



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: XAS measurements on rare earth doped nanocrystals	Experiment number: 26-01-872
Beamline: BM26A	Date of experiment: from: 08/06/10 to: 11/06/10	Date of report:
Shifts: 9	Local contact(s): Sergey Nikitenko	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

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Report:

The main purpose of the experiment was to investigate the class of rare earth (RE) doped alkaline earth sulfides (CaS:RE , SrS:RE and $\text{Ca}_{(1-x)}\text{Sr}_{(x)}\text{S:RE}$) for different values of x , different dopant concentrations and different dopants (Eu,Ce) prepared using a solvothermal method[1].

Measurements were performed at the RE L_{III} edge in fluorescence mode, using the nine element monolithic Ge-detector as available at BM26A. The samples were kept at 80K, using a cryostat (see Figure 1).

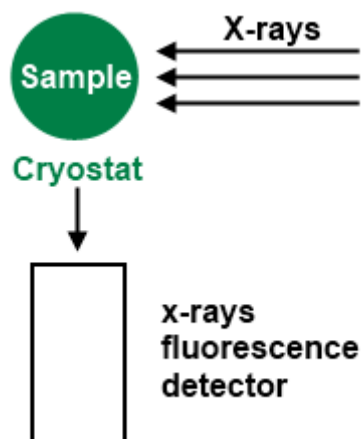


Figure 1: Experimental setup

The solvothermal synthesis technique allows us to produce micron-sized single crystalline sulfide particles at a low synthesis temperature and without the use of H_2S . Previous measurements at the Dubble beamline (26-01-830) indicated the presence of divalent and trivalent Eu in these particles.

We performed a detailed study of this phenomenon by measuring the XAS spectra for SrS:Eu particles with different dopant concentrations (0.25% to 2%), this was motivated by the fact that concentration quenching in SrS occurs already for rather low dopant concentrations (Figure 2).

In Figure 3 the XANES spectra are displayed, showing that trivalent Eu is present in all samples.

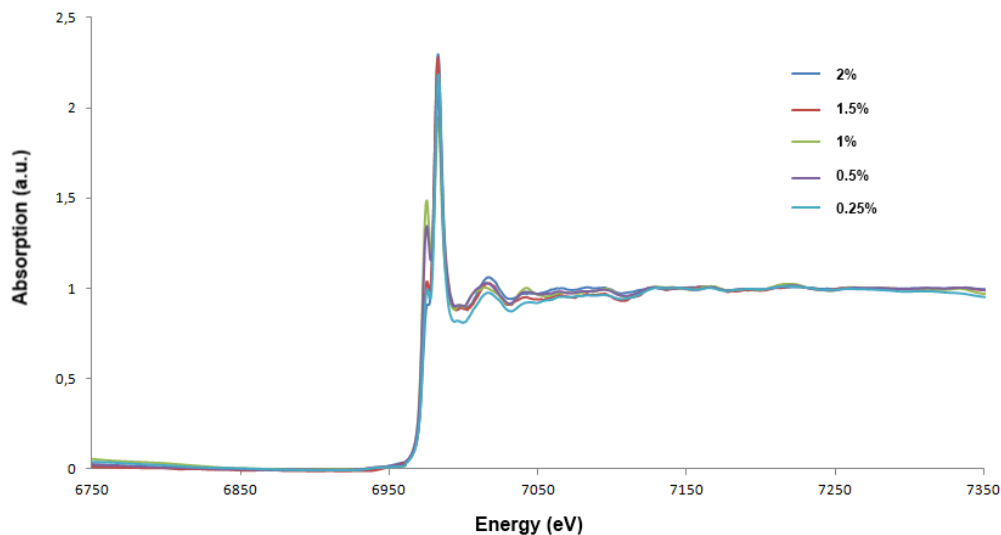


Figure 2: Exafs spectra of $\text{Sr}_{(1-x)}\text{S:Eu}_x$ for different values of x .

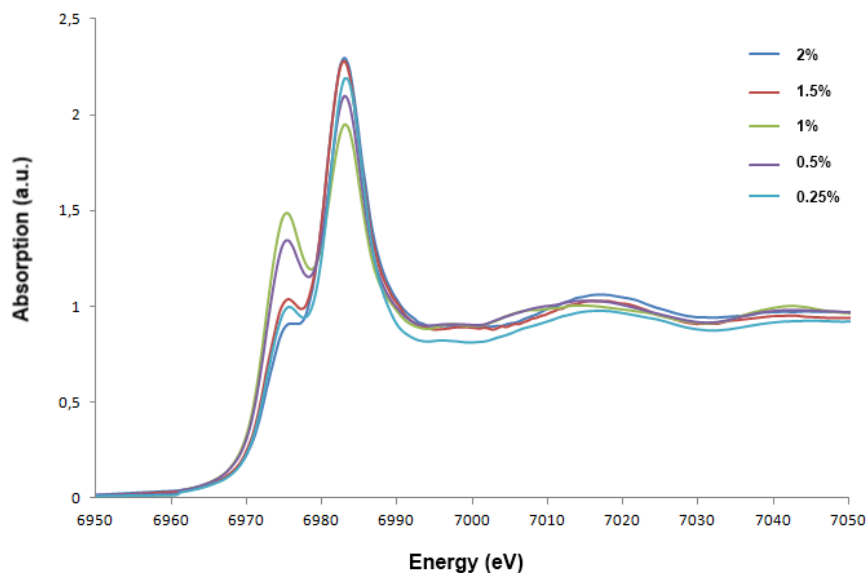


Figure 3: XANES spectra of $\text{Sr}_{(1-x)}\text{S:Eu}_x$

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 4 it is clear that upon increasing the dopant concentration, a higher fraction of trivalent Eu ions is present in the material. The reason for this is not clear yet, but this could be due to the formation of europium clusters within the material. This trivalent Eu can be due to the low synthesis temperature and/or by Eu ions that are not incorporated in the particles, but contaminate their surface. In addition, clustering of Eu ions at higher dopant concentrations is possible [1]

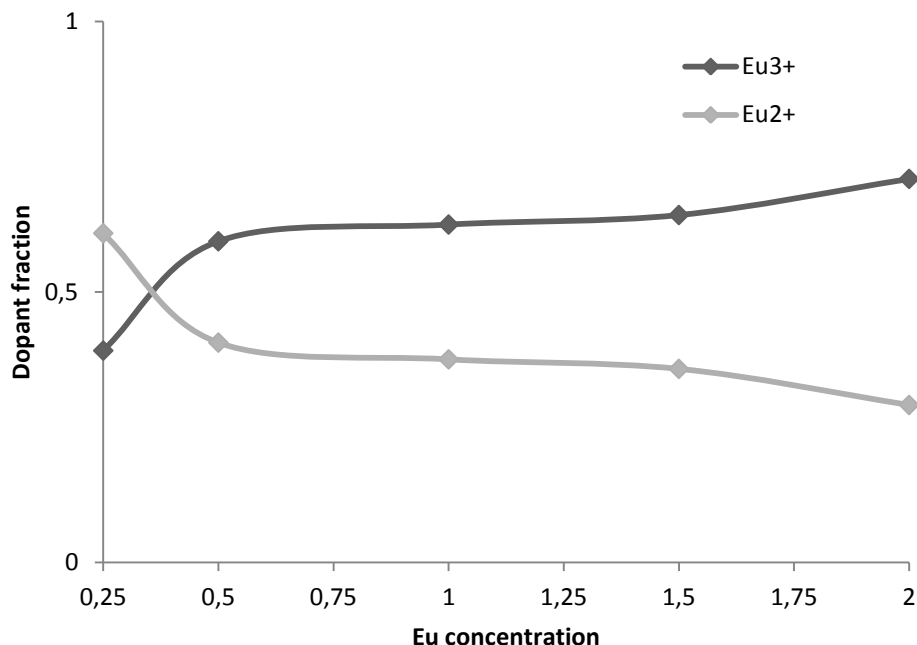


Figure 4: . Fractions of Eu^{3+} and Eu^{2+} contributions to the Eu L_{III} XANES spectra as a function of the Eu concentration

Supplementary measurements were performed on core-shell particles, whereby the doped monocrystalline particles are surrounded by a doped shell [2]. Due to the low dopant concentration and the strong x-ray absorption by the host crystal, measurements were performed only in fluorescence mode. Unfortunately, the signal-to-noise ratio was too small for reliable EXAFS analysis. Only in the XANES region the signal was good enough for analysis.

In Figure 5 the spectra are displayed for $\text{SrS:Eu}(1\%)|\text{SrS:Ce}(1\%)$ core shell particles. As can be seen for the measurements at the Eu L_{III} edge, the Eu ions are mainly in a trivalent state. Surprisingly, the Ce L_{III} edge measurements show an unexpected contribution of tetravalent Ce ions to the signal, which is known to be a luminescence killer.

Follow up measurements should be performed to be able to explain the large Eu^{3+} and/or Ce^{4+} fractions in the samples. Preparation of core|shell particles with a SrS:Eu core and an undoped shell may allow the Eu ions to be all incorporated in the sample, and not present as restfraction. Unfortunately this geometry worsens the data quality, i.e. the x-rays have to penetrate a larger layer of undoped SrS before they can be absorbed by the Eu ions. Since thr SrS host matrix is a strong absorber, the signal-to-noise ratio will diminish.

Preparation of Ca-based core|shell particles may bring a solution, since the CaS host matrix is less absorbing.

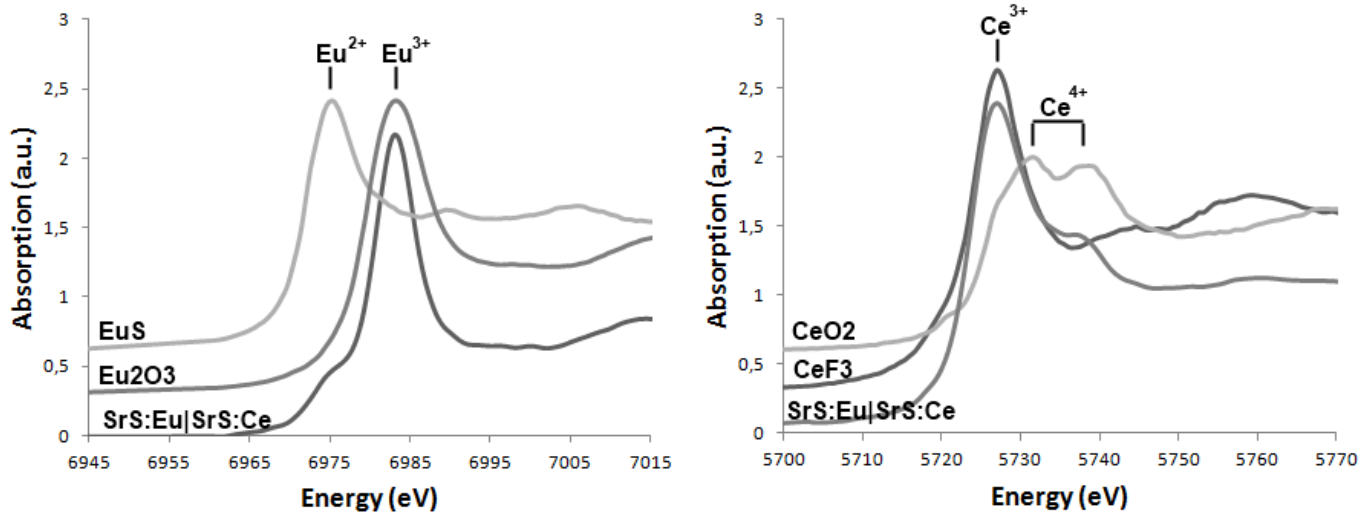


Figure 5: XANES spectra of SrS:Eu/SrS:Ce core shell particles.

Left panel measured at the Eu L_{III} edge, right panel, measured at the Ce L_{III} edge.

References:

- [1] J.E. Van Haecke *et al.*, J.Electrochem. Soc., **154**, J278-J284 (2007)
- [2] K.Korthout *et al.*, Appl. Phys.Lett., **98**, 261919 (2011)