EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

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://wwws.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.

ESRF	**Experiment title:** EXAFS of rare earth doped oxynitride phosphors for lighting applications	**Experiment number**: 26-01-937
Beamline: BM01B	**Date of experiment**: from: 23/08/2011 to: 30/08/2011	**Date of report**:
Shifts: 21	**Local contact(s)**: Hermann Emerich	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

$Ca_3Sc_2Si_3O_{12}:Ce^{3+}$ is an efficient green-emitting colour converter for white LEDs (these powders were prepared at the Hong Kong Baptist University) . Extended x- ray absorption fine structure (EXAFS) was used to probe the environment of the dopant ions in these phosphor materials. Introduction of rare earth ions (Ce^{3+} and/or La^{3+}) in $Ca_3Sc_2Si_3O_{12}$ could in principle lead to the replacement of Ca^{2+} as well as Sc^{3+} ions. Thanks to the EXAFS measurements performed at the SNBL beamline we were able to show that the La^{3+} and Ce^{3+} dopant ions occupy only the Ca sites in $Ca_3Sc_2Si_3O_{12}$.

As mentioned before the rare earth (RE) dopants could in replace the Ca ions as well as the Sc ions:

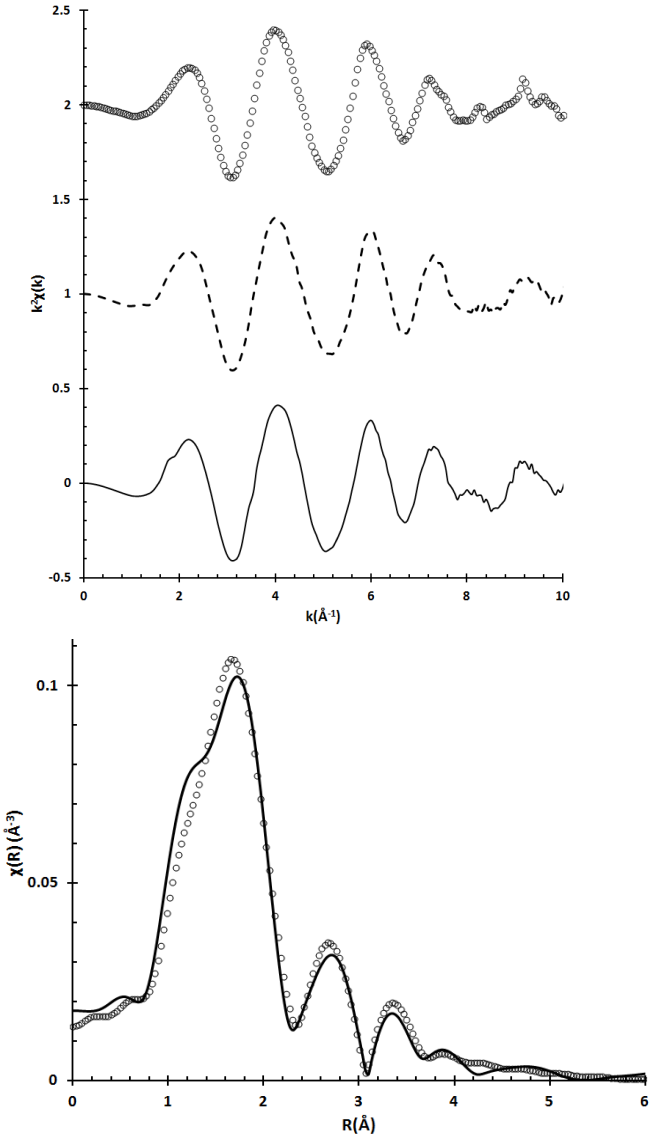
1. The substitution of Ca^{2+} by a RE^{3+} will lead to a charge mismatch, but the ionic radii are similar. The ionic radii of Ce^{3+} (114.3 pm) and La^{3+} (116 pm) in the 8-coordinated Ca site are almost the same as the one of Ca (112 pm).
2. The Sc^{3+} ions have the same charge as the dopant ions, however they have a much smaller ionic radius. The ionic radii of Ce^{3+} (101 pm) and La^{3+} (103.2 pm) are much larger than the one of Sc (74.5 pm) in the 6-coordinated Sc-site.

The EXAFS spectra were collected at the RE K edge, since L_{III} edge spectra provide not enough k space to perform a detailed analysis. The possibility of acquiring these high energies at the SNBL beamline encouraged us to perform these experiments at this beamline. In Figure 1 the K-edge extracted EXAFS spectra are shown.

We performed simulations on the RE K-edge EXAFS spectra, using the two different structural models. By using the Sc site model, we could not reproduce the experimental data, even with strong distortions of the first coordination shells, in contrast to the Ca site model. The simulated Ce K-edge spectra, compared to experimental data, are shown in Figures 1 and 2 (a). In this simulation we used the Ca site model, where the Ce dopant occupies a Ca site.

We used the same model to investigate the site occupancy of the La ions in $Ca_3Sc_2Si_3O_{12}$:Ce,La. The results of the fit can be found in Figure 2 (b). The experimental data are represented nicely by the Ca site model, whereby again a decrease in distance of the oxygen ions and an increase for the positively charged ions is observed.

Summarizing, we were able to conclude that the Ce and La ions occupy the Ca sites in the host crystal. Some structural disorder is observed around the dopant ions, which can be explained by the charge mismatch between Ca and the dopant ions.



Figre 1: (top) K edge extrated EXAFS spectra of La in $Ca_3Sc_2Si_3O_{12}:Ce^{3+}$, La^{3+} (circles), of Ce in $Ca_3Sc_2Si_3O_{12}:Ce^{3+}$, La^{3+}(dashed line) and of Ce in $Ca_3Sc_2Si_3O_{12}:Ce^{3+}$ (solid line). (bottom) Fourier transform of experimental solid line) and simulated (circles) of the Ce K-edge EXAFS spectra on $Ca_3Sc_2Si_3O_{12}:Ce^{3+}$.

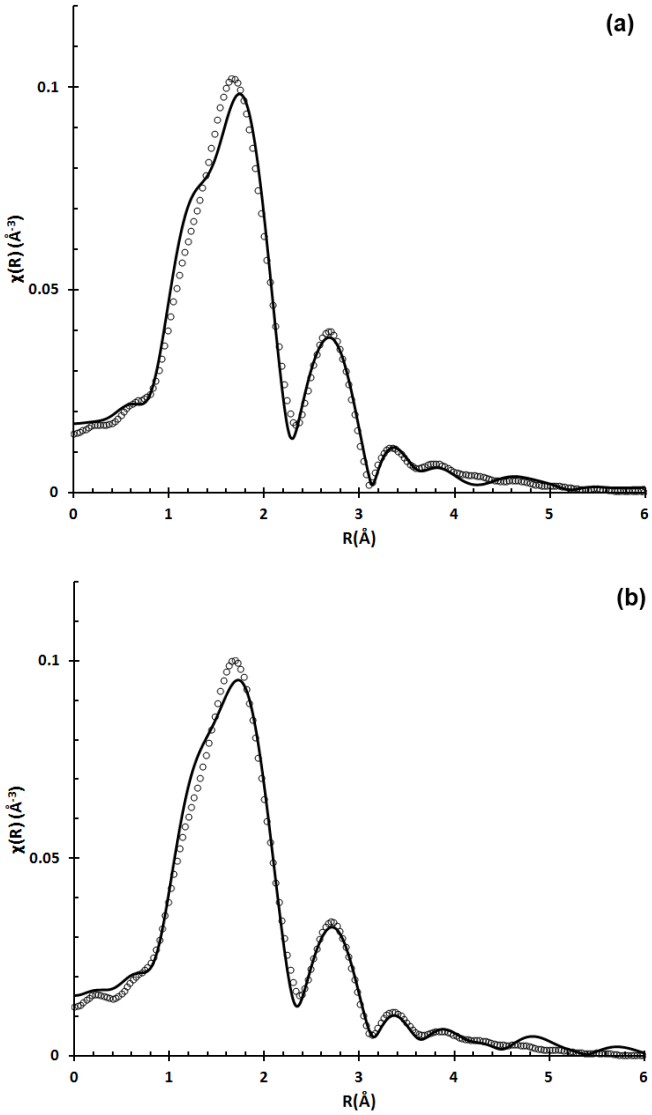


Figure 2: (a) Fourier transform of experimental (solid line) and simulated (circles) of the Ce K-edge EXAFS spectra on $Ca_3Sc_2Si_3O_{12}:Ce^{3+}$, La^{3+}. (b) Fourier transform of experimental (solid line) and simulated (circles) of the La K-edge EXAFS spectra on $Ca_3Sc_2Si_3O_{12}:Ce^{3+}$, La^{3+}.

These results are the subject for a publication in collaboration with Prof. Dr. Kok Wai Cheah, Hong Kong Baptist University.