeared that after 10s of seconds to one minute, the $SrAl_2O_4$:Eu,Dy phosphor is fully charged and no further valence state changes are then expected. Hence to study valence state changes when filling and emptying traps, the XANES experiments should be performed very fast, which was just possible at the BM26 beamline for the best available persistent phosphors (such as $SrAl_2O_4$:Eu,Dy). Future measurement campaigns will verify this behavior for other persistent phosphors, possibly at beamlines having a higher XANES acquisition rate.

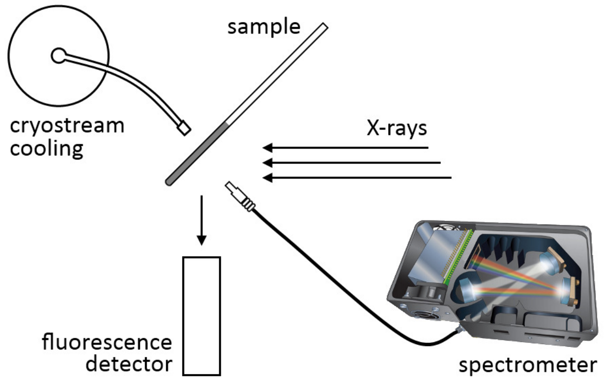

Fig. 1.Experimental setup.

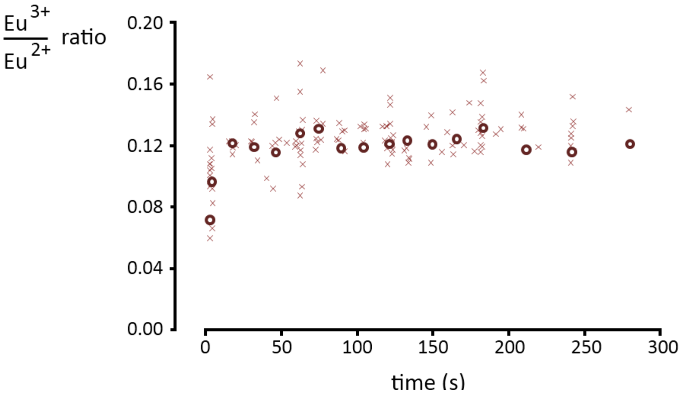

Fig. 2.Change in the Eu^{3+}/Eu^{2+} ratio as a function of the x-ray irradiation time.

From XANES spectral analysis (Fig.2), changes in the valence state for Eu, but not for Dy, could be detected. The implication of these observations for the existing models on persistent luminescence has been investigated, and was the subject for a publication submitted to Physical Review Letters (current status: under review). The abstract for this publication is mentioned below:

Luminescence and x-ray absorption measurements of persistent $SrAl_2O_4$:Eu,Dy powders: Evidence for valence state changes

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The development of new efficient afterglow phosphors is currently hampered by a limited understanding of the persistent luminescence mechanism. Radioluminescence and x-ray absorption measurements on the persistent phosphor $SrAl_2O_4$:Eu,Dy were combined to reveal possible valence state changes for the rare earth (co)dopants. Traps in the phosphor material are quickly filled when exposing thermally emptied $SrAl_2O_4$:Eu,Dy powder to x-rays. On the same time scale, a partial oxidation of Eu^{2+} to Eu^{3+} is observed by XANES (x-ray absorption near-edge spectroscopy), while for the trivalent dysprosium the valence state remains unchanged. The impact of these observations on the recently proposed models for persistent luminescence is discussed.

Several results of this campaign were also presented at the ESTE2010 conference, Piechowicze, Poland.