Defect clustering in $Ce_{1-x}Gd_xO_{2-x/2}$ using the PDF Analysis

**Michela Brunelli[a], Marco Scavini[b,c], Mauro Coduri[b], Mattia Allieta[b], Claudio Ferrero[d]**

[a]Institut Laue-Langevin, 6, rue J. Horowitz, BP 156, 38042 Grenoble Cedex 9, France; [b]Dipartimento di Chimica, Università di Milano, Via C. Golgi 19, I-20133 Milano, Italy; [c]ISTM-CNR and INSTM Unit, via Golgi 19, I-20133 Milan, Italy [d]European Synchrotron Radiation Facility, 6, rue J. Horowitz, BP 220, 38043 Grenoble Cedex 9, France

Introduction and motivation

$Ce_{1-x}Gd_xO_{2-x/2}$ solid solutions (CGO) are promising candidates as conducting electrolytes for electrochemical cells at intermediate temperatures (800-1000 K). However The ionic conductivity σ_i of CGO systems shows an anomalous behavior as a function of x. In particular, $>_i$ increases by enhancing the doping concentration up to a critical value (x~ 0.10) and, after a broad maximum, decreases when increasing x above ~ 0.2. It is a common opinion in the literature that the anomalous trend described above is related to the formation of complex defects, O vacancies ordering or even phase separation on the nanoscale, which should trap the O vacancies and then reduce the average O mobility.

Aim of this work is to unveil the complex positional disorder induced by gadolinium doping and oxygen vacancies formation in CGO solid solutions by means of the Pair Distribution Function (PDF) analysis
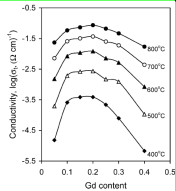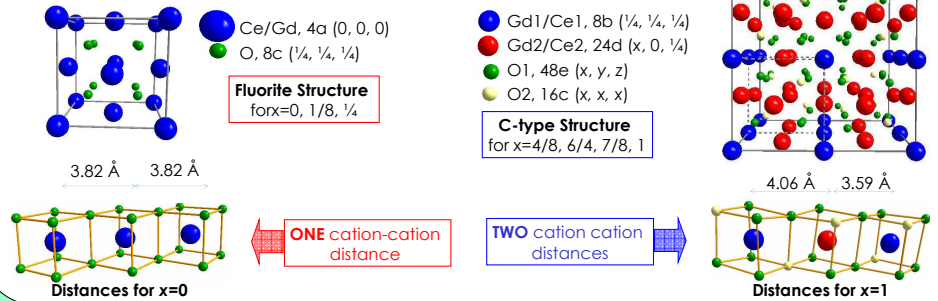

Z. Tianshu et al., Solid State Ionics **148** (2002) 567

Data Collection

Data were collected at **90 K** at **ID31** beamline of the **ESRF**, using $\lambda=0.30975(1)$ Å on powdered samples of $Ce_{1-x}Gd_xO_{2-x/2}$ with **x=0, 1/8, 2/8, 4/8, 6/8, 7/8, 1**

XRPD data quality for Pair distribution function (PDF) method, plus empty capillary and air background, were obtained by summing several scans (~7 hours total measuring time).
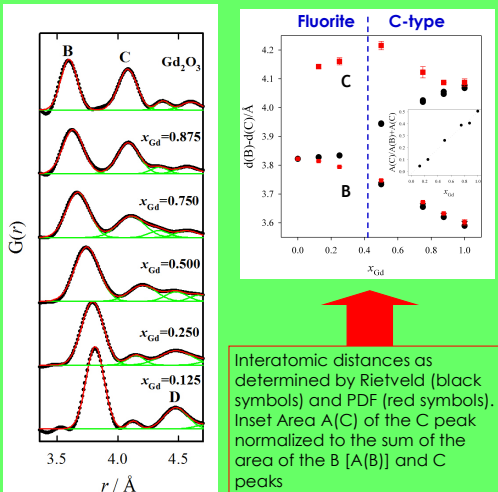
Average Structure from Rietveld analysis

Ce/Gd, 4a (0, 0, 0)
O, 8c (¼, ¼, ¼)

Gd1/Ce1, 8b (¼, ¼, ¼)
Gd2/Ce2, 24d (x, 0, ¼)
O1, 48e (x, y, z)
O2, 16c (x, x, x)

Fluorite Structure for x=0, 1/8, ¼

C-type Structure for x=4/8, 6/4, 7/8, 1

3.82 Å   3.82 Å

4.06 Å   3.59 Å

ONE cation-cation distance

TWO cation cation distances

Distances for x=0

Distances for x=1

PDF: Direct analysis

PDF peaks have been fitted with Gaussian functions after baseline subtraction.

In the figure below (left) the fits pertinent to the B (short cation-cation distance) and C (long cation-cation distance) peaks are shown

Interatomic distances as determined by Rietveld (black symbols) and PDF (red symbols). Inset Area A(C) of the C peak normalized to the sum of the area of the B [A(B)] and C peaks

Average and local structure don't match!!

➤The C peak is apparent even for the samples with average fluorite structure: x=1/8 and 2/8 while it should be absent

➤Moreover, the ratio A(C)/[A(B)+A(C)] increases linearly at increasing x

➤Finally PDF and Rietveld interatomic distances don't match for the C peak and for even longer interatomic distances.

Experimental PDF Functions
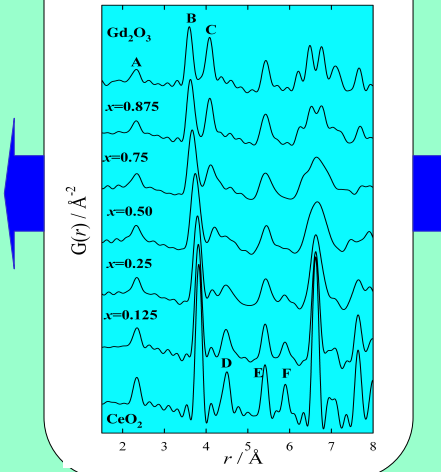

Pictorial model for short range structure

For **r>10 Å** the PDF data fairly agree with the average structure

For **r<6 Å** the PDF data are consistent with a biphasic model where Fluorite and C-type zones coexist.

Gd-rich and Ce-rich subnanometric "droplets" are present: for x≤0.25 the C-type droplets (in red) are embedded in the fluorite structure (in black). For x≥0.50 the Gd-rich zones percolate and the average structure is C-type.
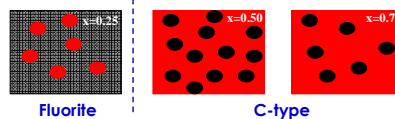
Fluorite   **C-type**

PDF: Real Space Rietveld
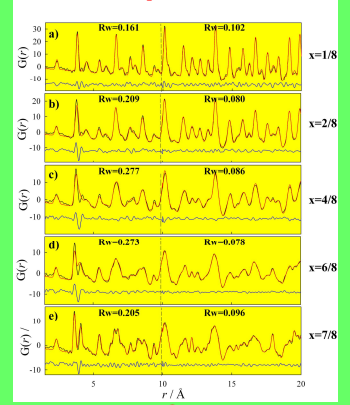
For r>10 Å PDF data fairly agree with the average model
For r<10 Å PDF data **don't match** the average model

PDF data for **r<6 Å** are consistent with a **biphasic model**: a fluorite CeO_2-like phase and a Gd_2O_3-like one appear together.

The fits with the **biphasic model** in the 1.5<r<6 Å are shown in the **left** part of the figure aside, together with the monophasic average models in the same r range