

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.



	Experiment title: Sm K-edge differential PDF study to unveil the short and medium range environment of Sm in Ce _{1-x} Sm _x O _{2-x/2} oxides	Experiment number: CH-3251
Beamline: ID31	Date of experiment: from: 10.11.2010 to: 15.11.2010	Date of report: 30.04.11
Shifts: 15	Local contact(s): Dr. Andy Fitch	<i>Received at ESRF:</i>
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Report:

Samarium doped ceria oxides (Ce_{1-x}Sm_xO_{2-x/2}, CSO) 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 CSO as a function of the doping concentration x .

Data were collected at 90K at two different wavelengths just below the Ce-K absorption edge ($\lambda_1 = 0.3099 \text{ \AA}$, and at $\lambda_2 = 0.3070 \text{ \AA}$) to obtain the so-called Differential Pair Distribution Function, which highlights the contribution of Ce to the experimental PDF. Data at $\lambda_1 = 0.3099 \text{ \AA}$ have been collected on samples of composition $x=n/16$, where $n=0-16$, while data at λ_2 have been collected on samples with $n=4,8$ and 12 .

The effect of doping on the *average* structure (i.e. on space group, *mean* atomic positions and atomic mean square displacements) has been determined using the conventional reciprocal space Rietveld analysis, while the Pair Distribution Function (PDF) Technique was used to explore structural distortions as well as the spatial extent of disorder in the real space.

Cerium oxide belongs to the fluoritic structure (space group $Fm-3m$) and is characterized by two wickoff positions (Ce, 4a, 0, 0, 0 and O, 8c, 0.25, 0.25, 0.25); while the C-type structure (space group $Ia-3$) is the stable form of the Sm sesquioxide at room temperature and is composed of 3 non equivalent positions: M1 (8b, 0.25, 0.25, 0.25); M2 (24d, x , 0, 0.25); O (48e, x , y , z). When Ce⁺⁴ ions enter the structure of a sesquioxide, oxygen is introduced in the 16c (x , x , x) site [1]. The whole solid solution compositional range has been investigated since there are contradictions among the literature reports regarding the miscibility gap between fluoritic and C-type structure[2, 3], as well as the structure of the high x compositions[2, 3]. Indeed samarium oxide (Sm₂O₃) undergoes an irreversible transition from the C-type to the B-type monoclinic phase (lower symmetry, higher density) when heated up to about 800°C [4], the opposite that one could expect by increasing temperature.

In Figure 1 are reported the lattice parameters as a function of x Sm content in Ce_{1-x}Sm_xO_{2-x/2}. The dashed lines represent the x dependence of lattice parameter expected according to the Vegard's law. Three regions in the whole x range can be clearly appreciated. However for $x > \sim 0.3$ and $x < \sim 0.5$ composition the Vegard's law

for the fluoritic and the C-type structures is not obeyed. At higher x the lattice parameter reaches a plateau (green dashed line), giving evidence of a Sm solubility limit in the C-type structure. In Figure 2 the fractional coordinate values related to the cation site (M2) in the C-type structure as a function of x are reported. As shown for the regression line in Figure 2, a linear trend is obtained, indicating a solubility of Sm^{3+} in the C-type structure even at high doping concentration. This behavior is in contrast with the lattice parameter evolution (see Figure 1) and it suggests that a complex mechanism has to be considered to describe the solubility of Sm^{3+} in the $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-x/2}$ solid solution.

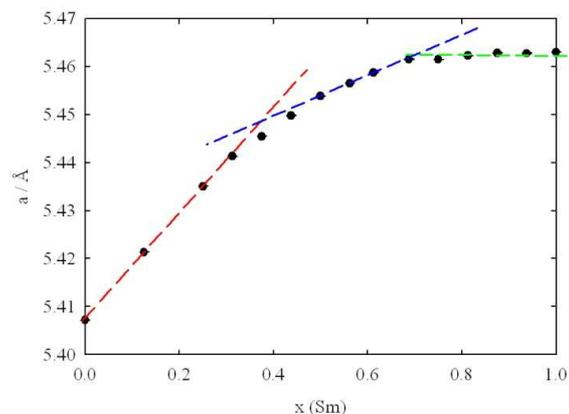


Figure1. Phase diagram at T=90K for $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-x/2}$. Red dashed line: fluoritic phase; blue dashed line: C-type phase; green dashed line: C-type + B-type phases.

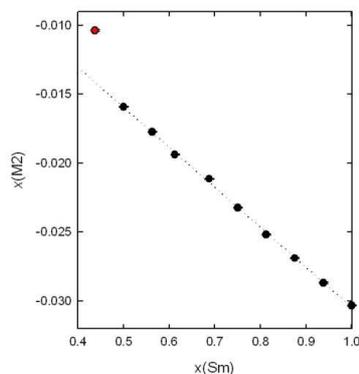


Figure2. $x(\text{M2})$ coordinate as a function of x samarium concentration. $R^2=0.9993$.

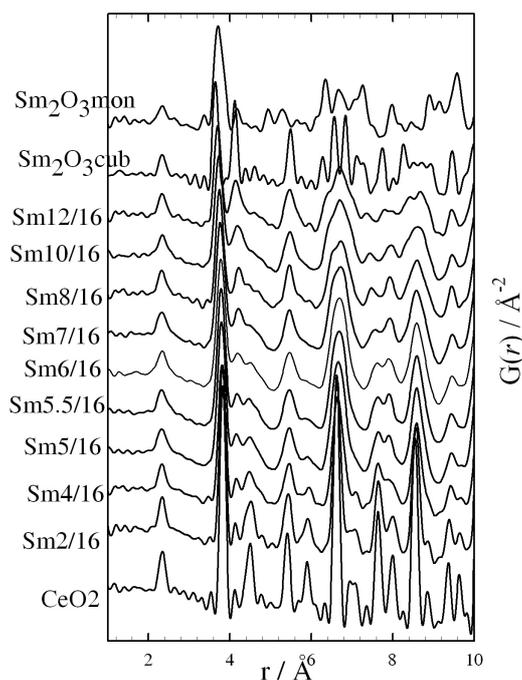


Figure2. Local structure as a function of radial distance for different Sm compositions

The real space analysis has been performed with the software PDFGetX2 [5] and PDFGUI [6]. 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 experimental PDF functions collected at λ_2 are plotted together in Fig. 2.

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. $r < \sim 10 \text{ \AA}$), this is true only for the solid solution end-members (CeO_2 and Sm_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 Sm_2O_3 -rich droplets embedded in a fluoritic CeO_2 matrix, or vice versa, depending on the overall composition.

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 , making difficult the comparison between the two

data sets.

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