ESRF	**Experiment title:** Local disorder and compositional fluctuations in double doped CeO_2-based fast ionic conductors: a combined EXAFS and PDF study	**Experiment number**: CH-4451
Beamline: BM01B ID22	**Date of experiment**: from: 07/10/2015 to: 12/10/2015 from: 17/02/2016 to: 23/02/2016	**Date of report**: *Received at ESRF:*
Shifts: 15 18	**Local contact(s)**: BRUNELLI Michela CODURI Mauro	

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Report:

In proposal CH-4451 we planned to investigate the local and middle range structure in $Ce_{1-x-y}RE'_xRE''_yO_{2-(x/2+y/2)}$ single- and double-doped fast ionic conductors (with x+y=0.125, 0.250, 0.375, 0.500 and RE'=La or Sm; RE'' Yb or Y) using X-ray Absorption Spectroscopy (XAS) and high resolution XRPD analysing data both in the reciprocal space and in the real space (PDF analysis).

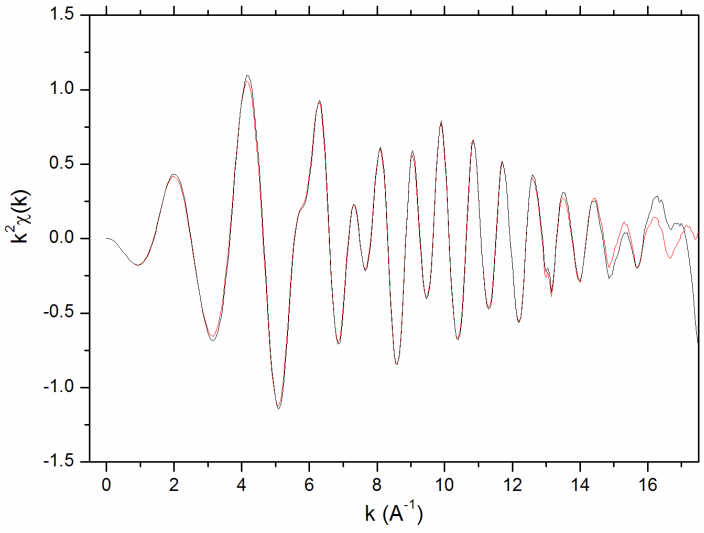

Fig. 1. Comparison between the EXAFS signal extracted after averaging 15 scans (red curve) and 5 scans (black curve).

XAS data should be useful to supply insights on the chemical environments of cations while PDF analysis to give information on the nature and extension of compositional and symmetry fluctuations induced by doping.

EXAFS measurements were performed at T = 90 K in transmission geometry at the four Ce, La, Sm, and Y K-edges. The samples, when needed depending on composition, were diluted in order to optimize the absorption edge and the total absorption at each edge considered.

During the 15 EXAFS shifts granted on BM01B we needed to acquire at least 15 scans for each edge and composition in order to reach a suitable signal to noise ratio also at high *k* values, as shown in Fig. 1. Please note that *k* values as high as 17 $Å^{-1}$ are requested to resolve cation-anion and cation-cation interatomic distances which differ of about 0.09 Å. Therefore we were able to measure all the single-doped compositions, two double-doped samples and the standard oxides at the above cited edges for a total of 27 samples. In this way we successfully separated different subshells, as shown in Figure 2.

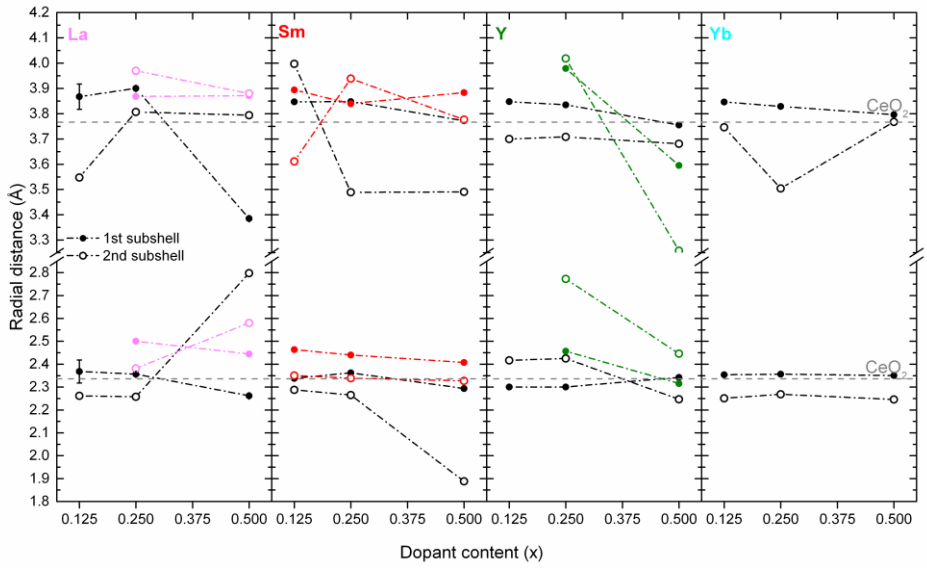

Fig. 2. First (lower) and second shell (upper) interatomic bond lengths of single-doped samples for the Ce-edge (black lines) and for the rare earth (RE) edges (colored lines), as a function of doping.

In Fig. 2 we show the interatomic distances behavior as a function of the dopant content for the first Ce-O or RE-O and for the second Ce-Ce/RE or RE-Ce/RE shells.
In all cases we observe a bimodal distribution of distances both in the first and in the second shell. The first subshell Ce-O (related to six oxygen atoms) is always characterized by an interantomic bond length very similar to those of pure CeO_2. The second subshell (2 atoms) is smaller in any case (except than for the Y edge).

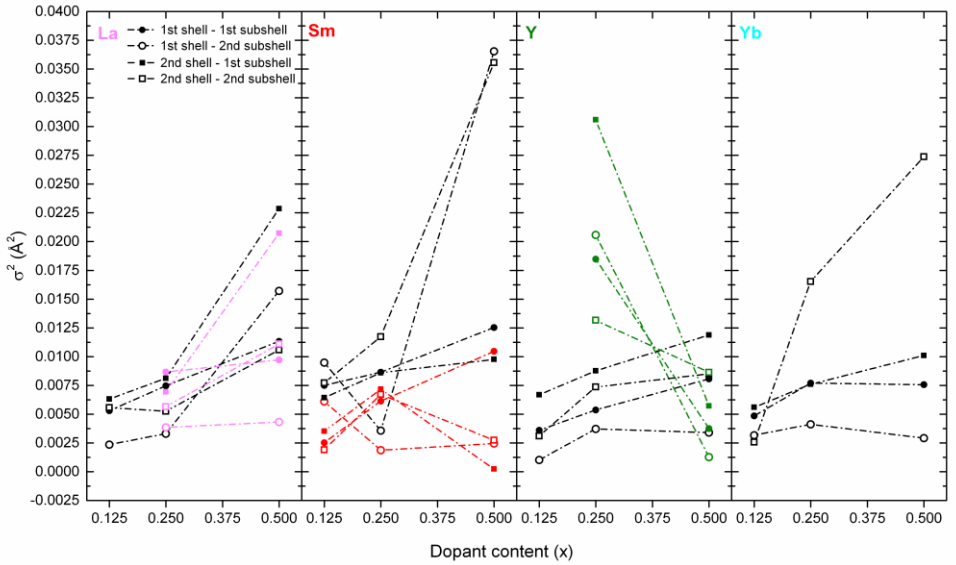

Fig. 3. First shell mean square relative displacement $\sigma^2(Å^2)$ of single-doped samples for the Ce-edge (black lines) and for the rare earth (RE) edges (colored lines).

The Debye-Waller σ^2(Å^2) factors of the single-doped compounds (Fig. 3) increase as a function of doping, except for the Y-edge where they decrease.
Taking into account the interesting results obtained, it would be essential for us to have the possibility to complete our EXAFS experiment by measuring the full compositional range of the double-doped samples. We will submit a continuation proposal in order to complete the full series of compositions (other 23 samples).

XRPD measurements have been collected at 90 K using wavelenghts of λ=0.326346(5) Å in the high *Q*-resolution setup (array of 9 point detectors) and λ=0.17712(1) Å using the 2 dimensional detector. High quality patterns have been collected on all the samples and the data are at present under analysis, since the experiment has been carried out at the end of February. In Figure 4 are shown, as examples, the low *r* portions of the PDF functions of the $Ce_{1-x}Yb_{x/2}La_{x/2}O_y$ samples.

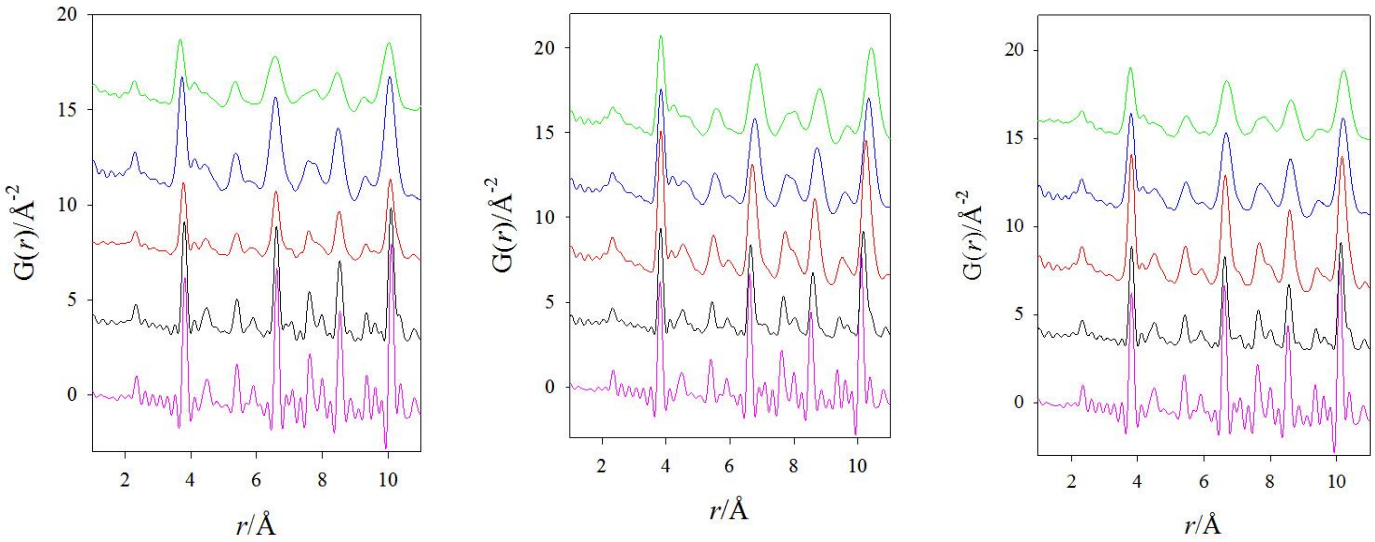

Fig. 4. G(r) function of the $Ce_{1-x}Yb_xO_y$ (left), $Ce_{1-x}La_xO_y$ (middle), $Ce_{1-x}Yb_{x/2}$ $La_{x/2}O_y$ (right) samples. Pink, black, red, blue and green lines refer to x=0, 0.125, 0.250, 0.375 and 0.500 samples respectively

In conclusion, we have successfully performed EXAFS and diffraction experiments and verified the suitability of the beamlines to reach the goals of the proposal. As to the diffraction part, all the samples have been measured and high quality PDF have been obtained. Data are at present under analysis. As to the EXAFS part, the time necessary to collect data of the desidered quality at sufficient high *k* values, was more than expected and only about half of the samples have been measured during the 15 shifts of the experiment.
We stress that *k* values as high as 17 Å^{-1} are needed to resolve interatomic distances which differ of less than 0.0.09 Å. Additional measuring time (about 15 shifts more) is needed for the EXAFS part at BM01B (now BM31).