



	Experiment title: An in-depth study of the defects architecture in $\text{Ce}_{1-x}(\text{Nd}_{0.74}\text{Tm}_{0.26})_x\text{O}_{2-x/2}$ through EXAFS measurements	Experiment number: HC-5046
Beamline: BM08	Date of experiment: from: 27 th Oct. 2022 to: 3 rd Nov. 2022	Date of report: <i>Received at ESRF:</i>
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Report:

With the experiment HC-5046, X-Ray absorption spectroscopy measurements were successfully performed on eight samples belonging to the $\text{Ce}_{1-x}(\text{Nd}_{0.74}\text{Tm}_{0.26})_x\text{O}_{2-x/2}$ system with $x = 0.05, 0.10, 0.15, 0.20, 0.30, 0.40, 0.50$ and 0.60 . The studied system belongs to the family of RE-doped ceria based electrolytes (RE indicates the trivalent rare earths) for solid oxide cells, characterized by a high ionic conductivity in the intermediate temperature range. The aim of the experiment was to gain as much information as possible on the local structure of such system, where different families of defects coexist, affecting the overall ionic conductivity of the material either in a positive or negative way, depending on the nature of the defects. 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 oxygen vacancies that make such systems O^{2-} ions conductors; on the other hand, the increasing amount of RE causes the growth of domains belonging to 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, according to the submitted proposal, the spectra of the samples were collected at the K-edges of Ce (40.44 KeV), Nd (43.57 KeV) and Tm (59.39 KeV), working in transmission mode, with an experimental set-up of the BM08 that employed the 311 monochromator crystal and no mirrors. Such spectra were collected at 100 K, up to $k=18$, to analyse their EXAFS region and to obtain information on the interatomic distances in the samples.

Moreover, further spectra for all the samples were collected at the L-III edges of Ce (5723 eV) and Nd (6208 eV), working in transmission and at room temperature, focusing the attention on the XANES region of the spectra, to obtain information on the valence of such ions in the structure. In the end, the spectra of the samples with $0.05 \leq x \leq 0.20$ were collected at the Tm L-III edge (8648 eV), working in fluorescence mode (due to the lower amount of such dopant with respect to Ce and Nd), up to $k=12$, to obtain information both from the XANES and the EXAFS region.

For both the K and L-III edges, the spectra of the pure oxides (CeO_2 , Nd_2O_3 , Tm_2O_3 and Ce_2O_3 only at the L-III Ce edge) were simultaneously collected with the spectra of the samples, to have a reference spectrum for each measurement.

The results obtained so far from preliminary analyses are hereinafter reported.

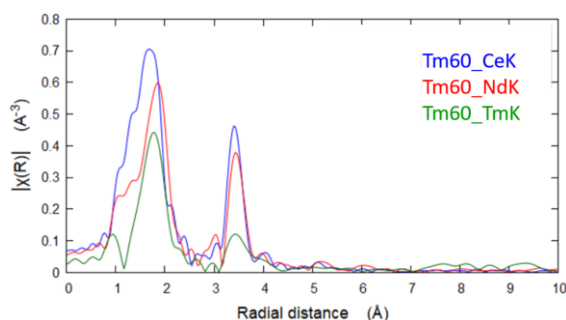


Figure 1 – Radial distances from spectra collected at the K-edges of the different elements for the $\text{Ce}_{0.40}\text{Nd}_{0.44}\text{Tm}_{0.16}\text{O}_{1.7}$ sample.

The study performed at the K-edges of the different elements shows a higher disorder for the Tm ions in the mixed oxides structure (Figure 1).

The EXAFS region of the spectra collected at the Ce K-edge was fitted according to the CeO_2 structural model, meanwhile the spectra collected at the Nd and Tm K-edges were analysed according to the pure Nd_2O_3 and Tm_2O_3 structures. Figure 2 shows the evolution of the Ce-O distance (first coordination shell), with the increasing dopant amount, which decreases from 2.33 to 2.27 Å with the increasing dopant amount, thus indicating that the Ce coordination number decreases from 8 to ~ 7 , according to the progressive formation of oxygen vacancies in the F lattice, and the progressive formation of RE_2O_3 defect clusters. The decreasing of the Ce-O radial distance is particularly evident for $x > 0.20$. An analogous trend was observed also for the Nd-O and Tm-O radial distances (first coordination shells), revealing a decrease in the coordination number from ~ 7 to ~ 6 , and an alignment of the RE-O distances with the ones expected for the pure RE_2O_3 oxides with the increasing RE content.

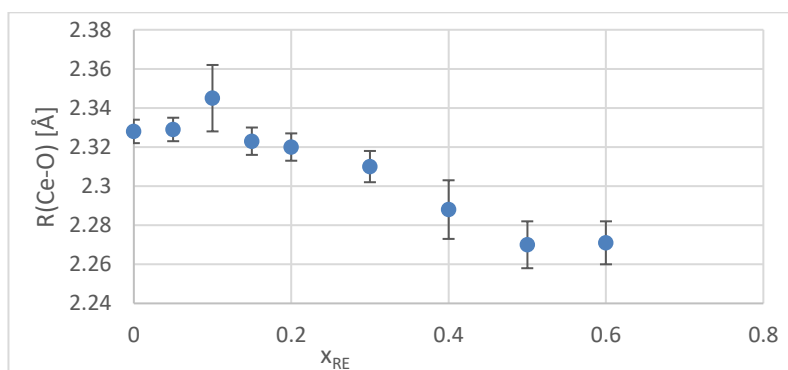


Figure 2 – trend of the Ce-O radial distance with the increasing dopant amount.

The study performed at the L-III edges showed the presence of the Ce mainly in the 4+ oxidation state: in fact, all the XANES spectra collected at the Ce L-III edge were tentatively described as a linear combination of the spectra of the Ce^{3+} and Ce^{4+} oxides. As a result, it was observed that the amount of Ce^{3+} in the mixed oxides samples, if present, is less than the 2%at. Of course, the doping ions (Nd and Tm) are present in the samples only in the commonly stable +3 oxidation state, as expected.