



## 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.



	<b>Experiment title:</b> <b>Cerium short and medium range environment in <math>Ce_{1-x}Gd_xO_{2-x/2}</math> oxides by means of differential pair distribution function obtained at the Ce-K edge</b>	<b>Experiment number:</b> CH-2907
<b>Beamline:</b> ID31	<b>Date of experiment:</b> from: 22.04.2009 to: 28.04.2009	<b>Date of report:</b> 01.09.09
<b>Shifts:</b> 18	<b>Local contact(s):</b> Dr. Andy Fitch	<i>Received at ESRF:</i>

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**Report:**

Gadolinium doped  $CeO_2$  materials ( $Ce_{1-x}Gd_xO_{2-x/2}$ , hereafter CGO) have been intensively studied in the last years as conducting electrolytes for electrochemical cells. In fact, CGO, solid electrolytes display an ion conductivity higher than conventional Ytria-Stabilized-Zirconia-based ones and would be able to operate at lower temperatures (500 - 700°C) [1]. Aim of the experiment was to determine the local and medium range structure of CGO as a function of  $x$ , which in turn is strictly related to the mechanism of ionic conductivity.

Micro-crystalline  $Ce_{1-x}Gd_xO_{2-x/2}$  samples with different Gd concentrations:  $x = 0, 0.125, 0.25, 0.50, 0.75, 0.875, 1.00$  have been prepared with Pechini sol-gel method and fired for 72 hours at 900°C.

Experimental  $G(r)$  have been obtained from XRPD data collected at  $\lambda_1=0.30975(1) \text{ \AA}$  (all the samples), and  $\lambda_2=0.30760(1) \text{ \AA}$ ; ( $x = 0.25, 0.50, 0.75$ ) at  $T = 90K$ , with a  $Q_{max} \sim 30 \text{ \AA}^{-1}$ . We collected experimental data at two wavelengths close to the Ce-K edge energy in order to obtain the so-called Differential Pair Distribution function [D- $G(r)$ ], in order to highlight the Ce contribution to the  $G(r)$ .

Data reduction have been carried on using PDFGetX2 software [2]. The  $G(r)$  data have been fitted using a so called *Real Space Rietveld analysis* applying symmetry constrains and varying cell parameters, atomic positions, thermal parameters [3].

For  $r > 12 \text{ \AA}$  the long range structural models obtained by the Rietveld analysis always fit well the experimental  $G(r)$  functions. In particular for  $x \leq 0.25$  the system belongs to a fluoritic phase (space group  $Fm-3m$ ) while for  $x \geq 0.50$  the structure is well described by a cubic C-type phase (space group  $Ia-3$ ) [4]. The agreement factors ( $R_w$ ) are in the 0.07-0.13 range.

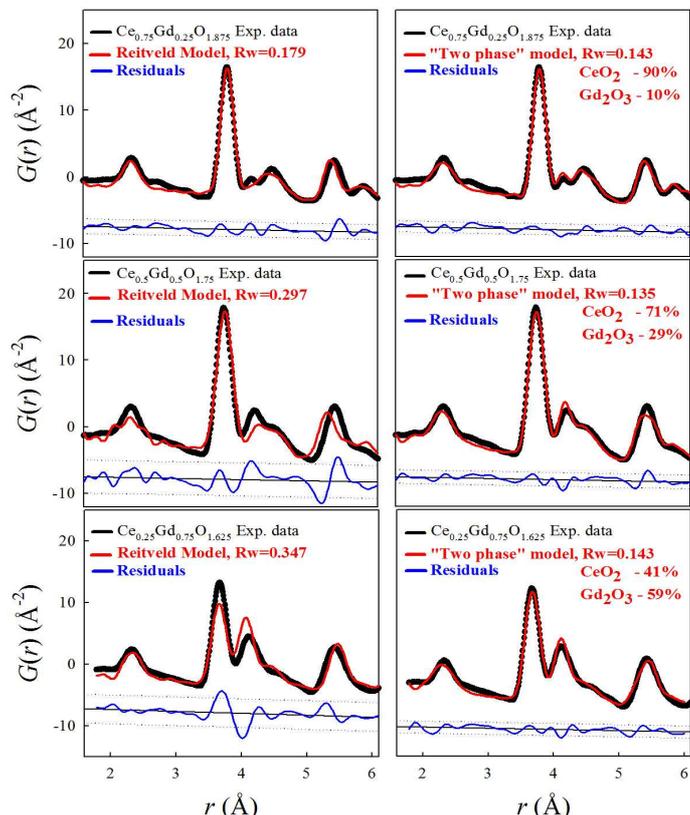
The same is obtained even at very low  $r$  for pure  $CeO_2$  and  $Gd_2O_3$  oxides. Conversely, for short interatomic distances ( $r < 12 \text{ \AA}$ ) the same structural models seems to be inadequate for all the intermediate compositions.

Attempts to fit the short range data supposing either random distribution or clustering of Ce/Gd ions did not bring to satisfying results.

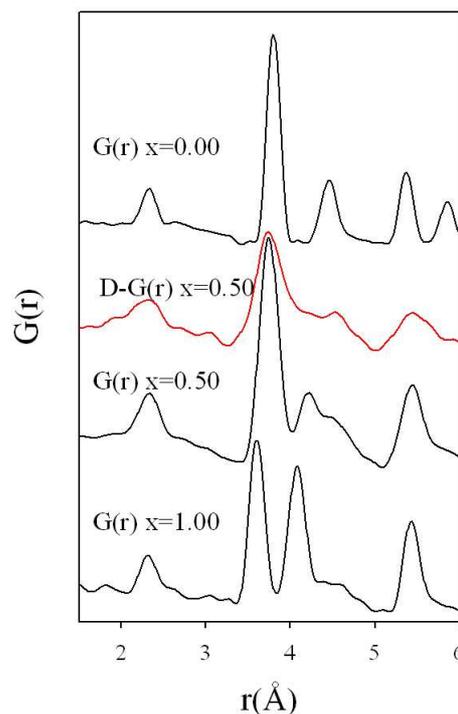
A net improvement of the fit was obtained only using a “two phases” model. This has been calculated taking into account the cubic phase of pure  $\text{CeO}_2$  and  $\text{Gd}_2\text{O}_3$ . Results from the model calculations together with the refined relative fractions (%) of the two nanoscale ‘phases’ are shown in Figure 1.

It should be noted that the relative fractions of Ce-rich (fluoritic) and Gd-rich (C-type) phases in the mixed crystals are not exactly what one would expect for completely segregated materials of the same chemical composition. This may be an indication of a partial mixing of Gd and Ce atomic species [5].

Considering the  $R_w$  values, a large improvement to the fit is obtained with the “two-phases” model. The system can be then described by an inhomogeneous mixture of  $\text{CeO}_2$  rich and  $\text{Gd}_2\text{O}_3$  rich phases, with a length of structural coherence limited to  $\sim 6\text{-}10\text{\AA}$ .



**Figure 1:** Experimental  $G(r)$  functions (black circles). Red lines represent the calculated  $G(r)$  using the long range structural models (left) and the “two phases” model.



**Figure 2:** Experimental  $G(r)$  functions of  $x=0, 0.50, 1$  samples (black lines). The  $D-G(r)$  relative to the  $x=0.50$  sample is also shown (red line).

Further insight can be obtained by the analysis of the Differential  $G(r)$  functions. In Figure 2 is shown the  $D-G(r)$  relative to the  $x=0.50$  sample (red line). For sake of comparison also the  $G(r)$  relative to the same sample and to pure  $\text{CeO}_2$  and  $\text{Gd}_2\text{O}_3$ , obtained at  $\lambda_1$  are also shown. Although the long range structure of the  $x=0.50$  sample is C-type (like  $\text{Gd}_2\text{O}_3$ ), the short range  $D-G(r)$  is strictly related to the  $G(r)$  function relative to  $\text{CeO}_2$  (if we neglect the broadening effect caused by the extraction of  $D-G(r)$ ). This seems to support the idea of the two-phase model described above. However we must underline that the analysis of the  $D-G(r)$  data is still in progress.

Since the CGO materials used for the electrochemical cells have fluoritic structure ( $x < 0.25$ ) it seems to be crucial to perform a Differential Pair Distribution Function experiment also at the Gd-K edge in order to highlight the Gd contribution to the  $G(r)$  and verify the presence of C-type subnanometric  $\text{Gd}_2\text{O}_3$  droplets within the Cerium rich  $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-x/2}$  fluoritic solid solution.

## References

- [1] J. Goodenough, *Ann. Rev. of Material Res.* **33** (2003) 91.
- [2] X. Qiu *et Al.*, *J. Appl. Cryst.* (2004), **37**, 678–678.
- [3] C. L. Farrow *et Al.*, *J. Phys.: Condens. Matter* **19** (2007) 335219.
- [4] V. Grover, *et Al.*, *J. Appl. Cryst.* **36** (2003) 1082.
- [5] M. Gateshki *et Al.*, *J. Phys.: Condens. Matter* **19** (2007) 156205.