	Experiment title: Yb-K-edge Anomalous Differential PDF study to unveil the short and medium range environment of Yb in $Ce_{1-x}Yb_xO_{2-x/2}$ oxides	Experiment number: CH-3618
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Report:

Doped ceria materials $Ce_{1-x}Ln_xO_{2-x/2}$ (hereafter CeLnO, Ln=4f elements plus Y) have been intensively studied in the last years for applications as conducting electrolytes in electrochemical cells. Ionic conductivity is obtained by oxygen diffusion via the vacancy mechanism. Impedance spectroscopy measurements carried out on several CeLnO systems show anomalous behaviours as a function of the Ln concentration *x*. In general, the ionic conductivity of Ln-doped ceria decreases by enhancing the doping concentration above a critical value (x~0.1-0.2, depending on Ln). **[1]** This behaviour has been attributed to Ln dopants and oxygen vacancies aggregates whose spatial extent as a function of *x*, *T* and RE is still matter of debate.

In this context the formation of defect clusters was suggested by EXAFS **[2]**. However, EXAFS experiments on CeLnO materials unveiled only the local structure around Ce and Ln. Conversely, the Pair Distribution Function (PDF/ G(*r*)), i.e. the real space analysis of a diffraction experiment, investigate both local and medium range deviations from an ideally periodic structure (i.e. the long range structure).**[3]** In a recent PDF experiment at the ID31 beamline of the ESRF we proved the presence of CeO_2-like and Gd_2O_3-like droplets in $Ce_{1-x}Gd_xO_{2-x/2}$ in the whole compositional range. **[4]**

Unfortunately, PDF is not element sensitive, at opposite to EXAFS, so that the attribution of a G(*r*) peak to a couple of atoms is not univocal.

This problem can be overcome by applying anomalous X-ray diffraction to the total scattering method in order to obtain the so-called Anomalous Differential Pair Distribution Function (AD-PDF).

In general, for AD-PDF experiments, diffraction data are measured at two slightly different energies E_1 and E_2 ($\Delta E = E_2 - E_1 \sim 2$, 400 eV) close to the desired absorption edge, obtaining two intensities I(*Q*), whose differences are essentially due to the anomalous components of the atomic structure factor of the *anomalous* element. **[5]**

However, applying the propter corrections to experimental data using the above strategy is a difficult task, because around an absorption edge many phenomena like absorption, fluorescence, coherent scattering, and resonant Raman scattering take place **[3,6]**, making it difficult to map the changes in cross section accurately.

In this experiment we applied a different strategy to unveil the local middle range structure around Yb in $Ce_{1-x}Yb_xO_{2-x/2}$ solid solution ($0 \le x \le 0.5$, x=1).

AD-PDF quality XRPD data have been collected at 70-80 energies around the Yb-K edge with high energy resolution, allowing an accurate mapping of absorption, fluorescence, Compton scattering, and resonant Raman scattering changes as a function of the photon energy. The suitable energy interval has been settled out collecting a fluorescence spectrum across the edge.

In figure 1 the fluorescence spectrum of Yb_2O_3 is shown as an example. Arrows indicate the energy range of XRPD measurements.
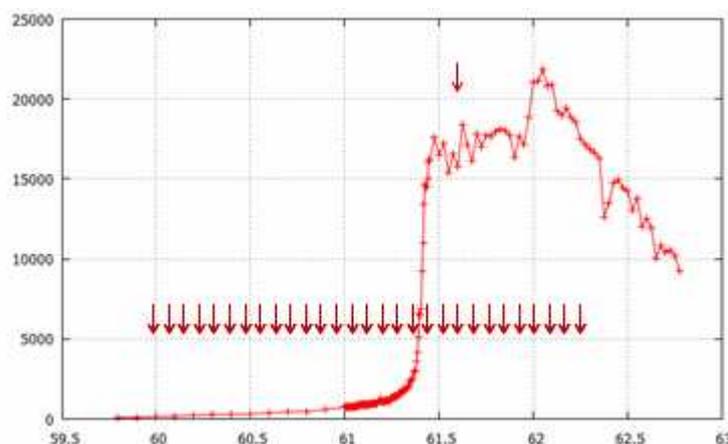
Figure 1. Fluorescence spectrum of Yb_2O_3 sample across the Yb K-edge (~61.332 keV). Arrows represent the energies selected for the AD-PDF experiment.

Data corrections and AD-PDF extraction have carried on using a software suite of programs under development by the members of our group at Columbia University.
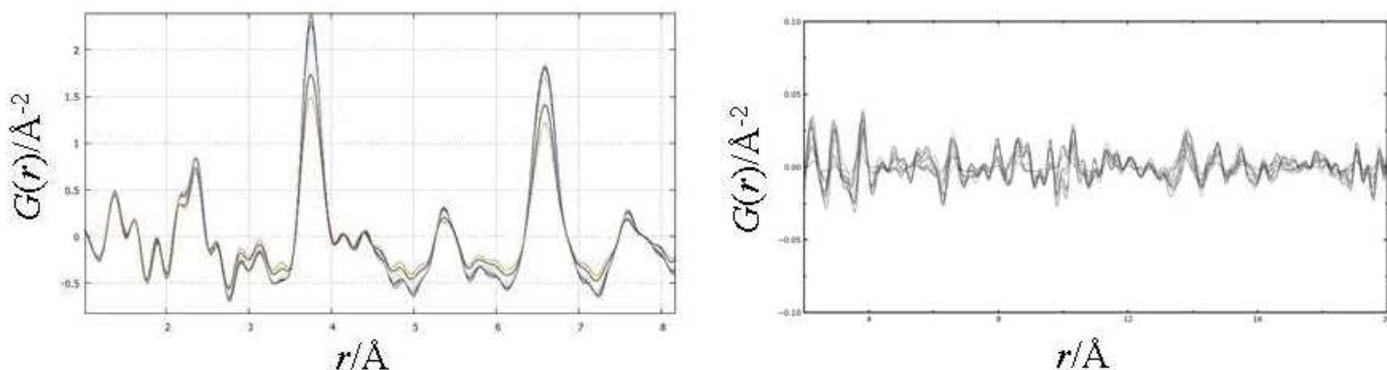
Figure 2. Left: total PDF functions collected at different energies on $Ce_{1-x}Yb_xO_{2-x/2}$, x=7/16 sample. Right: AD-PDF functions on the same sample.

In the left-hand side of figure 2, are shown the PDF functions obtained at different energies on the $Ce_{1-x}Yb_xO_{2-x/2}$, x=7/16 sample. The pertinent anomalous differential PDF functions are shown in figure 2, right-hand side.

REFERENCES
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