



## 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

- 1<sup>st</sup> March Proposal Round - **5<sup>th</sup> March**
- 10<sup>th</sup> September Proposal Round - **13<sup>th</sup> 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.



	<b>Experiment title:</b> Considering the exsolution process in ceria doped with transition metals - combining experiment with DFT calculations	<b>Experiment number:</b> A08-1-1105
<b>Beamline:</b> LISA	<b>Date of experiment:</b> from: 28.04.2023 to: 02.05.2023	<b>Date of report:</b> 29.07.2023
<b>Shifts:</b> 12	<b>Local contact(s):</b> PURI Alessandro (email: alessandro.puri@esrf.fr)	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): <b>Beata Bochentyn</b> , Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, 80-233 Gdańsk, ul. Narutowicza 11/12, Poland <b>Agnieszka Witkowska</b> , Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, 80-233 Gdańsk, ul. Narutowicza 11/12, Poland		

## Report:

A wide set of ceramic samples has been synthesized via the Pechini method. The following compositions with single metal have been given:

- $\text{Ce}_{0.9}\text{Co}_{0.1}\text{O}_{2-\delta}$
- $\text{Ce}_{0.9}\text{Cu}_{0.1}\text{O}_{2-\delta}$
- $\text{Ce}_{0.9}\text{Fe}_{0.1}\text{O}_{2-\delta}$
- $\text{Ce}_{0.9}\text{Ni}_{0.1}\text{O}_{2-\delta}$
- $\text{Ce}_{0.9}\text{Mn}_{0.1}\text{O}_{2-\delta}$
- $\text{CeO}_{2-\delta}$
- $\text{Ce}_{0.8}\text{Co}_{0.2}\text{O}_{2-\delta}$
- $\text{Ce}_{0.8}\text{Cu}_{0.2}\text{O}_{2-\delta}$
- $\text{Ce}_{0.8}\text{Fe}_{0.2}\text{O}_{2-\delta}$
- $\text{Ce}_{0.8}\text{Ni}_{0.2}\text{O}_{2-\delta}$
- $\text{Ce}_{0.8}\text{Mn}_{0.2}\text{O}_{2-\delta}$

and bimetallic compositions:

- $\text{Ce}_{0.8}\text{Ni}_{0.1}\text{Co}_{0.1}\text{O}_{2-\delta}$
- $\text{Ce}_{0.8}\text{Ni}_{0.1}\text{Cu}_{0.1}\text{O}_{2-\delta}$
- $\text{Ce}_{0.8}\text{Ni}_{0.1}\text{Fe}_{0.1}\text{O}_{2-\delta}$
- $\text{Ce}_{0.8}\text{Co}_{0.1}\text{Fe}_{0.1}\text{O}_{2-\delta}$

The samples were in a powder form in both as-prepared and reduced state. The reduction of as-prepared powders was performed in home laboratory in hydrogen atmosphere for 10h at 900°C, 1000°C and 1100°C.

The measurements at LISA beamline were performed in the transmission and fluorescence modes at 80K (cooled down with liquid nitrogen). The proper weight amount of particular powders was mixed with cellulose and pressed into pellets before the analysis. The measurements were taken at the near-edge and in the extended range spectra (up to 500 eV above the edge energy). The K-edges of transition metals were collected, as well as both CeK and CeL<sub>3</sub> edges were measured for comparison.

The exemplary figures presenting the obtained results are given below:

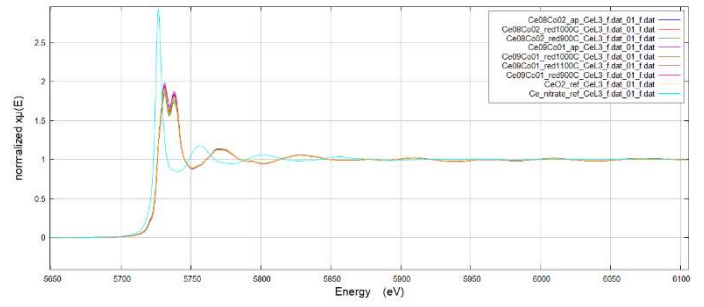
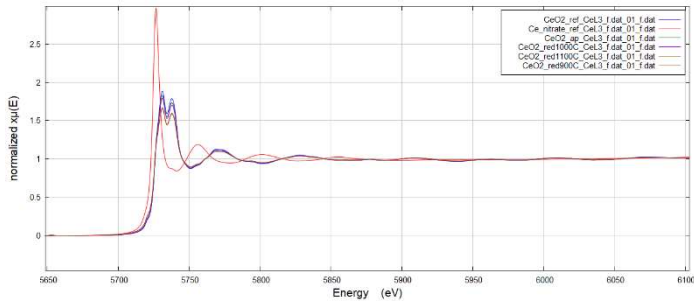


Fig.1: CeL<sub>3</sub>-edge XANES spectra of pure ceria (*left*) and ceria doped with Co (*right*) samples in both as-prepared and reduced states. Also the CeL<sub>3</sub>-edge XANES plot of Ce(NO<sub>3</sub>)<sub>3</sub> is given for comparison.

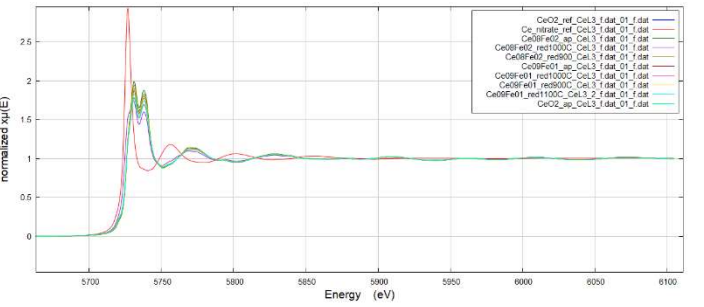
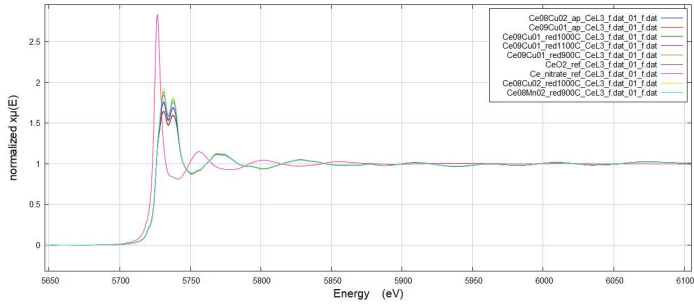


Fig.2: CeL<sub>3</sub>-edge XANES spectra of ceria doped with Cu (*left*) and Fe (*right*) samples in both as-prepared and reduced states. Also the CeL<sub>3</sub>-edge XANES plot of Ce(NO<sub>3</sub>)<sub>3</sub> is given for comparison.

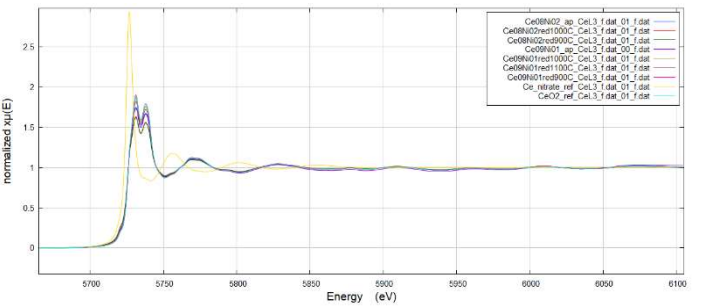
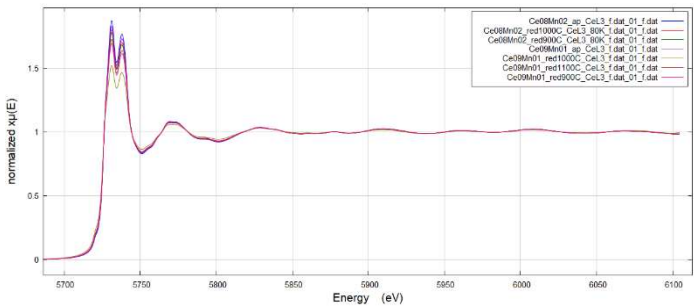


Fig.3: CeL<sub>3</sub>-edge XANES spectra of ceria doped with Mn (*left*) and Ni (*right*) samples in both as-prepared and reduced states. Also the CeL<sub>3</sub>-edge XANES plot of Ce(NO<sub>3</sub>)<sub>3</sub> is given for comparison.

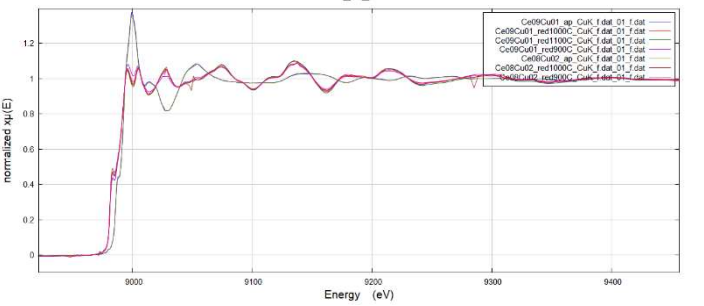
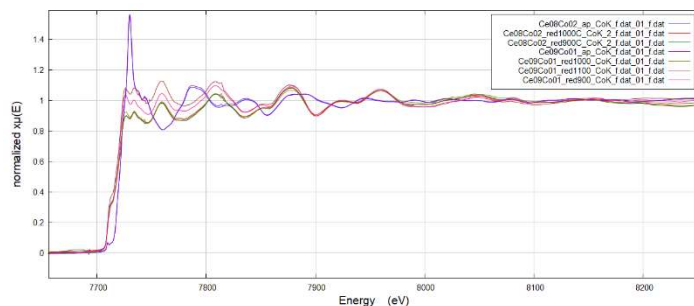


Fig.4: Co K-edge (*left*) and Cu K-edge (*right*) XANES spectra of ceria with Co or Cu dopants in both as-prepared and reduced states (after reduction at 900, 1000 or 1100°C in H<sub>2</sub>).

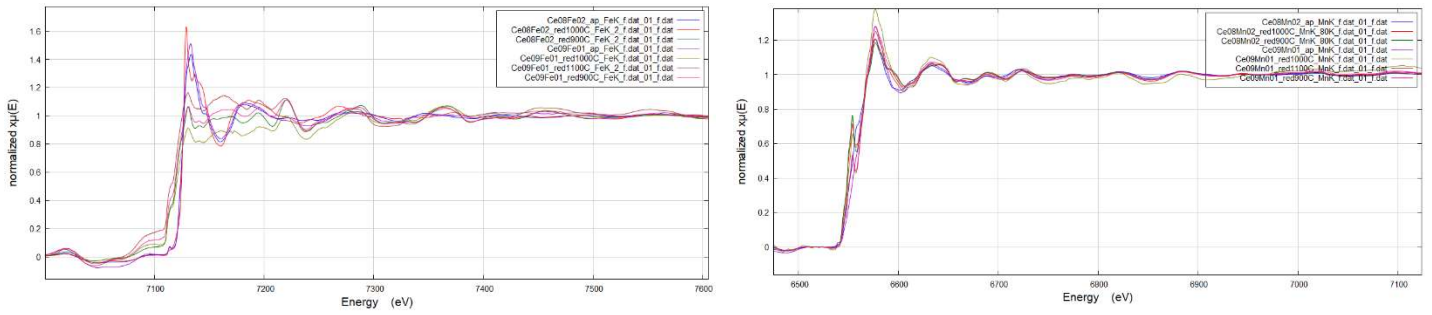


Fig.5: Fe K-edge (*left*) and Mn K-edge (*right*) XANES spectra of ceria with Fe or Mn dopants in both as-prepared and reduced states (after reduction at 900, 1000 or 1100°C in H<sub>2</sub>).

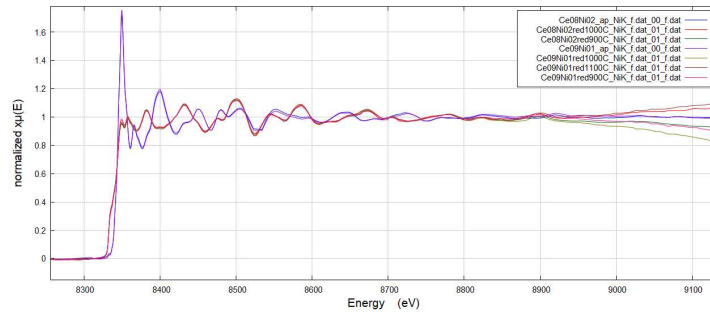


Fig.6: Ni K-edge XANES spectra of ceria with Ni dopant in both as-prepared and reduced states (after reduction at 900, 1000 or 1100°C in H<sub>2</sub>).

The metallic dopants were added to ceria fluorite structure in order to perform the exsolution process of metallic nanoparticles on the surface of the host material in reducing conditions. However, the reducibility of formed compounds strongly depends on both the type and amount of dopants, as well as the temperature of the reduction process.

The CeL<sub>3</sub>-edge XANES spectra of all analyzed samples (Figs 1, 2 and 3) indicate a partial reduction of cerium from Ce<sup>4+</sup> to Ce<sup>3+</sup> oxidation state. However, among them, the Fe-doped samples differ the most significantly from each other and seem to be the most prone to reduction. Particularly the Ce<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>2-δ</sub> compound after reduction at 1000°C in H<sub>2</sub> shows the highest content of Ce<sup>3+</sup>, the same as present in the Ce(NO<sub>3</sub>)<sub>3</sub> reference nitrate. Moreover, the pre-edge behaviour of different Fe-doped compounds allows distinguishing a reduction efficiency depending on the amount of introduced metal as well as the temperature of reduction.

The K-edge XANES spectra of all analyzed samples (Figs 4, 5 and 6) confirm that a high-temperature reduction in hydrogen shifted the edge position towards lower energies than it was observed for as-prepared samples. It's a consequence of a decreased oxidation state of particular metals. The most significant shift was found for Fe-containing samples. Moreover, the XANES spectra of Fe-doped compounds (Fig.5 *left*) are the most differential when compared to the other investigated compounds. It seems that metals other than iron are in a partially reduced state even in as-prepared samples, in order to provide the electroneutrality condition. Thus the edge shift to lower energies after a high-temperature reduction in H<sub>2</sub> is not so significant. In the case of Fe-doped samples iron is sensitive to reduction depending on various factors: local surroundings of aother atoms (composition), temperature, and even time of reduction. Therefore these XANES spectra (Fig.5 *left*) differ the most from each other. The same tendency can be observed in the case of the pre-edge behaviour.