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| | **Experiment title:**<br>Exploring the local structure of complex doped ceria systems by PDF analyses | **Experiment number**:<br>HC-4993 |
| **Beamline**:<br>ID22 | **Date of experiment**:<br>from: 6th Sept. 2022 to: 10th Sept. 2022 | **Date of report**:<br>10-02-23 |
| **Shifts:**<br>12 | **Local contact(s)**:<br>Ola Gjonnes Grendal | *Received at ESRF:* |


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**Report:**

The $Ce_{1-x}RE_xO_{2-x/2}$ systems (RE= trivalent rare earth) form a family of widely studied solid electrolytes for solid oxide fuel and electrolysis cells, characterized by a high ionic conductivity in the intermediate temperature range. With the experiment HC-4993, total scattering measurements were successfully performed on twentysix different samples: in particular, the pure $CeO_2$, $Nd_2O_3$, $Tm_2O_3$ and $Dy_2O_3$ commercial oxides were analysed, as references, togheter with eight samples with x= 0.05, 0.10, 0.15, 0.20, 0.30, 0.40, 0.50 and 0.60 belonging to the $Ce_{1-x}(Nd_{0.74}Tm_{0.26})_xO_{2-x/2}$ system, 8 samples with x= 0.05, 0.10, 0.15, 0.20, 0.30, 0.40, 0.50 and 0.60 belonging to the $Ce_{1-x}(Nd_{0.63}Dy_{0.37})_xO_{2-x/2}$ system and 6 samples with x= 0.10, 0.20, 0.30, 0.40, 0.50 and 0.60 belonging to the $Ce_{1-x}(Gd_{0.33}Sm_{0.67})_xO_{2-x/2}$ system. All the samples were obtained by a co-precipitation method.
The experiment was intended to collect total scattering data of very high quality, to perform a comprehensive study on the pair distribution function (PDF) of the samples, and on its evolution with the increasing RE content, thus gaining as much information as possible on the local structure of the considered systems, and on the differences in the oxides structure over a longer or a shorter range of distances. In fact, it is known that, in RE-doped ceria systems, the observed ionic conductivity is strongly influenced by the structure of the oxide and, in particular, by the different families of defects cohexisting in it. For instance, the partial substitution of $Ce^{4+}$ by RE in the fluorite-type lattice of pure ceria (F phase, Fm-3m space group), causes the occurrence of free oxigen vacancies that make such systems $O^{2-}$ ions conductors; on the other hand, the increasing amount of RE, also causes the growth of domains belonging to the the Ia-3 space group (C phase defects), a superstructure of F typically shown by the smallest $RE_2O_3$, which is characterized by a lower ionic conductivity.
During the allocated beamtime, the x-ray diffraction patterns of the doped ceria powders loaded in borosilicate capillaries (0.5 mm diameter) were collected at room temperature, with a $\lambda$= 0.35431 Å. The obtained diffraction patterns result from a series of 4 accumulations, progressively focused on higher $2\theta$ values. Togheter with the samples, data for an empty capillary were collected to substract its contribution to the total scattering; a standard $LaB_6$ sample was analysed too, to evaluate the experimental resolution effects.

The data analyses performed so far, showed that, with the increasing dopant amount, the occurrence of C-phase peaks is observed for all the systems. Figure 1 shows an enlarged view of the diffraction patterns collected on the NdDy-doped samples: the occurrence of superstructure peaks in such system is observed for x≥ 0.40.

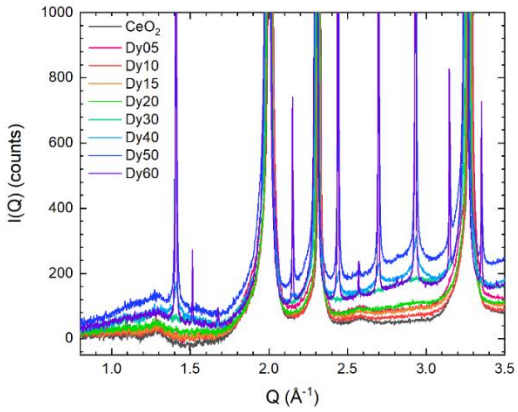


*Figure 1 – I(Q) patterns collected on pure ceria, and on the eight samples belonging to the NdDy-doped system.*

The G(r) function of all the samples was calculated via the PDFgetX3 software [1]. A study on its evolution in a long distance range (up to 3000 Å) showed that the oscillations in the PDF of the samples with x≤0.20 tend to dampen at gradually decreasing distances, indicating a reduction in the structural coherence of these samples; for x> 0.20, the structural coherence of the samples is constant.

So far, the majority of the performed data analyses focused on the NdDy-doped system: in particular, the G(r) function of all the NdDy-doped samples was tentatively fitted according to the $CeO_2$ structural model, in the 1.5 < *r* < 30 Å range, though the progressively increasing structural disorder, given by the chemical substitution. It was observed that, up to x= 0.30, the fluorite-type structure provides a good description of the system; for the samples with x> 0.30, on the other hand, a biphasic F+C model is necessary to properly describe the system. However, such analyses highlighted that, in all the samples, even at very low dopant amounts, and even in pure ceria, a significant deviation of the local structure with respect to the ideal one is observed (for r ≤ 10 Å).
A parallel test was performed by fitting the PDF functions of the samples with x≤0.30 with the same biphasic model employed for the samples with a higher RE content, to investigate the structural properties of the system at the local scale. As a result, an improvement in the G(r) fitting process was obtained, managing to describe in a proper way even the 1.5 < *r* < 6.15 Å range (an example for the $Ce_{1-x}(Nd_{0.63}Dy_{0.37})_xO_{2-x/2}$ sample with x= 0.30 is reported in Figure 2).

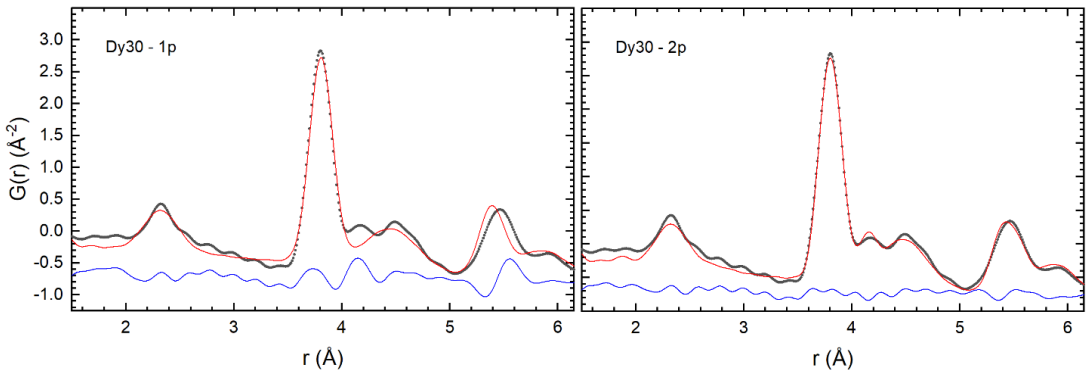


*Figure 2 – Comparison between a singl phase fit (left, only F phase considered) and a fit performed with a two phases model (right, F+C phases) in the 1.5 < r < 6.15 Å range for the $Ce_{1-x}(Nd_{0.63}Dy_{0.37})_xO_{2-x/2}$ sample with x= 0.30.*

[1] Juhás, P., Davis, T., Farrow, C. L. & Billinge, S. J. L. (2013). J. Appl. Cryst. 46, 560