

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Probing electron transfer in rare earth doped storage phosphors	Experiment number: 26-01-951
Beamline: BM26A	Date of experiment: from: 8/3/2013 to: 12/3/2013	Date of report:
Shifts: 12	Local contact(s): Dipanjan Banerjee, Sergey Nikitenko	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Van den Eeckhout, Koen Smet, Philippe F. Poelman, Dirk (*) Korthout, Katleen Meert, Katrien (*) De Roo, Nico (*) Sijbom, Heleen (*) LumiLab, Dept. Solid State Sciences, Ghent University, Krijgslaan 281-S1, B-9000 Ghent, Belgium		

Report:

In this experiment we performed time dependent XAS experiments on the high brightness persistent phosphors $\text{SrAl}_2\text{O}_4:\text{Eu,Dy}$ and $\text{CaAl}_2\text{O}_4:\text{Eu,Nd}$. These experiments allow us to gain information on the charge trapping and storage mechanism in persistent luminescent materials, also called afterglow phosphors or glow-in-the-dark materials.

The fascination of many researchers by the phenomenon of persistent luminescence has led to the development of different models explaining the storage and release mechanism. Most of these models involve a valence state change of the rare earth dopants. In previous experiments we already evaluated the application of XANES to study these materials (26-01-873).

XANES spectra were collected at the L_{III} edge of the dopant ions, i.e. the lanthanides. Given the low dopant concentration and the large self-absorption of the samples, measurements were performed in fluorescence mode.

During this campaign we performed *pump-probe* experiments, with an optical excitation source as pump and the x-rays as probe. In earlier experiments the x-ray beam was used as pump and probe simultaneously. In these experiments, 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 in Physical Review B [1].

The novel technique, which uses an optical excitation source as pump, appeared to be successful. Moreover we could detect a valence state change of the dopants and the codopants, simultaneously (see Figure 1).

In Figure 1 the main results of this campaign are depicted. The L_{III} XANES spectra of Eu and Dy were measured with and without optical excitation. The difference between the normalized XANES spectra with and without optical excitation clearly indicates a change of the spectra. The white line resonances of divalent and trivalent rare earth ions are separated by approximately 8 eV [1-2] (the resonance for the divalent ions is 8 eV below the one of trivalent ions). By comparing the measured spectra with spectra of reference compounds, we can conclude that a change in the XANES spectra is due to a valence state change of the dopants and codopants. Additional measurements using higher power optical excitation and time-dependent measurements at fixed energy are planned in a follow-up campaign to confirm these results, which indicate a real breakthrough in the modeling of persistent luminescent materials.

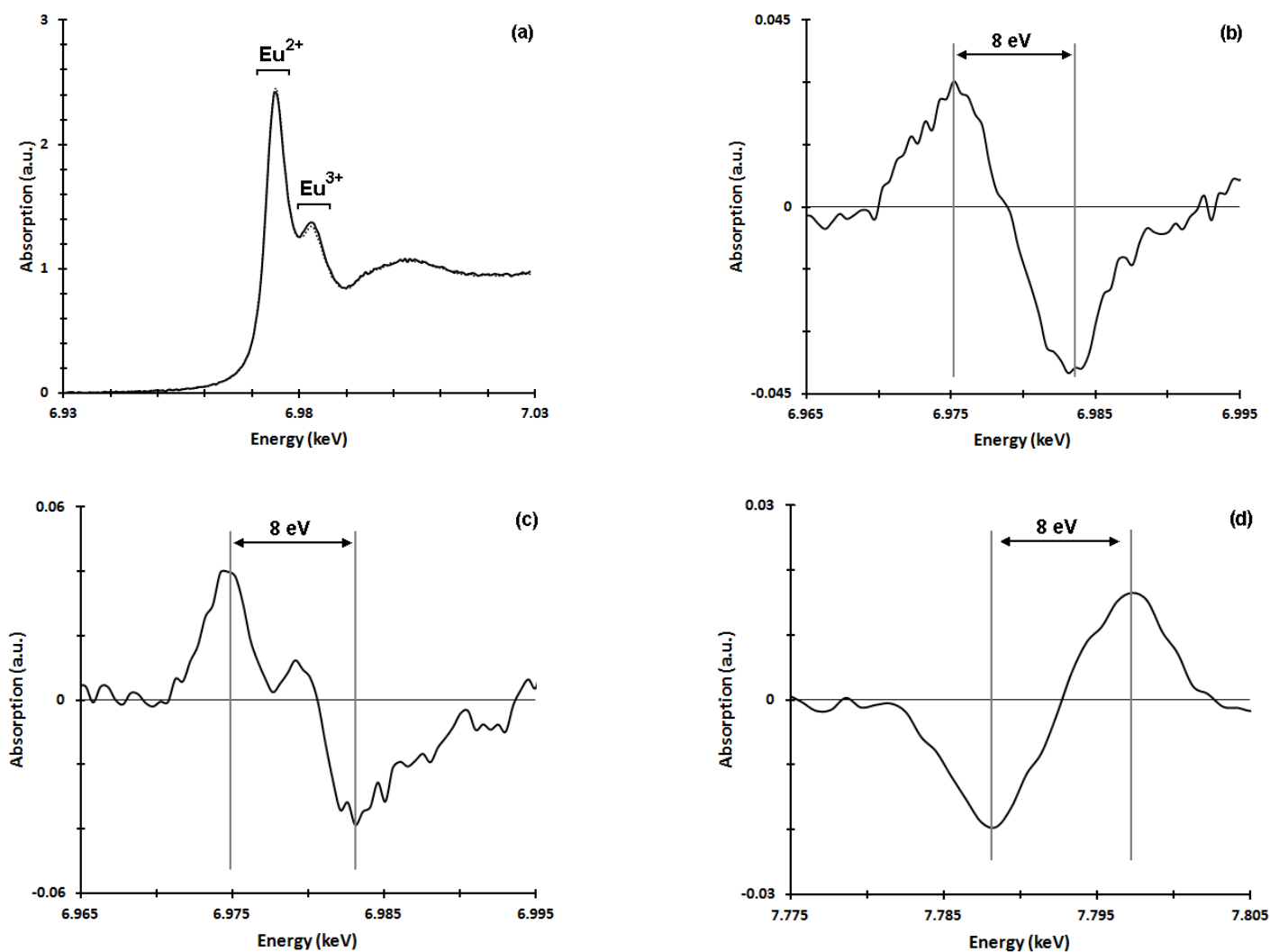


Figure 1: XANES spectra results of campaign 26-01-951. (a) Normalized Eu L_{III} XANES spectrum of $SrAl_2O_4:Eu, Dy$, **before** optical excitation (solid line) and **during** excitation (dotted line). (b) Difference spectrum of the XANES spectra depicted in (a), the intensity of the white line caused by the divalent ions increases, while the resonance of the trivalent Eu ions decreases upon optical excitation. (c) Idem as (b), but for the normalized Eu L_{III} XANES spectra of $CaAl_2O_4:Eu, Nd$. (d) Idem as (b), but for the normalized Dy L_{III} XANES spectra of $SrAl_2O_4:Eu, Dy$.

References:

- [1] K. Korthout, K. Van den Eeckhout, J. Botterman, S. Nikitenko, D. Poelman, P. F. Smet, *Luminescence and x-ray absorption measurements of persistent $SrAl_2O_4:Eu, Dy$ powders: evidence for valence state changes*, Physical Review B **84** (2011) 085140

[2] Z. Hu, G. Kaindl, G. Meyer, *X-ray absorption near edge structure at the L_{I-III} thresholds of Pr, Nd, Sm, and Dy compounds with unusual valences*, Journal of Alloys and Compounds **246** (1997) 186