

## 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> <b>HAXPES of ceria redox materials for solar thermochemical H<sub>2</sub>O and CO<sub>2</sub> splitting</b>	<b>Experiment number:</b> <b>HC-1165</b>
<b>Beamline:</b>	<b>Date of experiment:</b> from: 02 July 2014 at 08:00 to: 08 July 2014 at 08:00	<b>Date of report:</b> 28.08.2014
<b>Shifts:</b> 18	<b>Local contact(s):</b> Dr. Juan Rubio-Zuazo and Dr. German Castro	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> <b>Matthäus Rothensteiner* ETH Zurich/ Paul Scherrer Institut</b> <b>Simone Sala* Paul Scherrer Institut</b> <b>Alexander H. Bork* ETH Zurich</b> <b>Christian Proff Paul Scherrer Institut</b> <b>Jeroen Anton van Bokhoven ETH Zürich/Paul Scherrer Institut</b>		

## Report:

### 1) Technical problems

A significant amount of beam time could not be used because of technical problems: Due to a short circuit in the heating system, the UHV chamber had to be vented on Wed 02 07 2014. Repair work and pumping the analyzer chamber to sufficient vacuum conditions took at least until Thu 03 07 2014 19:00, but even after that sparks were frequently disturbing data acquisition.

### 2) Sample preparation and mounting



Figure 1

Three different ceria-based materials and a perovskite were investigated before and after thermal reduction. 6 pellets (2 in each run) were introduced into the analyser chamber:

sample 'ceria' was synthesized using a polymerized complex method. A pellet (38 mg, 5mm diameter, pressed at 1 ton) was prepared and exposed to several thermochemical H<sub>2</sub>O splitting redox cycles in our laboratory setup. 2. sample ceriaHf10 was synthesized via Pecchini type route by cooperation partners at EMPA. A pellet 38 mg, diameter 5mm, 1 ton) was prepared and exposed to several thermochemical H<sub>2</sub>O splitting redox cycles in our laboratory setup. 3. Hf01 was prepared using a polymerized complex method (same as sample ceria). ca. 120 mg of the powder were pressed into a pellet (13 mm diameter, 3 tons) and sintered on a zirconia crucible by ramping to 1300 °C in air and keeping the temperature constant for 3 hours. Pellets had a distorted, curved geometry after the heat treatment. 4. Hf01b was prepared in the same way as Hf01. 5. perovskite La 0.6 Sr 0.4 Cr 0.8 Co 0.2 O 3 was prepared via a Pecchini synthesis. The preparation of pellets was performed in the same way for samples Hf01, Hf01b and perovskite samples.

### 3) Heating – in situ thermal reduction

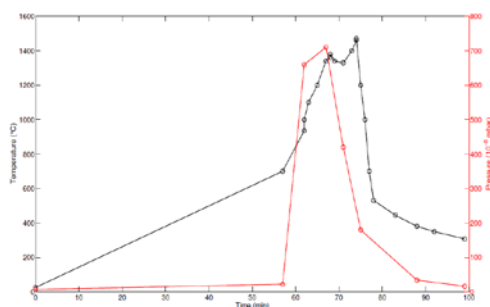


Figure 2  $T$  and  $p$  during reduction.

### 4) Results and discussion

XPS 12 keV; Ce2p<sub>3/2</sub> (Figure 4), Ce3p<sub>3/2</sub> and Ce3d (Figure 5) spectra were recorded before and after thermal reduction.

XPS 9 keV: Due to bad S/N ratio, measurements at 9 keV were not successful.

1.2536 keV (Mg X-ray tube): Ce3d spectra (Figure 5) of the reduced samples were taken.

XRD: Simultaneously to XPS at 12 keV photon energy, XRD measurements were performed by scanning the range  $8 \leq 2\theta \leq 40$  in 1600 steps and a dwell time of 2 s. Figure 3 shows XRD patterns of sample ceriaHf01 recorded before and after thermal reduction, the Mo sample holder as well as reference patterns (bottom). Figure 7 shows that thermal reduction leads to new peaks in the perovskite sample.

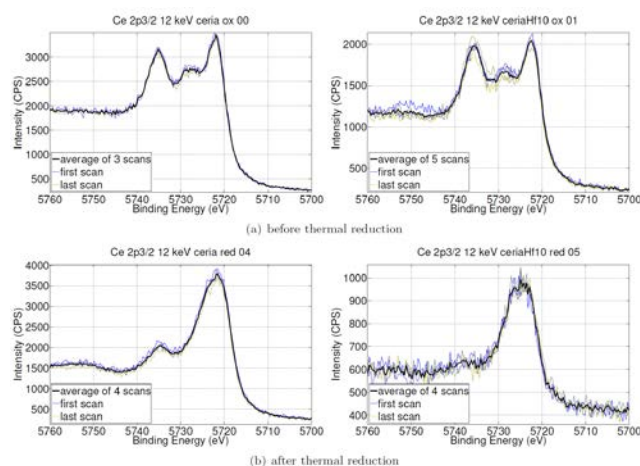


Figure 5

### 5) Conclusions

Photoemission spectra of Ce 2p<sub>3/2</sub>, Ce3p<sub>3/2</sub> and Ce3d were successfully recorded at 12 keV and 1.2536 keV before and after thermal reduction at high temperature (1470 °C and 1200 °C). Spectra show differences when both recorded different photon energies (12 and 1.2536 keV) as well as before and after thermal reduction. A more detailed analysis is hampered by the high noise level and the incompleteness of the dataset due to technical problems.

### 6) Strategies for improving the experiment

We propose the following strategies to improve the S/N ratio and reduce charging effects:

- improve sample holder geometry to improve contact pellet-sample holder to reduce charging effects and keep the sample from falling from the sample holder in case it breaks due to thermal stress during fast heating and cooling. This

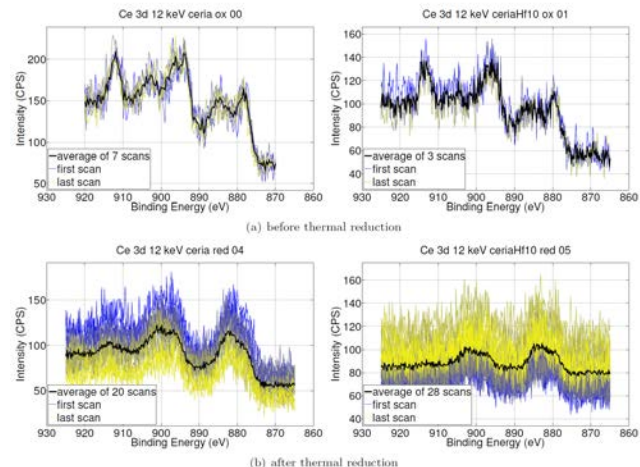


Figure 5

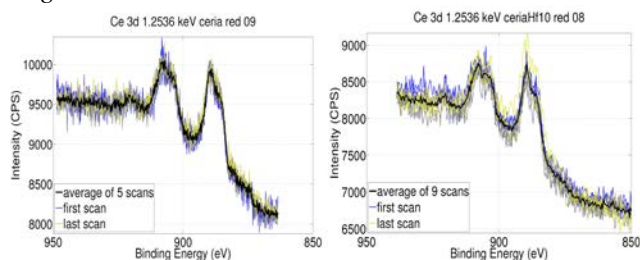


Figure 5

could be done by using two layers of Mo sheets with differently sized bores for the samples or a Mo mesh.

- improve sample geometry and surface of pellet - make flat pellets and reduce surface roughness
- find optimal temperature for reduction - in UHV lower T are sufficient for reaching the desired non-stoichiometry  $\delta$  and avoid total reduction to  $\text{Ce}_2\text{O}_3$  and phase changes or decomposition.
- reduce the number of time consuming sample changes by mounting up to 4 samples with a custom-made sample-holder.
- clean the surface by heating to moderate temperatures (ca. 400 °C) before measuring samples in the oxidised state.

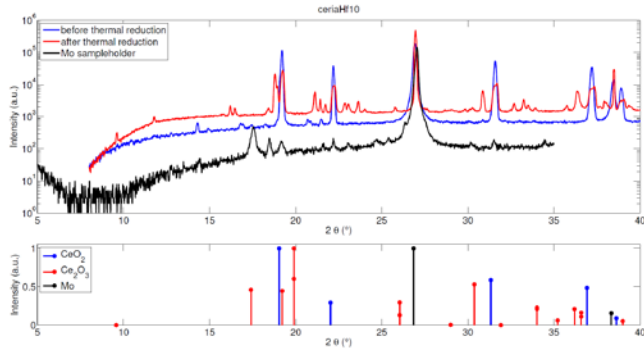


Figure 7

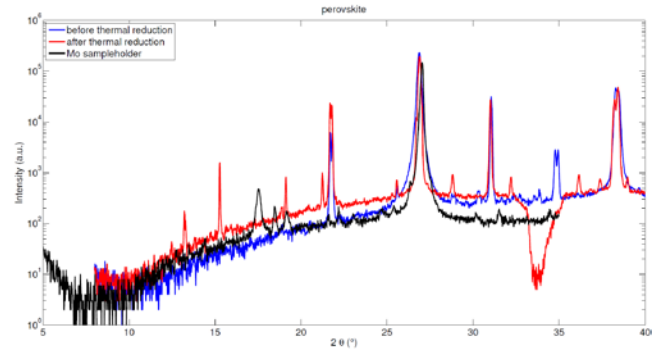


Figure 7