

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 using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now 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: Combined XAS and optical measurements of Eu-doped luminescent materials	Experiment number: 26-01 830
Beamline: BM26A	Date of experiment: from: 15 Jun 2009 to: 19 Jun 2009	Date of report: 16 Feb 2010
Shifts: 9	Local contact(s): Sergey Nikitenko, Marika Vespa	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): *Dirk Poelman (main proposer), *Philippe Smet (co-proposer), *Katleen Korthout, *Nursen Avci, *Anthony Partmentier, *Koen Van den Eeckhout, Lumilab, Dept. Solid State Sciences, Ghent University, Krijgslaan 281-S1, B-9000 Gent, Belgium		

Report:

The main purpose of the experiment was to investigate the class of europium doped alkaline earth sulfides (CaS:Eu , SrS:Eu and $\text{Ca}_{(1-x)}\text{Sr}_{(x)}\text{S:Eu}$) and thiosilicates ($\text{Ca}_{(2-x)}\text{Sr}_{(x)}\text{SiS}_4\text{:Eu}$ for different values of x as well as different dopant concentrations). In these compounds Eu is normally in a divalent valence state.

Measurements were also performed on $\text{Ca}_2\text{Si}_5\text{N}_8$ doped with europium and thulium, these are so-called **persistent phosphors**. These phosphors can glow for up to several hours after optical excitation.

Since the emission is very sensitive to the coordination of the Eu, we conducted optical emission measurements simultaneously with the XAS measurements. The XAS measurements were performed at the L_{III} edge of Eu, resp. Tm to study the valence state and the local environment. The experiment also consisted of measuring the PL-intensity and spectrum (1) by excitation with an LED **before** the synchrotron radiation hit the sample, (2) **during** the XAS measurements since the beam excited the sample and (3) by excitation with an LED **after** the synchrotron radiation hit the sample.

To carry out the experiments we used a fiber-coupled CCD spectrometer and a LED. On the LED an optical fibre was attached, so the light could be transmitted towards the sample. The position of the light beam on the sample was controlled by a xyz-stage. In this way we were able to measure the PL-intensities at the same spot on the sample as the position of the incoming x-rays. The CCD spectrometer was installed in the hutch and controlled by a PC from outside the hutch; the experimental setup is given in Figure 1.

Determination of the edge position, background subtraction and normalization of the raw data was done with Athena [1]. Moreover, peak fitting has been applied for the region around the edge (-20 eV to 20 eV) to quantify the ratio of $\text{RE}^{2+}/\text{RE}^{3+}$, since in some of the samples both valence state were observed in some spectra.

1. Measurements on the alkaline earth sulfides:

The PL spectrum before and after irradiation with the x-ray beam is given in Figure 2, no evidence for Eu^{3+} is found. The intensity is the same, this indicates that the phosphor indeed does not lose its luminescent properties due to irradiation.

Figure 3 depicts the influence of the beam on the samples: the ratio of the beam intensity to the XL-intensity (= luminescence due to x-rays) of the samples. Since this value is constant, no special features are found. These are promising results in view of future measurement campaigns, as there was some fear the synchrotron beam would influence the state of the sample.

In Figure 4 the XANES data on the rare-earth doped alkaline earth sulfides can be found. The samples prepared solvothermally clearly contain Eu^{3+} , which is not seen in the PL and XL measurements on the samples. This can be caused by surface defects or by Eu ions which are not incorporated in the samples.

The Fourier transforms of some EXAFS spectra are shown in Figure 5. Those transforms suggest different positions for the Eu-atoms depending on the preparation method.

2. Measurements on the thiosilicates:

The PL and XL measurements did not reveal any significant influence of the x-rays on the thiosilicates: no changes in the Eu-state were observed.

Although the PL-measurements only indicate the presence of Eu^{2+} , the XANES spectra of the samples with low dopant concentrations (2% and 10%) clearly show the presence of Eu^{3+} (see Figure 6).

3. Measurements on the persistent luminescent materials:

The mechanism of persistent luminescence in $\text{Ca}_2\text{Si}_5\text{N}_8: \text{Eu}, \text{Tm}$ is not clear yet. One possible mechanism suggests the creation of Eu^+ and Tm^{4+} ions. We used XANES spectroscopy to determine the valence state of the rare earth ions.

The spectra at the L_{III} -edge of Eu exhibit a double-peaked white line structure, indicating a mixed-valence state of the compounds (Figure 7). We observe the presence of Eu^{2+} and Eu^{3+} (probably caused by Eu^{3+} ions that did not fully reduce to the Eu^{2+} state during sample preparation) in the spectra but no Eu^+ .

At the L_{III} -edge of Tm no tetravalent Tm characteristic peak was observed (not shown).

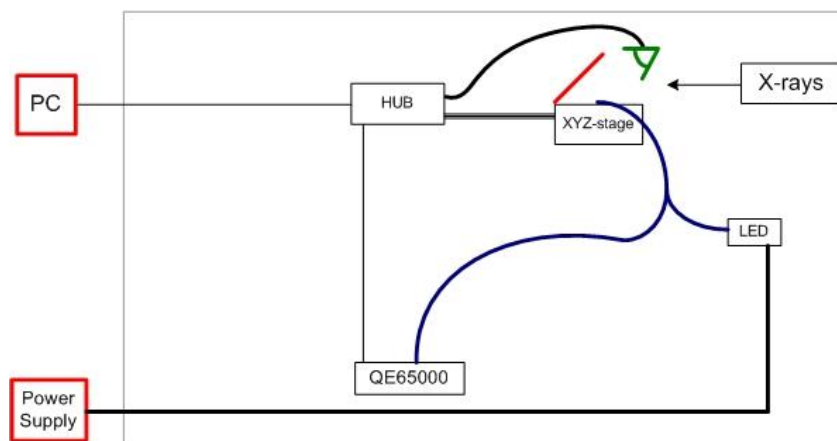


Figure 1: Experimental setup.

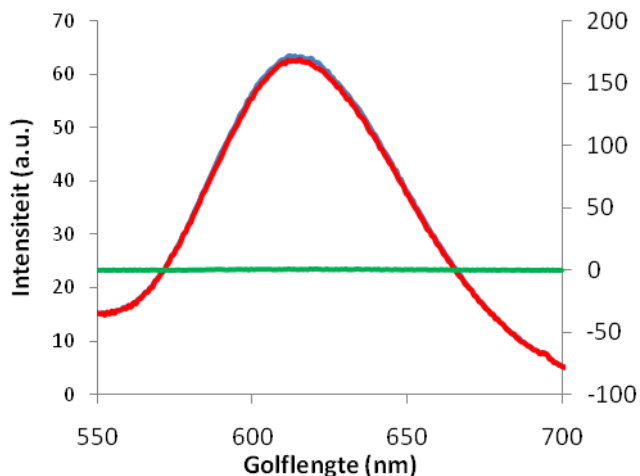


Figure 2: PL emission of the rare-earth doped particles (SrS:Eu). PL spectrum before (red), PL spectrum after (blue), Subtraction of both spectra (green).

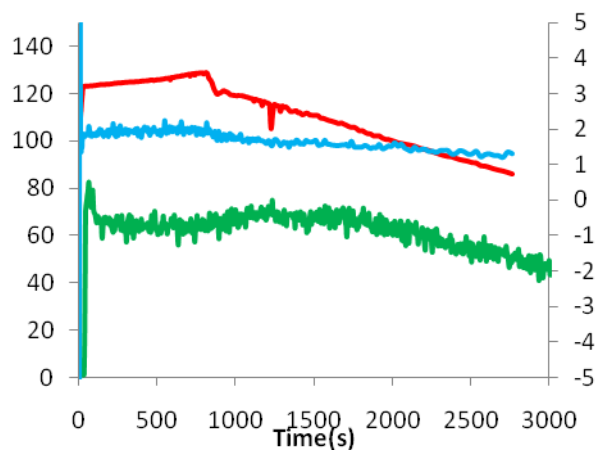


Figure 3: Influence of the beam on the samples emission intensity. Intensity of the beam (red), integrated emission intensity (green) and ratio of the intensities (blue) as a function of time.

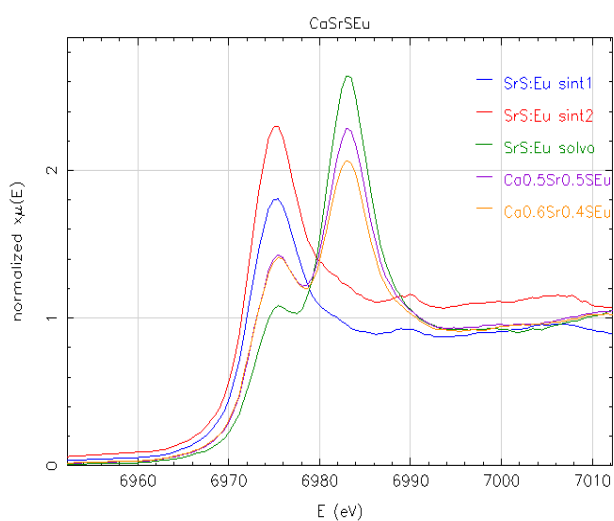


Figure 4: Xanes spectrum of the rare-earth doped alkali earth sulfides. The particles prepared in a solvothermal way (green, purple, yellow) have a large fraction of Eu^{3+} , which is not visible in the sintered particles (blue, red).

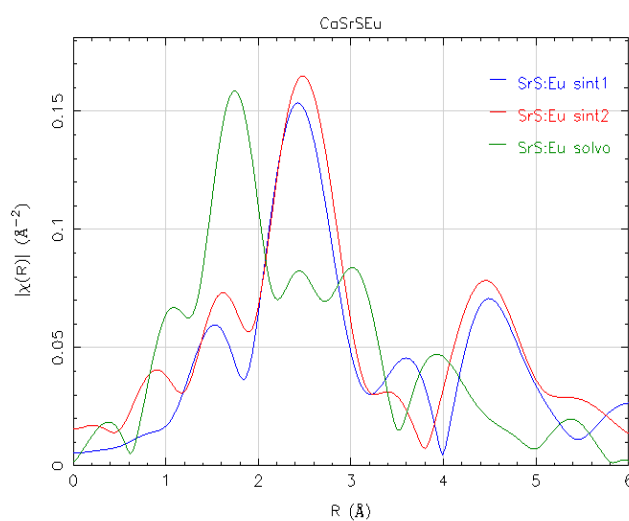


Figure 5: Fourier transform of the EXAFS signal

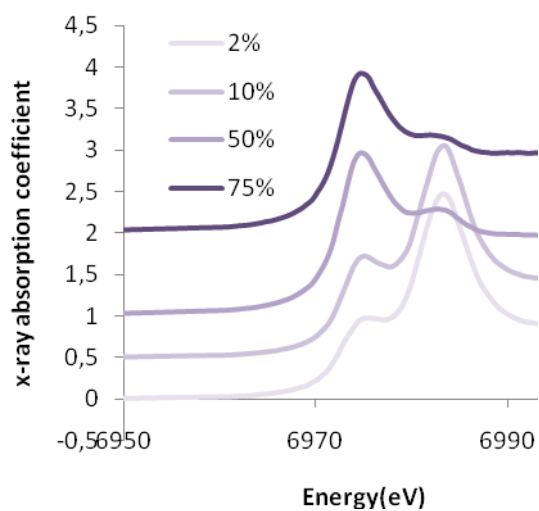


Figure 6: Xanes spectra of $\text{Ca}_{(1-x)}\text{EuxSi}_4$ for different values of x (see Figure)

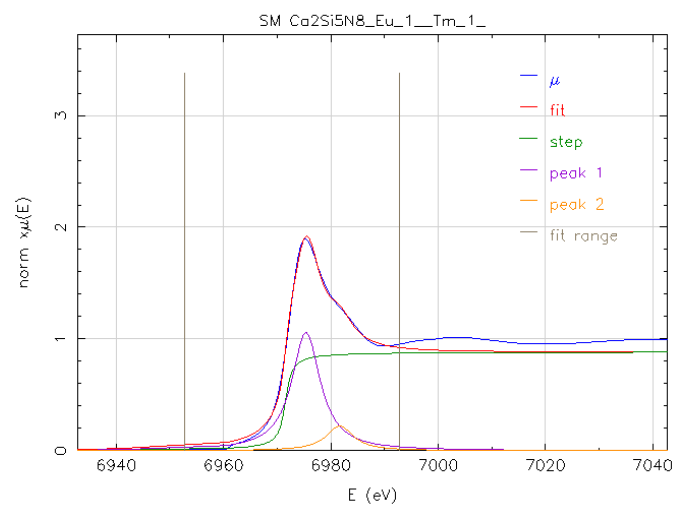


Figure 7: XANES spectrum of $\text{Ca}_2\text{Si}_5\text{N}_8:\text{Eu}(1\%), \text{Tm}(1\%)$. The double peaked white line can be fit by using 2 Lorentzians and one arctangent. The need of 2 Lorentzians indicates the existence of 2 valence states.

References:

[1] B.Ravel, M.Newville, J. Synchrotron Rad. 12 (2005), 537