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Local disorder in yttrium doped ceria (Ce$_{1-x}$Y$_x$O$_{2-x/2}$) probed by joint X-ray and Neutron Powder Diffraction

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Abstract. Yttrium doped ceria materials (Ce$_{1-x}$Y$_x$O$_{2-x/2}$) are widely studied for their application in Solid Oxide Fuel Cells devices. An anomalous decrease in the isothermal ionic conductivity at increasing Y$^{3+}$ concentration above a critical value has been observed and attributed to the formation of defect clusters / domains at the nanometric scale, the crystallographic structure of which is still under debate. In this context we present a combined Synchrotron Radiation and Neutron Powder Diffraction study. In particular, neutrons allow to determine accurately oxygen related parameters, the contribution of which in terms of X-ray scattering power is almost negligible when compared to that of cations. The effect of doping on the average structure is investigated using conventional Rietveld analysis, while the Pair Distribution Function (PDF) technique is used to explore structural distortions and the spatial extent of disorder as well. The local structure observed in the real space is not consistent with the mean crystallographic one and is better modeled considering a biphasic model.

1. Introduction

In recent years, doped ceria materials (Ce$_{1-x}$Y$_x$O$_{2-x/2}$, hereafter CYO) have attracted increasing attention as electrolytes for Solid Oxide Fuel Cells (SOFCs) because of their high ionic conductivity [1]. In a SOFC, oxygen gas on the cathode side of the cell reduces to O$^2-$, diffuses through the electrolyte layer and combines with hydrogen (or other fuels) producing water and electrons. The most common electrolyte used in SOFC is Yttria-Stabilised-Zirconia (YSZ), which is very stable in both reducing and oxidizing atmosphere, but requires high operating temperature (~1000°C) in order to exhibit high ionic conductivity [2]. Such high temperature requires an all-ceramic construction which raises the cost of the fuel cell. Overall manufacturing costs can be considerably reduced by operating at lower temperature. This is the case of doped ceria electrolytes, which maintain a high ionic conductivity even at intermediate temperatures (e.g. 500-700°C).

Although pure ceria (CeO$_2$) does not show a significant ionic conductivity, this can be raised by doping its fluorite structure with a lower valent oxide, such as Y$_2$O$_3$. For each trivalent ion substituting...
a Ce(IV) ion 0.5 oxygen vacancies appear to maintain electroneutrality. Ionic conductivity occurs by oxygen diffusion via the vacancy mechanism:

\[ Y_2O_3^{4+} \rightarrow 2Y^{3+} + 3O^{2-} + V_0^{\cdot} \quad (1) \]

As a consequence the isothermal ionic conductivity \( \sigma \) should increase monotonically at increasing doping concentration. Conversely a maximum of \( \sigma \) is generally observed at a critical \( Y^{3+} \) concentration \( x \), above which \( \sigma \) decreases (see e.g. [3,4]).

Local probes like EXAFS and NMR have been adopted in order to investigate the structural origin of the anomalous behavior of the conductivity. In particular EXAFS measurements [5,6] suggested the appearance of defect clusters formed by substitutional cations and oxygen vacancies. Kim et Al. [7] drew the same conclusion using solid state NMR experiments. These results are also supported by first principle atomistic calculations which suggest that: (i) it is energetically favorable for a vacancy to be in a first neighbor position with respect to the \( Y^{3+} \) substitutional ion [8]; (ii) the reduced concentration of effective free mobile vacancies (i.e. the conductivity drops) is due to the formation of defect associates of the oxygen vacancy with the solute cation [9].

It should be noted that the EXAFS technique can be successfully employed to explore only the local structure of \( Ce^{4+} \) and \( Y^{3+} \) ions and cannot provide further information in case of more extended defects (e.g. on the nanometric scale). The same applies for the solid state NMR measurements. Anyway, HRTEM [10], SAED and EELS [11] measurements suggested that at higher doping concentrations complex defect clusters (a few nanometers large) form and act as deeper traps for oxygen vacancies. However, it is well known that the main limitation of electron beam-based techniques is that the investigated region could not be representative of the whole sample, particularly in highly defective oxides.

For this reason a bulk technique, able to investigate both the very local structure (first coordination shells) and the mesoscopic scale (i.e. a few nanometers) would be required to shed light on such a complex system. The Pair Distribution Function (PDF, i.e. the real space analysis of diffraction data) can be considered to be the right technique to solve this problem: Since both Bragg and diffuse scattering contributions are taken into account, it is a unique tool to determine the local and medium range deviations with respect to an ideally periodic structure [12, 13].

The Pair Distribution Function \( G(r) \) is experimentally determined via sine Fourier transform of the corrected total scattering function \( S(Q) \):

\[ G(r) = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1] \sin(Qr) \, dQ \quad (2) \]

where \( r \) is the radial distance. In order to compare or to fit the experimental \( G(r) \) against a structural model, the \( G(r)_{\text{calc}} \) can be calculated from a set of structural parameters according to:

\[ G(r)_{\text{calc}} = \frac{1}{r} \sum_v \sum_\mu \left[ \frac{b_v b_\mu}{b^2} \delta(r - r_{v\mu}) \right] - 4\pi r \rho_0 \quad (3) \]

where \( v \) and \( \mu \) are the ions involved, \( b \) is the coherence scattering length and \( \rho_0 \) is the number density. The function \( G(r) \) indicates the probability of finding a couple of atoms at a certain \( r \)-distance with an integrated intensity dependent on the coherence scattering length \( b \) of the elements involved (see equation 3). The effect of the reciprocal space resolution on real space data is reported elsewhere [14].

Aim of this work is to provide a crystallographic description of the local disorder induced by yttrium doping in CYO materials. For that reason we performed X-Ray (XRPD) and Neutron Powder Diffraction (NPD) experiments since both techniques can be seen as complementary probes for the CYO system: X-ray scattering lengths \( b \) are proportional to the atomic number, thus the main contributions are due to the cations, especially cerium. On the other hand, neutron scattering lengths depend on the single isotopes. In particular, considering a natural isotopic compositions, the neutron \( b \)-values for Ce, Y and O are 4.84, 7.75 and 5.803 Å, respectively [15]. For that reason, neutrons are far
more sensitive to oxygen related parameters than X-rays. Moreover, Ce, Y and O have an almost negligible neutron absorption cross section, which makes them very suitable for a NPD investigation.

Experimental data have been analyzed using both reciprocal space Rietveld analysis and atomic Pair Distribution Function.

2. Experimental

Micro-crystalline CYO samples with Y concentrations $x = 0.125$, 0.250 were prepared with the Pechini sol-gel method and fired at 900°C for 72 hours. XRDP patterns were collected at the ID31 beamline of the ESRF, Grenoble [16] in the $2\theta$ range $0<2\theta<120^\circ$ up to $Q_{\text{max}}=29.4$ Å$^{-1}$, where $Q=4\pi \sin\theta/\lambda$ is the transferred momentum. We collected experimental data (plus empty capillary and air background) at incident X-ray wavelength $\lambda=0.35413(3)$ Å. Additional data were collected also on CeO$_2$ (Aldrich $\geq 99.0\%$) and Y$_2$O$_3$ (Aldrich 99.9%). In order to attain XRDP data quality for experimental PDF all patterns were obtained summing intensity counts over several scans performed at fixed temperature ($T=90$ K).

NPD patterns for reciprocal space analysis were collected at the D20 instrument at ILL, Grenoble [17], warming the samples at the rate of 0.75 K/min from 4 K to room temperature at incident neutron wavelength $\lambda=1.3595(3)$ Å in the $2\theta$ range $13<2\theta<144^\circ$. About 10 minutes acquisition time diffraction patterns were collected at 4 K and room temperature, whilst shorter acquisitions (2 minutes) were collected upon heating.

NPD patterns for real space analysis were collected at the D4c instrument at ILL [18] at incident neutron wavelength $\lambda=0.4975(3)$ Å, covering a $Q$-range between 0.35 and 23.6 Å$^{-1}$ at fixed temperature ($T = 90$ K) for all the samples. Empty cryostat, vanadium rod, empty cans and boron powder patterns were also measured in order to properly subtract the background and for normalization. The backgrounds were measured periodically during the experiment in order to check their stability. PDF quality patterns were collected for each sample within 3-4 hours.

3. Results and discussion

We performed the data analysis using a multi-step approach. First the average crystallographic structure (i.e. cell parameter, atom positions and thermal parameters) was obtained for each sample by means of the reciprocal space Rietveld method. Then the average structural models were applied to the same data in real space, using the PDF approach to detect local deviations from the mean structure. Finally a structural model is proposed to interpret the local structure of CYO samples.

3.1. Reciprocal space analysis

The XRDP and NPD patterns were analyzed via the Rietveld method [20] as implemented in the GSAS software suite of programs [21] which features the graphical interface EXPGUI [22]. The background was fitted by Chebyshev polynomials. For XRDP data, absorption correction was performed through the Lobanov empirical formula [23] and line profiles were fitted using a modified pseudo-Voigt function [24] accounting for asymmetry correction [25]. In the final refinement cycles, cell parameter, positional coordinates (in Y$_2$O$_3$) and isotropic thermal parameters were allowed to vary as well as background and line profile parameters. For NPD data, absorption correction was considered as negligible. Line profiles were fitted only in the longer acquisition patterns. Since line profile parameters do not vary passing from low to high temperature, they were kept fixed in the refinements upon warming, where only the cell parameter and the isotropic thermal parameters were allowed to vary.

Cerium oxide exhibits fluoritic structure (space group $Fm\overline{3}m$). Cerium lies in the (0, 0, 0) site and O in ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$). The stable form of the Y$_2$O$_3$ sesquioxide in the investigated temperature range is the so called C-type structure ($Ia\overline{3}$) [19]. The cations lie in two non equivalent positions: M1 ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) and M2 (x, 0, $\frac{1}{4}$), while oxygen occupies a (x, y, z) site.
The C-type structure is very close to the CeO$_2$-fluorite: It can be obtained from a 2x2x2 fluorite supercell by removing two oxygen ions in each of the single fluorite cells. In this way the space group symmetry is lowered to $Ia\overline{3}$ and the cations gain a 6-fold coordination.

Both $x=0.125$ and $x=0.250$ samples both exhibit a CeO$_2$-like fluoritic structure. In figure 1 the NPD and XRPD patterns collected at $T = 90$ K for the $x = 0.250$ composition are shown as an example. All the peaks are well fitted by the fluoritic model and no noteworthy residual is observed. The same applies for the whole temperature range investigated. Since no positional degree of freedom is allowed in such a structure owing to symmetry constraints, the only structural parameters varied in the Rietveld refinements were the lattice parameter and the isotropic mean square displacements ($msd$) parameters. The Ce/Y site occupations were fixed based on the nominal compositions.

The cell parameter is found to decrease upon Y doping. In particular, from the XRPD analysis at 90 K, $a=5.407228(3)$, 5.405631(5) and 5.403207(9) Å for CeO$_2$, $x=0.125$ and $x=0.250$, respectively. In figure 2 the isotropic mean square displacement parameters of metal (left) and oxygen (right) ions are shown.

A rigid shift of the $msds$ of doped samples towards higher values can be clearly observed. In absence of disorder, $msds$ are related only to the square of the amplitude of atomic vibration around their equilibrium position. When disorder is present, ions occupying the same site in different cells can
occupy equilibrium positions which differ from the average one, adding a contribution to the thermal parameter often defined as “static contribution”. The observed shift can be then regarded as a clear fingerprint of doping induced disorder [26]. The msd parameters obtained at \( T = 90 \text{ K} \) through XRPD and NPD refinements are in fairly good agreement and are shown in table 1 for a sake of comparison.

### Table 1. Mean square displacements msd (in Å^2) of cations (M) and anions (O) obtained by XRPD and NPD refinements at 90 K. The samples exhibit fluoritic structure (space group \( Fm\overline{3}m \)): Cations lie in (0, 0, 0) and anions in (1/4, 1/4, 1/4).

<table>
<thead>
<tr>
<th></th>
<th>X-Rays</th>
<th>Neutrons</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>( \text{msd (M)} )</td>
<td>( \text{msd (O)} )</td>
</tr>
<tr>
<td>( \text{CeO}_2 )</td>
<td>0.00091(1)</td>
<td>0.00302(6)</td>
</tr>
<tr>
<td>( x=0.125 )</td>
<td>0.00338(1)</td>
<td>0.00633(7)</td>
</tr>
<tr>
<td>( x=0.250 )</td>
<td>0.00813(2)</td>
<td>0.0127(2)</td>
</tr>
</tbody>
</table>

The analysis of msds clearly indicates the increasing of structural disorder upon Y doping.

### 3.2. Real space analysis

In order to gain insight into the local deviations that occur in such a disordered material, a PDF study was performed. As stated above, data were collected for both X-ray and neutron at \( T = 90 \text{ K} \) in order to minimize thermal motion. X-ray real space data were processed using the PDFGetX2 software [27]: Data were corrected for background, sample self-absorption, multiple scattering and Compton scattering. Neutron real space data were processed by regrouping repeated scans of the D4c detectors over the available range of scattering angles in the reciprocal space. For each sample, empty container and sample environment contributions were subtracted from the raw data, taking into account absorption effects [28] as well as the incoherent-scattering contribution. A standard multiple-scattering [29] and Placzek [30] corrections were applied. The PDF analysis was performed by fitting the experimental \( G(r) \) using the software PDFGui [31]. The agreement between model and experimental data is given by the \( R_w \) factor:

\[
R_w = \left( \frac{\sum_{i=1}^{n} \omega(r_i) \left[ G_{\text{obs}}(r_i) - G_{\text{calc}}(r_i) \right]^2}{\sum_{i=1}^{n} \omega(r_i) G_{\text{obs}}^2(r_i)} \right)^{1/2}
\]  

where \( \omega(r_i) = 1/\sigma^2(r_i) \) and \( \sigma(r_i) \) is the standard deviation at a distance \( r_i \).

Due to its well ordered structure, \( \text{CeO}_2 \) can be considered a reference material for a PDF study. Moreover, since only special positions are occupied, it is possible to know a priori the positions of the peaks and which couples of atoms are involved, by simple geometric considerations. In table 2 the list of the first distances is reported considering the cell parameter \( a=5.407\text{Å} \), as measured at 90 K.

### Table 2. List of distances of the first coordination shells in a CeO\(_2\)-like structure. Values are referred to the case of CeO\(_2\) measured at 90 K.

<table>
<thead>
<tr>
<th>Distance</th>
<th>Value</th>
<th>Distance</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d(\text{Ce} - \text{O}) \text{NN} )</td>
<td>( a \frac{\sqrt{3}}{4} \approx 2.34 \text{ Å} )</td>
<td>( d(\text{Ce} - \text{Ce}) \text{NN} \equiv d(\text{O} - \text{O}) \text{NN} )</td>
<td>( a \frac{\sqrt{3}}{2} \approx 3.82 \text{ Å} )</td>
</tr>
<tr>
<td>( d(\text{O} - \text{O}) \text{NN} )</td>
<td>( d \frac{\sqrt{3}}{2} \approx 2.70 \text{ Å} )</td>
<td>( d(\text{Ce} - \text{O}) \text{NN} )</td>
<td>( a \frac{\sqrt{3}}{4} \approx 4.48 \text{ Å} )</td>
</tr>
<tr>
<td>( d(\text{O} - \text{O}) \text{NN} )</td>
<td>( a \frac{\sqrt{3}}{2} \approx 4.68 \text{ Å} )</td>
<td>( d(\text{O} - \text{O}) \text{NN} )</td>
<td>( a )</td>
</tr>
</tbody>
</table>
In figure 3a the G(r) curves obtained for CeO$_2$ using NPD (red) and XRPD (blue) are shown. As stated above, one advantage of neutrons is that they allow to study O-O distances which are undetectable through X-rays. On the other hand, high energy and high reciprocal-space resolution X-ray data from ID31 allow to reach higher Q$_{\text{max}}$ values (i.e. to increase the real space resolution) and to explore a wider r range, due to the very high angular resolution and very narrow instrumental resolution function [16]. In figure 3b the experimental G(r) curves for the Y$_2$O$_3$ sample are also reported.

![Figure 3](image)

**Figure 3.** Experimental G(r) curves for CeO$_2$ (a) and Y$_2$O$_3$ (b) obtained by NPD (red) and XRPD (blue). Labels indicate to which couple of atoms every peak is referred.

The NPD G(r) curves are shown in figure 4. The arrows are guides to the eye to indicate the amplitude and position shifts of the different peaks at increasing Y concentration. According to a considerable local structural disorder, the G(r) peaks related to doped sample look broader than in pure ceria and in most cases Y doping causes the peak features to resemble those of Y$_2$O$_3$.

Moreover, since the cell parameter decreases by enhancing the doping concentration, all peaks are expected to shift toward lower distances. However, this is true only for the NN (Nearest Neighbors) M-O and the NN M-M distances, while the NN O-O distances increase as well as the third M-M and O-O neighbors (which correspond to the cell parameter). All these findings indicate that disorder affects not only the first coordination shells: Shifts of peak positions are observed even at higher distances (see figure 4). It’s worthwhile noticing that such a widespread structural disorder cannot be detected with other techniques such as EXAFS, which is sensitive only to the first coordination shells. Besides, interatomic distances involving only light atoms, such as O-O, are precluded.

The extent of the disorder induced by doping was determined by fitting the XRPD G(r) curves monitoring the residual R$_{\text{wu}}$ as a function of r. A fluoritic model has been applied: The cell parameter is fixed to the average structure value and the presence of two metals ions is taken into account by randomly populating the cation positions with Ce$^{4+}$ and Y$^{3+}$ ions in due proportions. Thermal parameters and scale factor only have been refined.
Figure 4. NPD experimental G(r) curves for CeO$_2$ (red), $x=0.125$ (black), $x=0.250$ (blue) and Y$_2$O$_3$ (grey). Arrows are guides for the eye to highlight the effect of doping on peak positions and width.

X-Ray diffraction patterns from ID31 were chosen for this purpose since they don’t suffer from limited reciprocal space resolution effects. Conversely, oscillations in neutrons G(r) curves are subjected to damping at increasing $r$, due to the lower resolution of the D4c instrument.

Whilst for CeO$_2$ the fluoritic model fits very well even the shortest distances, this is not true for the doped samples. At the subnanometric scale, (i.e. for $r < 10$ Å) R$_w$ values increase dramatically by enhancing the doping rate and, most importantly, the peak positions of the calculated G(r) curves are not consistent with the experimental ones (see figure 5a for $x=0.250$). In particular, the fluoritic model cannot account for the peak at $\sim 4.1$ Å which roughly appears at the same r-distance of the long M-M distance in the C-type structure (see figure 3b). The refinement against NPD data yielded similar outcomes (see figure 5b). In particular, in the $1 < r < 6$ Å range the following R$_w$ values were obtained: 0.080 for CeO$_2$, 0.127 for $x=0.125$ and 0.197 for $x=0.250$. This indicates that the structure of CYO is distorted only locally to accommodate for the presence of two distinct metal ions, but on average it still exhibits a fluoritic symmetry.

A possible explanation could be the tendency of the two cations to retain their local environment within some coordination shells. This can be tentatively accounted for by a model composed of the two end-member phases, CeO$_2$ and Y$_2$O$_3$.

In figure 5d the refinements performed using the biphasic model are shown for the NPD case. Scale factors, atoms positions and two thermal parameters, one for cations and the other for oxygen ions, were refined. A similar model has been successfully employed to describe the local structure in the CeO$_2$-ZrO$_2$ solid solution [32]. The biphasic model (69.4% of CeO$_2$ and 30.6% of Y$_2$O$_3$) yields a reduction of the residual down to R$_w=0.141$, from 0.197 using the single fluorite phase.

Furthermore, when the results of the neutron PDF biphasic model are applied to the X-ray G(r) (see figure 5c), the peak at $\sim 4.1$ Å is well fitted by refining only the overall scale factor and the thermal factors, whereas the single fluoritic model fails (see red circle in figure 5a). At the same time a noticeable decrease of R$_w$ values is observed.
Figure 5. XRPD and NPD $G(r)$ curves for the $x=0.250$ composition. (a): fluoritic model against XRPD data, (b): fluoritic model against NPD data; (c): biphasic model against XRPD data; (d): biphasic model against NPD data. Points: experimental data; solid lines: calculated (up: fluoritic model; down: biphasic model). Residuals are also shown. The red circles in (a) and (c) highlight the improvement obtained with the biphasic model in fitting the 4.1 Å peak from the XRPD data.

The coordination of Ce$^{4+}$ and Y$^{3+}$ cations in fluorite and C-type structure, respectively, are shown in figure 6. The distance values are obtained by applying the biphasic model and refer to cation-cation pairs. The fluorite CeO$_2$ structure exhibits only one Ce-Ce distance (see figure 6a) and all ions are arranged in a perfect cubic environment. In the C-type structure (see figure 6b) two non-equivalent cation sites are present, labeled in black (Y1) and in blue (Y2), respectively: They differ in their oxygen vacancies distributions and lie in a slightly distorted cubic environment, thus gaining a 6-fold coordination. Two cation-cation distances are hence present.

It should be noted that the fit yields cell parameters which are quite different from the ones of the average structure: In the biphasic model the CeO$_2$ cell parameter changes from 5.4072 Å (pure ceria) to 5.3849 Å, while for the $x=0.25$ composition the measured cell parameter is 5.4032 Å; the biphasic model cell parameter for Y$_2$O$_3$ is 10.879 Å, which is larger than that of pure Y$_2$O$_3$, which is 10.602 Å.
However, rather than actual cell parameters of the CeO$_2$ and Y$_2$O$_3$ pure phases, the refined cell parameter values obtained through the biphasic model were considered here just variable parameters. Indeed, since disorder is localized on a sub-nanometric scale, M-M and M-O distances are not supposed to relax to the CeO$_2$ and Y$_2$O$_3$ values as expected for a true phase separation. However, the fit improvement after the application of this simple biphasic model suggests that complex defects as well as compositional fluctuations occur at the sub-nanometric scale.

4. Conclusion
Although there is growing evidence that short- and medium-range structural distortions deeply affect the physical properties of materials, a comprehensive description of the local structure in doped ceria materials is still lacking. To this purpose, an experimental approach involving XRPD, NPD and the related Pair Distribution Function analysis was performed in order to determine the average crystallographic structure and the local distortions arising from disorder. The study of the thermal parameters in the reciprocal space clearly indicates that the doping introduces disorder in the ceria structure. X-Ray real space refinements show that the coherence length of disorder is about 8-10 Å.

The first coordination shells are not consistent with the average fluoritic structure and are better described by a biphasic model, i.e. describing the chemical environment of the cations in their pure oxides. Although the model proposed in this work is very simple, it allows to improve considerably the fit of the first coordination shells. However, deviations from the mean structure are not limited to the first coordination shells and complex defect clusters may need to be considered to provide a comprehensive description of the local structure in the CYO solid solution.

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