

## 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.



	<b>Experiment title:</b> EXAFS of rare earth doped oxynitride phosphors for lighting applications	<b>Experiment number:</b> MA1400
<b>Beamline:</b> BM23	<b>Date of experiment:</b> from: 31/08/2011 to: 04/09/2011	<b>Date of report:</b>
<b>Shifts:</b> 12	<b>Local contact(s):</b> Mark Newton	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Poelman, Dirk Smet, Philippe F. Korthout, Katleen (*) Van den Eeckhout, Koen (*) Parmentier, Anthony B. (*) Botterman, Jonas (*) LumiLab, Dept. Solid State Sciences, Ghent University, Krijgslaan 281-S1, B-9000 Ghent, Belgium		

## Report:

The main purpose of the experiment was to investigate europium doped phosphors for lighting applications at the K edge of the europium ions. Different phosphor materials were investigated but the main results were obtained for the europium doped thiosilicates.

Due to their efficient yellow-to-red emission, europium doped calcium thiosilicates are very interesting materials for use in phosphor converted light-emitting diodes (pc-LEDs). Their emission spectrum results from  $4f^65d \rightarrow 4f^7$  transitions of the  $\text{Eu}^{2+}$  ions and the presence of two inequivalent lattice sites for  $\text{Eu}^{2+}$ ; emission properties and crystal structure are, therefore highly dependent on the europium concentration and incorporation of these ions.

Extended x-ray absorption fine structure (EXAFS) is a powerful technique to investigate the environment of particular ions in materials. With this technique, it is possible to determine which crystallographic sites are substituted for upon adding dopant ions in the case of impurity doped luminescent materials. For instance, upon introduction of Eu in  $\text{Ca}_2\text{SiS}_4$ , it is assumed that the dopant ions replace Ca ions. By means of EXAFS measurements at the Eu K edge (48.518 keV) we are able to show that the Eu dopant ions occupy the two different sites in  $\text{Ca}_2\text{SiS}_4$ , albeit some preferential substitution is observed. BM23 is one of the very few beamlines in Europe wherein such high energy EXAFS measurements can be made with sufficient quality to allow such analysis.

From earlier measurements, (Eu L<sub>III</sub> edge at the Dubble beamline (ESRF)), we know that Eu<sup>2+</sup> and Eu<sup>3+</sup> ions coexist in all samples; the fraction of trivalent Eu diminishing with increased concentration. However, there are two possible substitutional positions for the Eu atoms in the Ca<sub>2</sub>SiS<sub>4</sub> lattice. What the high energy Eu K edge EXAFS from BM23 allows to be understood is: that, at low dopant concentrations (<10%), and within a global, Ca<sub>2</sub>SiS<sub>4</sub>, orthorhombic structure, the dopant ions *substitute* for the Ca ions at both inequivalent crystallographic sites and the partitioning of Eu between these sites can be established.

The EXAFS data analysis on the lightly doped samples show that the divalent Eu ions preferentially occupy the Ca1 site in the crystal structure. Moreover the relative occupancy of the Ca1 site increases upon increasing the dopant concentration from 2% to 10%. This effect agrees well with the photoluminescence spectra: upon increasing the dopant concentration the relative intensity of the emission band caused by the Ca1 site increases.

The trivalent Eu ions in Ca<sub>2</sub>SiS<sub>4</sub> were found to form defect clusters in the lattice. This effect can be caused by charge compensation. If one trivalent Eu ion occupies a divalent Ca site, a charge mismatch occurs. By introducing one Ca vacancy a compensation for two triavalent Eu ions is obtained. These cluster defects were indeed observed during the EXAFS analysis.

At higher concentrations (>50%), where a monoclinic Eu<sub>2</sub>SiS<sub>4</sub> structure is adopted, the Ca ions occupy both europium sites; unexpectedly a large fraction Eu<sup>3+</sup> ions is also found for low doped thiosilicates, though this is not reflected in their photoluminescence.

From the EXAFS results we can conclude that the Ca ions in heavily doped samples preferentially occupy the Eu2 site in the monoclinic lattice. The preferential substitution decreases with an increase of dopant concentration, so we obviously obtain an equal distribution of the Eu ions in Eu<sub>2</sub>SiS<sub>4</sub>.

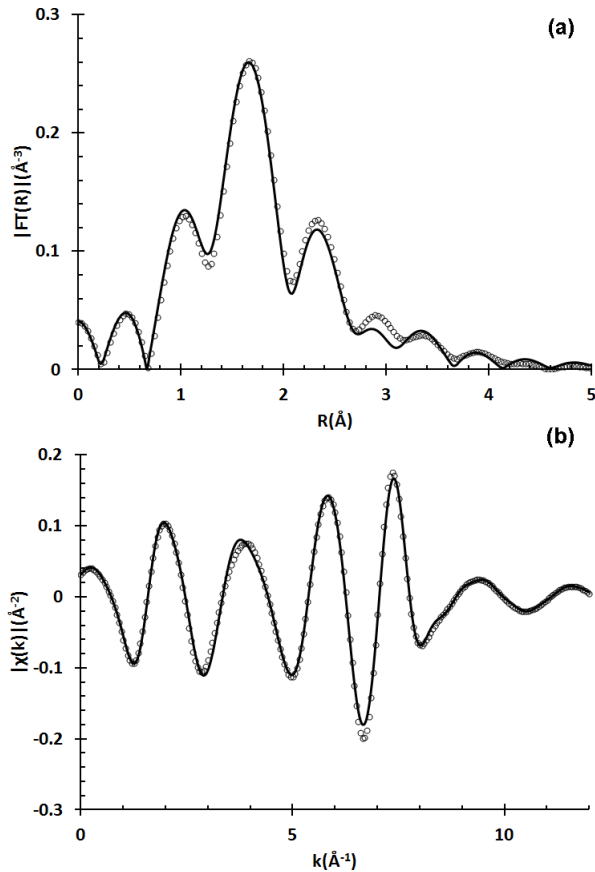


Figure 1: (a) Fourier transform of experimental (solid line) and simulated (circles) of Eu K-edge EXAFS on Ca<sub>2</sub>SiS<sub>4</sub>:Eu (7.5%), i.e. Ca<sub>1.85</sub>Eu<sub>0.15</sub>SiS<sub>4</sub>. (b) Back transformation of the data in (a) to k-space.

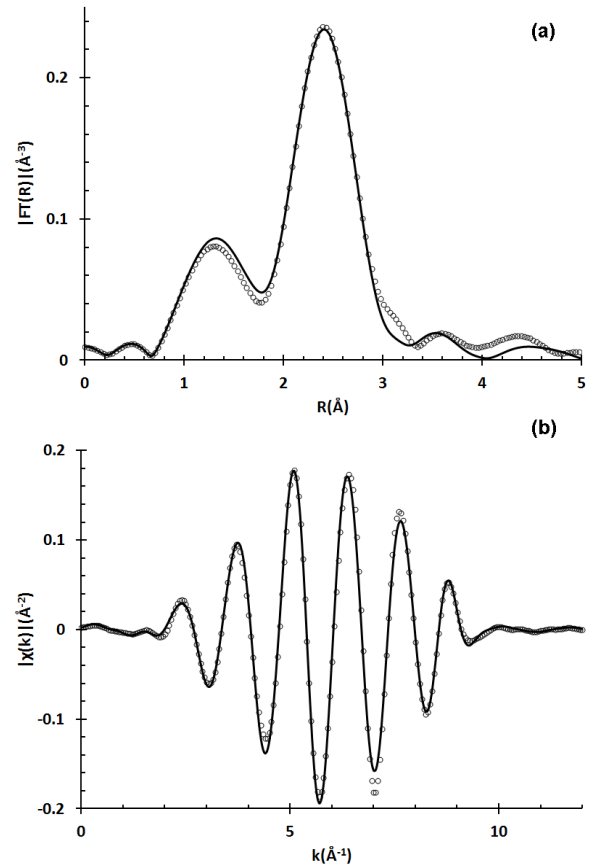


Figure 2: (a) Fourier transform of experimental (solid line) and simulated (circles) of Eu K-edge EXAFS on Ca<sub>2</sub>SiS<sub>4</sub>:Eu (95%), i.e. Ca<sub>0.1</sub>Eu<sub>1.9</sub>SiS<sub>4</sub>. (b) Back transformation of the data in (a) to k-space.

These results are the subject for a publication accepted by Physical Chemistry Chemical Physics. The abstract for this publication is mentioned below:

### **A XAS study of the luminescent Eu centers in thiosilicate phosphors**

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Due to its bright yellow-to-red emission, europium doped  $\text{Ca}_2\text{SiS}_4$  is a very interesting material for phosphor converted light emitting diodes. The emission spectrum is highly depending on the Eu concentration and can consist of more than one emission band. We combined X-ray absorption fine structure and photoluminescence measurements to analyze the structure of europium centers in  $(\text{Ca},\text{Eu})_2\text{SiS}_4$  luminescent powders. This paper provides an explanation for the concentration dependency of the emission spectra. We find that at low dopant concentrations a large fraction of trivalent europium ions is unexpectedly present in the powders. These trivalent europium ions tend to form defect clusters in the luminescent powders. Furthermore we observe a preferential substitution of the europium ions over the two different substitutional Ca sites, which changes upon increasing the dopant concentration. At high dopant concentration, the powder crystallizes in the monoclinic  $\text{Eu}_2\text{SiS}_4$  structure. Once more a preferential substitution of the europium ions is observed. Summarizing, the influence of the concentration on the emission spectrum is explained by a difference in preferential occupation of the Eu ions in the lattice.

Several results of this campaign were also presented at the XAFS15 conference, Beijing, China