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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

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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

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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;
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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:** Gd K-edge differential PDF study to unveil the short and medium range environment of Gd in Ce1-xGdxO2-x/2 oxides	**Experiment number**: CH-3148
Beamline: ID31	**Date of experiment**: from: 14.04.2010 to: 20.10.2010	**Date of report**: 30.04.11
Shifts: 18	**Local contact(s)**: Caroline Curfs	*Received at ESRF:*

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Report:

Gadolinium doped ceria oxides ($Ce_{1-x}Gd_xO_{2-x/2}$, CGO) 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 CGO by means of anomalous PDF. Seven samples (x=0, 0.125, 0.250, 0.500, 0.750, 0.875, 1) were measured at 90 K at λ_1=0.2496 Å and some of them (x=0.25, 0.50, 0.75) were measured also at λ_2=0.2475 Å. We collected data at two different wavelengths just below the Gd-K absorption edge in order to obtain the so-called Differential Pair Distribution Function, which in principle highlights only the contribution of Gd to the experimental PDF.

PDF quality data were obtained after summing several scans for about 8-10 hours of total counting time, reaching a Qmax value of ~ 30 $Å^{-1}$.

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]**, while for the real space analysis PDFGetX2**[3]** and PDFGUI**[4]** were used.

In figure 1 the mean square atomic displacements (*msd*) as a function of the doping concentration are shown, which clearly indicate the occurrence of disorder.

In order to deepen the description of such disorder, the local structure has been studied by means of PDF. The observed G(*r*) functions are shown in figure 2a. The real space peaks have been fitted using normalized gaussian functions and the corresponding metal-metal interatomic distances are reported in figure 2b.

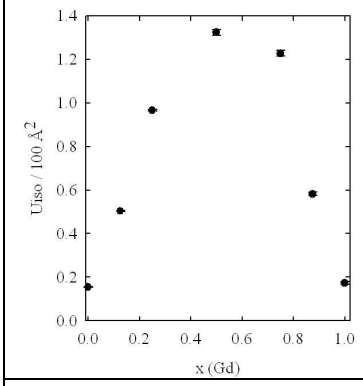

Figure1. Mean square displacements in doped ceria samples as a function of *x* concentration.

The same distances obtained through the reciprocal space analysis are also plotted in the same figure. Some important differences can be noted. According to the reciprocal space analysis the fluoritic structure shows one Ce/Gd-Ce/Gd distance whereas in the C-type structure one set of "long" and "short" distances are present. By comparing the values obtained in both spaces it should be noted that the Ce/Gd-Ce/Gd distance in the fluoritic structure decreases by enhancing the doping concentration. Moreover the "long" distances values in the C-type structure obtained from the $G(r)$ functions are clearly overestimated with respect to the reciprocal space analysis. These distances increase as a function of the cerium concentration x and, in contrast with the reciprocal space insights, they are present even when the structure is long range fluoritic. This disagreement between the short range and the long range structure gives evidence about the presence of some kind of disorder on the nanoscale: The local structure obtained through the PDF analysis is not consistent with the average crystallographic model (F*m*-3*m* for $x<0.5$ and I*a*-3 for $x\geq0.5$) and has been interpreted using a "biphasic model", i.e. supposing the formation of Gd_2O_3-rich droplets extending about 10 Å embedded in a fluoritic CeO_2 matrix, or vice versa, depending on the overall composition.

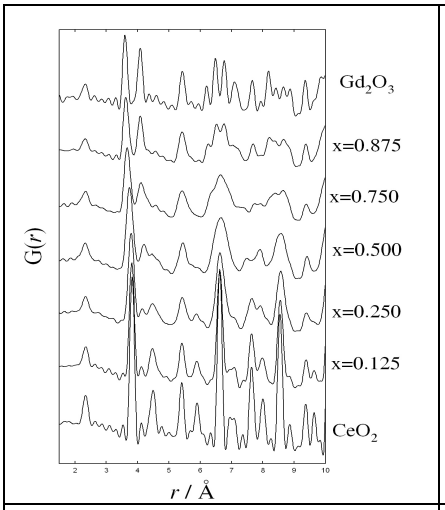

Figure2a. Observer PDF functions.

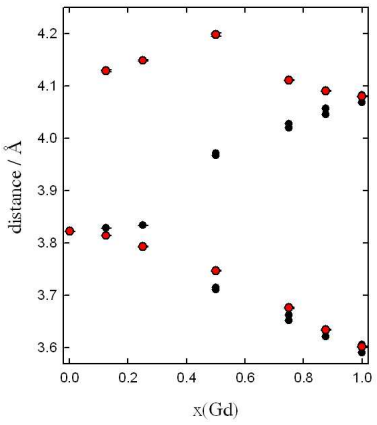

Figure2b. Metal-metal interatomic distances as determined by Rietveld (black circles) and PDF (red circles).

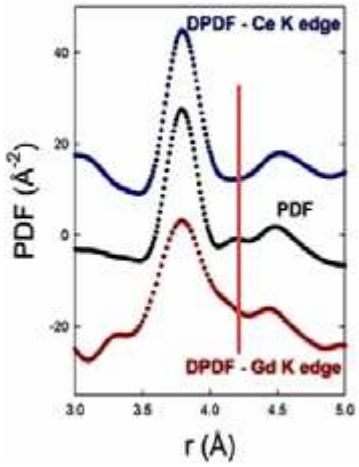

Figure2c. Experimental PDF (black), Ce-DPDF (blue) and Gd-DPDF (red) for the x=0.25 composition

In order to support the idea that Ce and Gd ions retain their local environment, a differential Pair Distribution Function study has been performed. The method to obtain has been reported in **[5]**.

In figure2c the experimental PDF for the composition x=0.25 is compared to the Gd - DPDF (red) and the Ce - DPDF (blue). A hump at about 4.1 is present only in Gd - DPDF: this suggests that only Gd cations contribute to the corresponding PDF peak.

In order to compare all the samples and to avoid a poor signal to noise ratio, the DPDF have been calculated by considering data collected up to a Qmax =24 A^{-1}.

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.

[5] M. Allieta *et Al., Zeitschrift für Kristallographie*, in press