

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: In situ optical and x-ray absorption measurements of persistent luminescent materials	Experiment number: MA1401
Beamline: BM23	Date of experiment: from: 28/09/2011 to:02/10/2011	<i>Received at ESRF:</i>
Shifts: 12	Local contact(s): Mark Newton	

Names and affiliations of applicants (* indicates experimentalists):
Dirk Poelman (proposer)
Philippe F. Smet (co-proposer)
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Report:

The main purpose of the experiment was to investigate the class of rare earth (RE) doped alkaline earth aluminates ($\text{SrAl}_2\text{O}_4:\text{Eu}$, (Dy) and $\text{CaAl}_2\text{O}_4:\text{Eu}$, (Nd)). These materials **show** persistent luminescence, meaning that they exhibit a considerable afterglow when the optical excitation has ended. Several theoretical models exist to explain the phenomenon of persistent luminescence, but the exact mechanism behind the storage and release of energy in these materials is still shrouded in mystery. Most models expect a valence state change of the rare earth dopants upon charging and subsequent slow decay [1]. XANES is in principle a perfectly suited technique to evaluate the valence state changes of these dopants [2].

In applications, the persistent luminescent materials are excited using light, but they can also be charged (and made to emit light for a long time) using x-rays; as such, the measurement beam during the XAS experiment simultaneously charges the material. The proposal aimed at a dedicated investigation on the valence state changes upon charging of the persistent phosphor by x-ray irradiation. Quick XANES measurements on the L_{III} edges of the rare earth dopants would enable us to determine these changes. Unfortunately we were not able to perform the quick-XANES measurements, as they were requested in the proposal, due to the low dopant concentration and the strong absorbance of the host matrix.

$\text{CaAl}_2\text{O}_4:\text{Eu},(\text{Nd})$ samples were prepared via non-aqueous sol-gel technique and a heat treatment in air at 1000°C . Subsequently these samples were annealed at different temperatures (500°C - 1100°C) under H_2/N_2 atmosphere to reduce Eu^{3+} to Eu^{2+} . In this way a series with increasing $\text{Eu}^{2+}/\text{Eu}^{3+}$ photoluminescent signal is obtained.

We were able to perform XAS measurements on the L_{III} edge of Eu in $\text{CaAl}_2\text{O}_4:\text{Eu}$, (Nd). The results are displayed in Figure 1. During the annealing, i.e. reduction process, the trivalent europium ions reduce to

divalent europium. In Fig. 1 we can see that because of the reduction process, a shoulder appears on the lower half of the absorption edge.

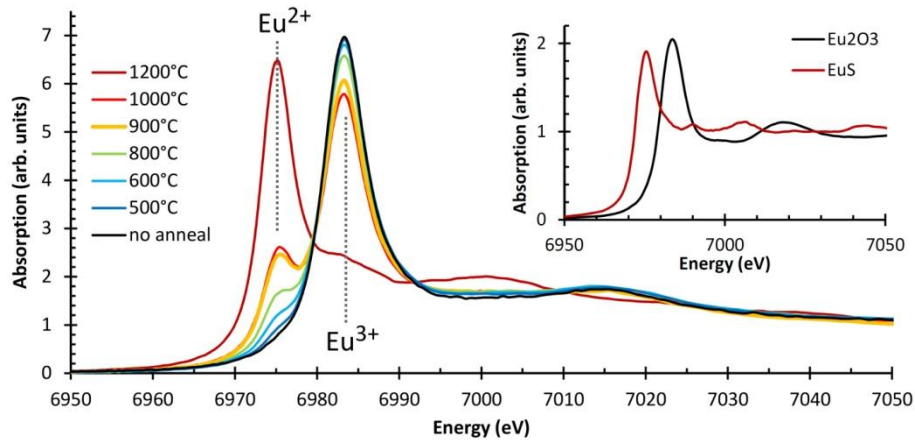


Figure 1: XANES spectra for $\text{CaAl}_2\text{O}_4:\text{Eu}$ heat-treated at 1000°C as a function of the temperature of the post-annealing in H_2/N_2 . The inset shows the XANES spectra for the reference compounds EuS and Eu_2O_3 .

We performed a detailed investigation of the XANES spectra, whereby the white line of the divalent and trivalent Eu ions was fitted using arctangent and lorentzian functions. From Figure 1 it is clear that upon increasing the annealing temperature, a higher fraction of divalent Eu ions is present in the material.

The results depicted in Figure 1 can be correlated with the photoluminescence (PL) of these samples: without annealing only line emission, arising from the trivalent ions is visible. By annealing the samples the band emission from the divalent Eu ions becomes more dominant in the PL spectra. This correlation is visualized in Figure 2.

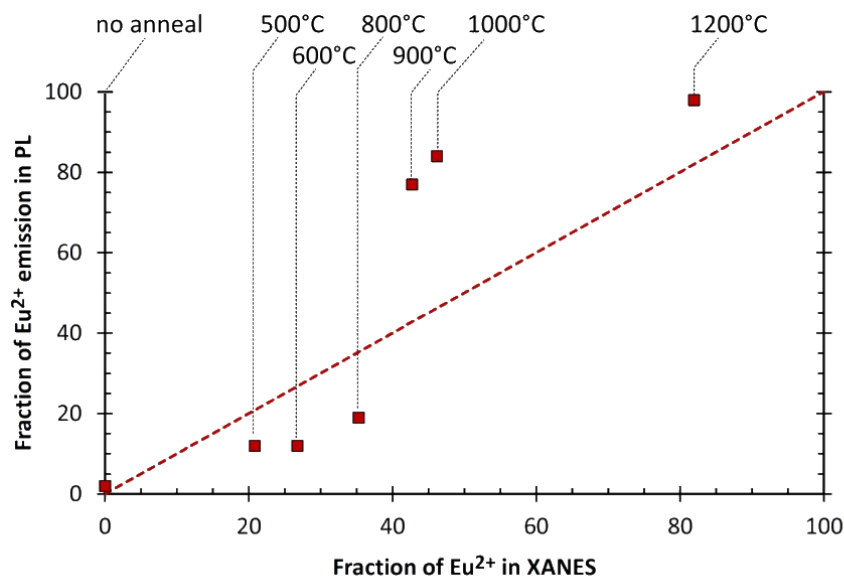


Fig. 2. Influence of the temperature during the post-annealing in H_2/N_2 on the fraction of Eu^{2+} emission with respect to the total emission intensity upon excitation at 260nm . All data points are plotted against the fraction of Eu^{2+} as derived from the XANES measurements.

From Figure 2 it is clear that there is a large difference between both valence states of europium derived from photoluminescence measurements and from the ratio derived from x-ray absorption spectroscopy. A

considerable fraction of Eu^{3+} ions can be present in the powders, although this is not necessarily reflected in the photoluminescent spectrum.

These results are part of a publication in *Optical Materials Express* [3]. The abstract for this publication is shown below:

Valence states of europium in $\text{CaAl}_2\text{O}_4:\text{Eu}$ phosphors

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Persistent luminescent $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Nd}^{3+}$ powders were prepared by a non-aqueous sol-gel technique. The crystallization of calcium aluminate by heat-treatment of the sols is described in detail. After heat treatment in air, the europium dopant ions are mainly in a trivalent state. For the reduction to the divalent state post-annealing in a reducing nitrogen-hydrogen atmosphere is used. The reduction of europium ions is monitored by photoluminescence and x-ray absorption (XANES) spectroscopy. The degree of reduction is strongly dependent on the annealing temperature. Although for high temperature a strong enhancement of the Eu^{2+} emission is observed, this also leads to powders with a gray body color.

Perspectives

Unfortunately the time resolved measurements on persistent materials in fluorescence mode were not possible during this beamtime allocation. Although we realize that these measurements are very challenging, a dedicated investigation on the valence state changes upon charging of these phosphors by x-ray irradiation would enable us to discriminate between and fine tune different existing models for this phenomenon.

References:

- [1] K. Van den Eeckhout, P. F. Smet, and D. Poelman, *Materials* **3**, 2536 (2010)
- [2] Y. Takahashi, G. R. Kolonin, G. P. Shironosova, I. I. Kupriyanova, T. Uruga, and H. Shimizu, *Mineral. Mag.* **69**, 179 (2005)
- [3] N. Avci, K. Korthout, M.A. Newton, P.F. Smet, and D.Poelman, *Optical Materials Express* **2**, 321 (2012)