



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>

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

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.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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 measurement of cerium reduction during calcination of Ce-doped phosphate phases	Experiment number: A20-1-855
Beamline: BM20	Date of experiment: from: 23.06.23 to: 26.06.23	Date of report:
Shifts: 9	Local contact(s): Elena Bazarkina, Kristina Kvashnina	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Theresa Lender*, Institute of Crystallography, RWTH Aachen Julien Marquardt*, Institute of Geosciences, Goethe University of Frankfurt		

Report:

During this beamtime the temperature-dependent change of the oxidation state of Cerium in rhabdophane was analyzed through in-situ measurements. During a previous beamtime in 2022 at beamline BM20 ex-situ measurements were performed at the end products of the reaction, Ce(IV)-doped monazite. These measurements revealed that though the precipitation reaction started with a tetravalent Cerium compound after heating the precipitated rhabdophane to 800 °C most of the Cerium had turned trivalent. Based on these observations, time- and temperature-resolved experiments were planned in order to study the Cerium reduction more closely and possibly conclude ways to increase the tetravalent portion in the final product.

Experiments were performed on 4 compositions of the two solid solutions $\text{La}_{1-x}(\text{Ca,Ce})_x\text{PO}_4$ and $\text{Gd}_{1-x}(\text{Sr,Ce})_x\text{PO}_4$, respectively. These had been precipitated and dried at 50 °C before measurement. Room temperature XANES measurements of the powders were performed before pellet pressing to exclude any effect of the pressing on the oxidation state. Afterwards, pellets of all compositions were pressed, glued to an oven and heated with controlled heating rates. These were varied between 15 °C/min for measurements with a maximum temperature of 800 °C and 1.5 °C/min for measurements with a maximum temperature of 500 °C. Long holding times at high and low temperatures were allowed in some experiment to study the behaviour of the samples at constant temperatures.

While quantification is still in progress, qualitatively the same behaviour has been observed in all samples. Starting from surprisingly Ce(III)-rich precipitates the remaining tetravalent Cerium is reduced rapidly upon heating. As soon as temperatures are decreased again Cerium is oxidized to a degree similar to the Ce(III)/Ce(IV)-ratio observed before the experiment. This behaviour is visualized in figure 1 and was reproducibly observed in all samples.

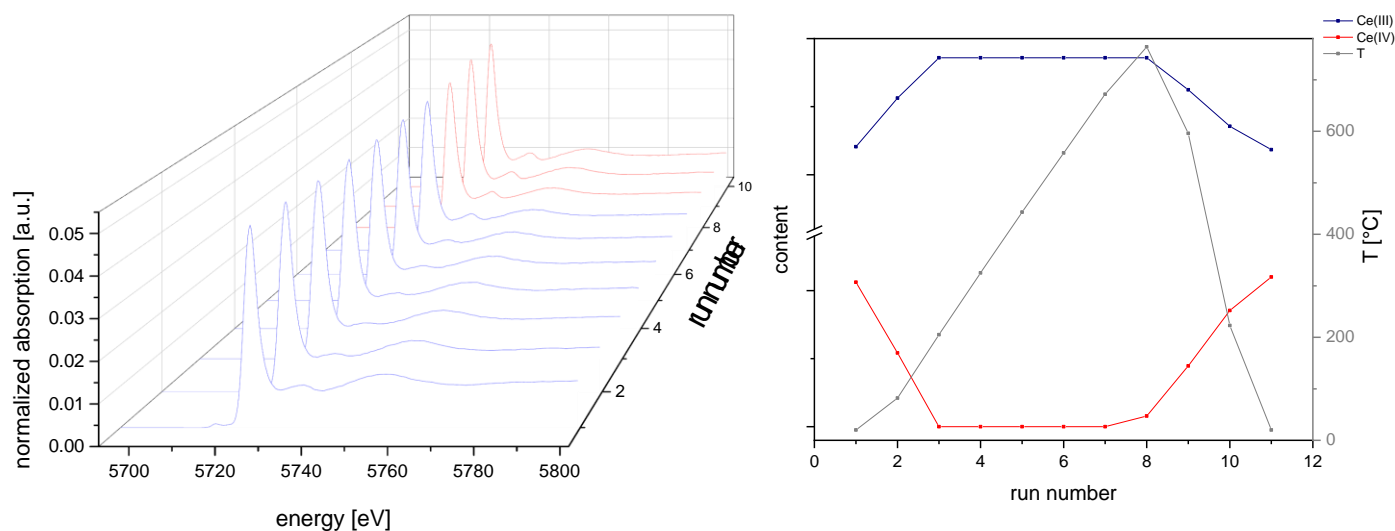


Figure 1: The temperature dependent behaviour of Cerium is very well visible in the post-edge region (left). Upon heating all remaining Ce(IV) is reversibly reduced. The Ce(III)/Ce(IV) ratio before and after the experiment is comparable (right).

Based on experiments with low heating rates the onset temperature for the Cerium reduction could be determined between 100 °C and 150 °C. According to Mesbah *et al.* between room temperature and 150 °C rhabdophane is dehydrated from $\text{LnPO}_4 \cdot 0.667 \text{ H}_2\text{O}$ to $\text{LnPO}_4 \cdot 0.5 \text{ H}_2\text{O}$ (both monoclinic, C2). The remaining water is eliminated below 250 °C leading to a hexagonal anhydrous rhabdophane phase [1]. The dehydration and phase change are reversible [2]. The phase transformation from rhabdophane to monazite between 600 °C and 700 °C [3], however, is irreversible. Powder XRD measurements of the pulverized pellets after the end of the experiments confirm that the phase transition occurred even during short experiments. The driving forces behind the reduction and oxidation of Cerium during heating and cooling have not been established yet.

Overall, the experiments were very successful. This heating setup was used for the first time in combination with the XAS equipment and allowed very good temperature control. It was possible to induce and record changes in the oxidation state of Cerium. The high reproducibility of the observed behaviour is a strong indication that the method works reliably.

[1] Mesbah, A., Clavier, N., Elkaim, E., Szenknect, S., & Dacheux, N. (2017). In pursuit of the rhabdophane crystal structure: from the hydrated monoclinic $\text{LnPO}_4 \cdot 0.667 \text{ H}_2\text{O}$ to the hexagonal LnPO_4 (Ln= Nd, Sm, Gd, Eu and Dy). *Journal of Solid State Chemistry*, 249, 221-227.

[2] Mesbah, A., Clavier, N., Elkaim, E., Gausse, C., Kacem, I. B., Szenknect, S., & Dacheux, N. (2014). Monoclinic form of the rhabdophane compounds: $\text{REEPO}_4 \cdot 0.667 \text{ H}_2\text{O}$. *Crystal growth & design*, 14(10), 5090-5098.

[3] Akers, W. T., Grove, M., Harrison, T. M., & Ryerson, F. J. (1993). The instability of rhabdophane and its unimportance in monazite paragenesis. *Chemical Geology*, 110(1-3), 169-176.