



	Experiment title: Local environment of yttrium, cerium and barium in the protonic conductor $\text{BaCe}_{1-x}\text{Y}_x\text{O}_{3-x/2}$	Experiment number: ME-1125
Beamline: BM8	Date of experiment: from: 9/11/2005 to: 13/11/2005	Date of report: 7/12/2005
Shifts: 12	Local contact(s): Dr. Chiara Battocchio	<i>Received at ESRF:</i>
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Report:

Introduction

Barium cerate-based solid electrolytes constitute a class of materials of great interest for SOFC (Solid Oxide Fuel Cell) technology. Perovskite-type cerates show the highest conductivities among protonic conductors in the high temperature range (600-1000 °C) [1]. In particular, yttrium-doped barium cerates, with the general formula $\text{BaCe}_{1-x}\text{Y}_x\text{O}_{3-\delta}$ show the highest conductivity between cerates. The mechanism of proton conduction is determined by the partial substitution of Ce^{4+} with Y^{3+} : charge neutrality is achieved by formation of oxygen vacancies; hydroxyls coming from water dissociation can then be hosted according to the reaction: $\text{H}_2\text{O} + \text{O}^\times_{\text{O}} + \text{V}^\circ_{\text{O}} \rightleftharpoons 2 \text{OH}^\circ_{\text{O}}$. Protons so introduced can migrate between anionic sites by a hopping mechanism enhanced by high temperature [2]. From neutron diffraction analysis on protonated $\text{BaCe}_{1-x}\text{Y}_x\text{O}_{3-\delta}$ [3,4] it is evident that doping of cerium sites with yttrium modifies the structure by peculiar local tilting and distortion of oxygen octahedra. This fact can influence the conduction mechanism, by modifying the O-O distances and therefore the hopping probability of protons between neighbouring anions. XAFS provides a detailed description of the local environment of Y^{3+} and of the way the introduction of doping cations is effective also in modifying the environment of Ce^{4+} and Ba^{2+} . This information will contribute to the elucidation of the mechanism of proton conduction, so far investigated only by molecular dynamics simulations.

Experimental aspects

$\text{BaCe}_{1-x}\text{Y}_x\text{O}_{3-\delta}$ ($x = 0.02, 0.1, 0.2, 0.3$) samples were synthesized by a sol-gel route. The protonated samples obtained after calcination in wet air at 1000 °C of the gels were constituted by a single perovskite-type phase, as demonstrated by Rietveld analysis carried out on laboratory XRD data. The dry samples were then obtained by heating at 800 °C in dry O_2 flux. X-ray absorption experiments on yttrium K-edge (17038 eV) were carried out at the BM8 CRG beamline using both a liquid nitrogen cryostat and a thermochemical cell for *in situ* measurements [5]. Reference sample of Y_2O_3 was measured at LN temperature in transmission mode. The barium cerate samples with $x = 0.1, 0.2, 0.3$ were measured in transmission mode. The 2%-doped

samples were measured in fluorescence mode with dynamical focusing, using a high-purity 13-elements Ge detector. In order to elucidate the structure under operating conditions, *in situ* measurements were made at 480 °C, both in dry O₂ and in wet O₂ flux. Finally, to investigate the structural modifications due to protonation, the dry 10%-doped sample was treated *in situ* with wet O₂ at 480 °C, and the XAS spectrum was taken at LN temperature.

Results

Raw absorption data was analyzed using GNXAS package [6], simultaneously fitting structural parameters and atomic background, and taking into account multiple electron edges. In all samples, yttrium environment is axially distorted, with four O atoms at about 2.24 Å, and two other O atoms at about 2.35 Å (fig. 1 & 2) [7]. The distance splitting is increased upon hydration. The Debye-Waller factors of the four nearest oxygens also increase with increasing water content, while the other two remain unchanged. These results point out that the protons reside in the vicinity of nearest oxygen atoms, locally perturbing the yttrium environment.

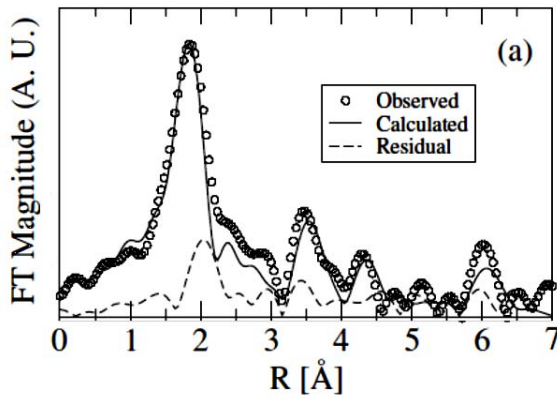


Fig 1 - EXAFS data and fitting for dry BaCe_{0.98}Y_{0.02}O_{3-δ} assuming a regular octahedral environment

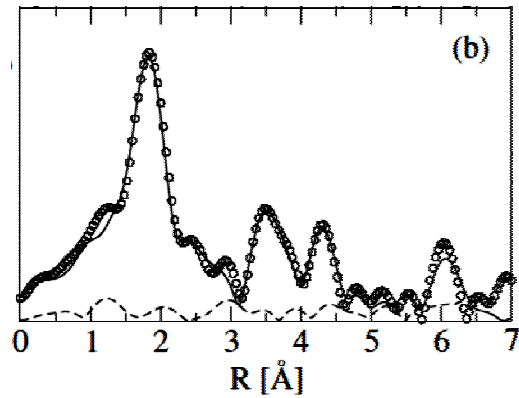


Fig 2 - EXAFS data and fitting for dry BaCe_{0.98}Y_{0.02}O_{3-δ} with a distorted octahedral environment

It is worth of notice that the splitting effect is retained in near-operative condition also, as the high-temperature EXAFS spectrum shows (fig. 3), suggesting that proton-dopant clustering is still effective. The effect of proton insertion on the second and third shells is even more striking (fig. 4): while the interatomic Y-Ba and Y-M (with M=Ce,Y) distances are only slightly elongated with increasing proton content, the Debye-Waller factors are largely affected. As an example, in re-hydrated samples, with maximum proton content, the variance associated with Y-O-M angles (corresponding to corner-sharing octahedra) is as high as 20 degrees.

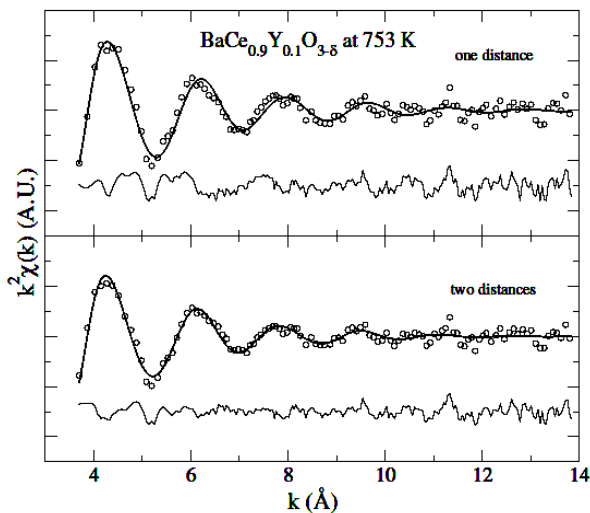


Fig. 3 - Axial-equatorial distortion in BaCe_{0.9}Y_{0.1}O_{3-δ} at high temperature.

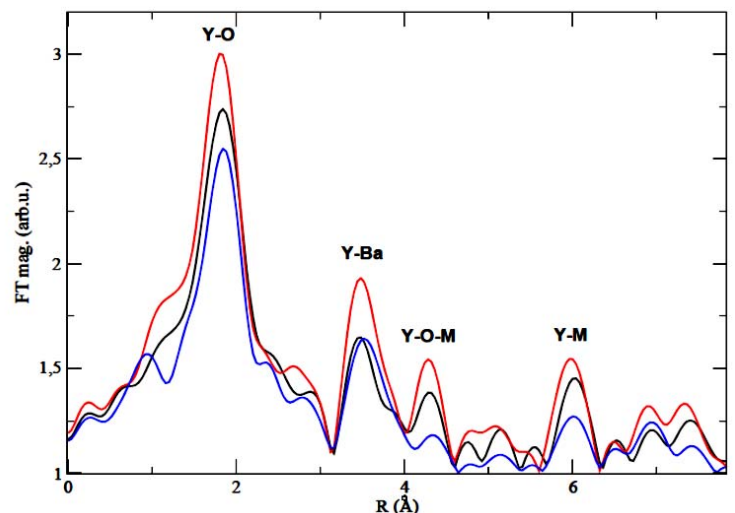


Fig. 4 - EXAFS data of fresh (black), dry (red) and rehydrated (blue) BaCe_{0.9}Y_{0.1}O_{3-δ}

References

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