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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 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.

ESRF	**Experiment title:** Anomalous Ce K-edge differential PDF study to investigate the short and medium range environment of Ce in Y-doped Ce1-xYxO2-x/2 oxides	**Experiment number**: CH-3250
Beamline: ID31	**Date of experiment**: from: 03.11.2010 to: 09.11.2010	**Date of report**: 30.04.11
Shifts: 15	**Local contact(s)**: Dr. Andy Fitch	*Received at ESRF:*

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Report:

Yttrium doped ceria oxides ($Ce_{1-x}Y_xO_{2-x/2}$, CYO) have been intensively studied in the last years since they find application in Solid Oxide Fuel Cells. Aim of the experiment was to determine the local and medium range structure of CYO as a function of the doping concentration *x*. Seven samples (x=0,0.125, 0.250, 0.500, 0.750, 0.875,1) were measured at 90 K at λ_1=0.3099 Å and some of them (x=0.25, 0.50, 0.75) were measured also at λ_2=0.3070 Å. Data were collected at two different wavelengths just below the Ce-K absorption edge in order to get the so-called Differential Pair Distribution Function, which in principle highlights only the contribution of Ce to the experimental PDF. PDF quality data were obtained after summing several scans for about 8-10 hours of total counting time, reaching a Q_{max} value of ~ 28.5 $Å^{-1}$.

The effect of doping on the *average* structure (i.e. on space group, *mean* atomic positions and atomic mean square displacements) was analyzed using the conventional Rietveld analysis while Pair Distribution Function (PDF) Technique was also used to explore structural distortions as well as the spatial extent of disorder in the real space. The reciprocal space analysis has been performed using the software GSAS **[1]** and its graphic interface EXPGUI **[2]**. It shows that the *average* structure is fluoritic (space group F*m*-3*m*) for $x \leq 0.25$ and C-type (space group I*a*-3) for $x \geq 0.50$. Moreover, the increase of the mean square atomic displacements (*msd*) as a function of the doping concentration clearly indicates the occurrence of disorder. In the C-type part of the solid solution, the low symmetry allows for the use of anisotropic *msd*s at least for cation sites: As an example in figure 1a the ellipsoids related to the anisotropic *msd*s indicate that the disorder is strongly localized. The local environment of the two different cation sites (labeled as M1 and M2) is shown in figures 1b and 1c. The real space analysis has been performed with the software PDFGetX2 **[3]** and PDFGUI **[4]**. The high total counting time allows for a sufficiently high signal to noise ratio at high angle, thus reducing the amplitude of noise in the real space. The F(Q) function for the sample x=0.25 obtained at λ_1 is shown in figure 2a.

Due to its noticeable Q resolution, ID31 is the ideal beamline to study both the local and the mesoscopic scale. For all the measured samples the real space long range structure is in keeping with the average

crystallographic model. However, considering the local structure (i.e. r < ~10 Å), this is true only for the end-members(CeO_2 and Y_2O_3). Indeed the local structure obtained through the PDF analysis is not consistent with the average crystallographic model and has been interpreted using a "biphasic model", i.e. supposing the formation of Y_2O_3-rich droplets embedded in a fluoritic CeO_2 matrix, or vice versa, depending on the overall composition.

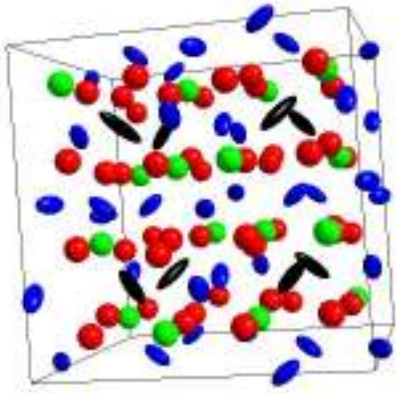

Figure**1**a. Ellipsoids for x(Y)=0.75. Black: M1; blue: M2, red: O1, green: O2.

Figure**1**b. Coordination of M1 site. Black: M1; red: O1, green: O2.

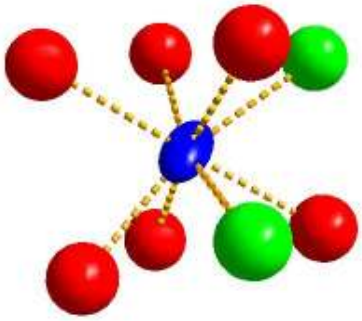

Figure**1**c. Coordination of M1 site. Blue: M2; red: O1, green: O2.

In figure 2b the local range refinement for the sample x=0.25 is shown: On the left is the fit obtained using a biphasic model, while on the right just the average model is applied.

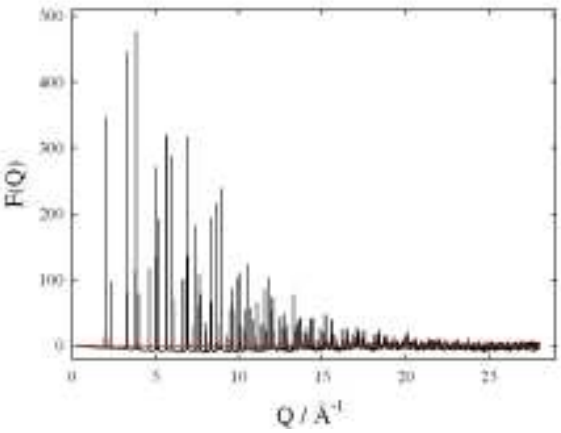

Figure2a. F(Q) function for the composition x=0.25

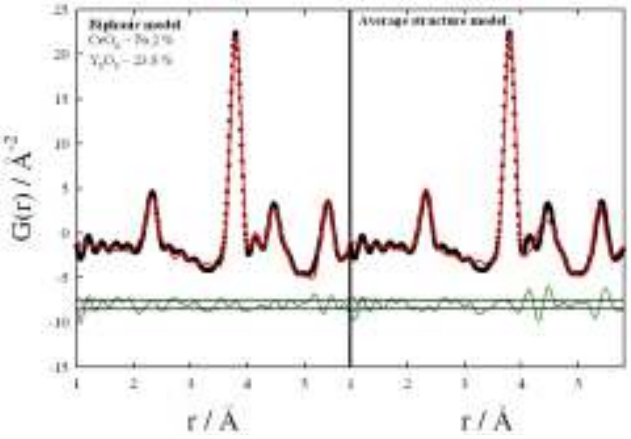

Figure2b. Average (right) and biphasic model (left) in red, experimental data in black, difference in green.

The same model apply for the other Yttrium compositions.
This experiment was also aimed to obtain the Ce - Differential Pair Distribution Function in order to define to which atom pair every real space peak is referred. This part of the work is still in progress since a strong fluorescence contribution is observed at high Q at λ_2, which make difficult the comparison between the two data sets.

REFERENCES

[1] Larson, A. C.; Von Dreele, R. B. *General Structural Analysis System (GSAS)*; Los Alamos National Laboratory Report LAUR 86-748; Los Alamos National Laboratory, 2004.
[2] Toby, B. H. *J. Appl. Crystallogr.* **2001**, *34*, 210–214.
[3] X. Qiu *et Al.*, *J. Appl. Cryst.* (2004), **37**, 678–678.
[4] C. L. Farrow *et Al.*, *J. Phys.: Condens. Matter* **19** (2007) 335219.