

Report experiment MA-4582

Background

Perovskite materials with with Ba, Sr, La on the A site and Fe, Zn, Y, Zr on the B site are potential cathode materials for protonic ceramic fuel cells (PCFC). However, their proton uptake (only max. 1/10 of oxygen vacancies hydrated) is still much lower than for Y-doped BaZrO₃ electrolyte materials (fully hydrated at T≤300°C). Using defect chemical analysis, we recently elucidated the importance of the covalency of the TM-O bonds and defect interactions (hole-hole and proton-hole) for proton uptake.

For (Ba,Sr,La)(Fe,Zn,Y)O_{3.δ} perovskites, this interpretation is supported by recent XRS (X-ray Raman Scattering) and EXAFS results [1] obtained from the experiments MA-4144 and MA-4015. We extended our experimental work to the BaZr_{0.88-x}Y_{0.12}Fe_xO_{3.δ} solid solution series. In these materials, even 10% of iron drastically decrease the protonation, transitioning from an electrolyte-like to cathode-like behavior. These experimental results will be complemented with the one from XRS O-K edge [2] to have a comprehensive understanding on local lattice distortions and electronic modification around the perovskites' B-cations.

Experimental details

We measured 11 samples in total for each edge: BaZr_{0.88-x}Y_{0.12}Fe_xO_{3.δ} (x=0, 0.06, 0.1, 0.3, 0.7) and BaZr_{0.2}Fe_{0.8}O_{3.δ} oxidized and reduced.

All the samples were measured at the Fe K-edge using SrFeO_{3.5} in the oxidized and reduced form, Fe₂O₃ as a standard for Fe⁴⁺ and Fe³⁺. Additionally Zr- containing and Y-containing samples were measured at the Zr-edge and Y-edge using YSZ (17%Y) as a standard.

The samples were measured in the form of pressed pellet (composition of interest+cellulose matrix) in a cryostat at 10 K. Most of the measurement are performed in transmission mode, except for the Fe K-edge of low iron containing samples (x=0.06-0.1) which are performed in fluorescence mode.

The energy resolution in the XANES region is of ≈0.2eV; in the EXAFS region we acquired until k≈20 Å⁻¹ for the iron and zirconium and until k≈15 Å⁻¹ for the yttrium.

We acquired 2-4 scan per sample in transmission and 4-10 scan for the samples in fluorescence.

Fe K-edge

In Fig.1 e Fig.2 the XANES and the FTs of all the oxidized and reduced samples are reported.

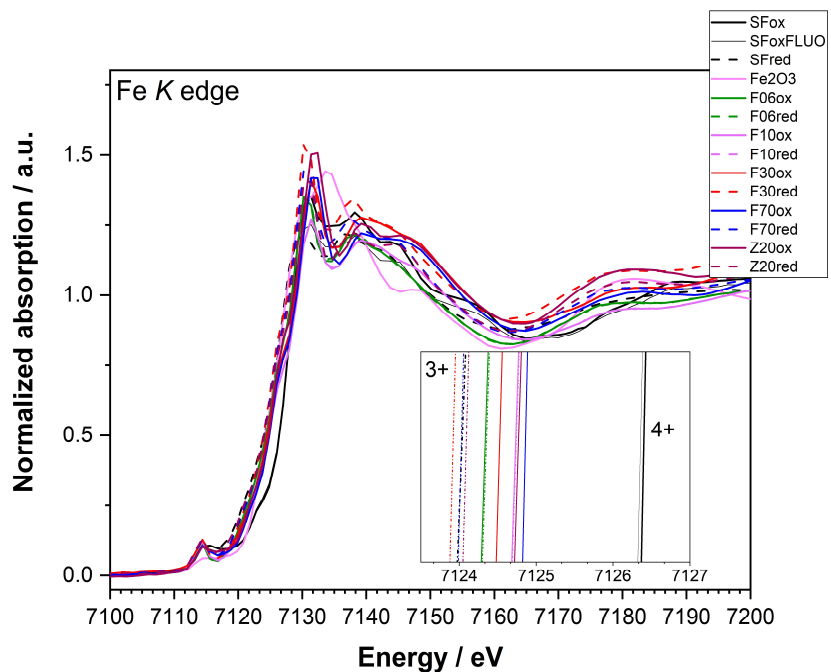


Figure 1 Fe K edge XANES of all the measured samples.

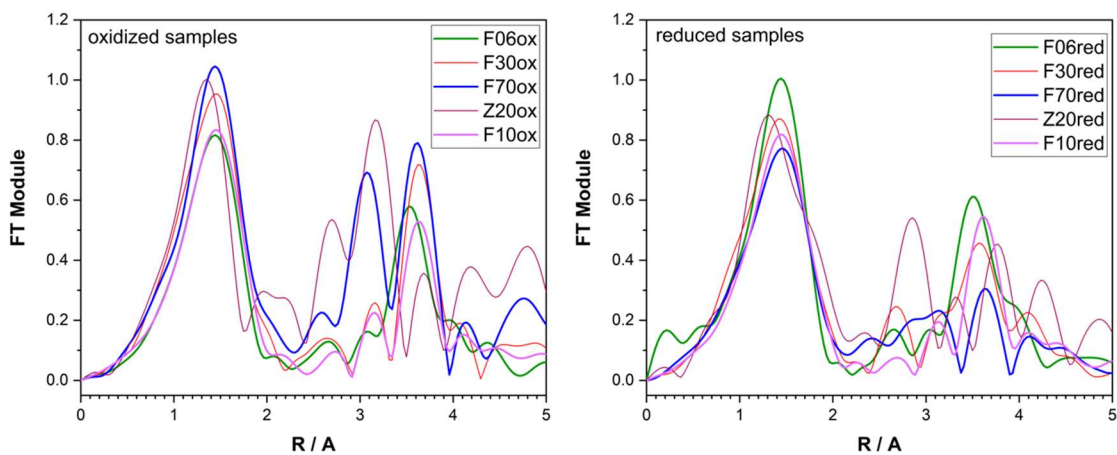


Figure 2 Fe K edge FTs of all the measured samples: oxidized (left) and reduced (right).

Y K-edge

In Fig.3 e Fig.4 the XANES and the FTs of all the oxidized and reduced samples are reported.

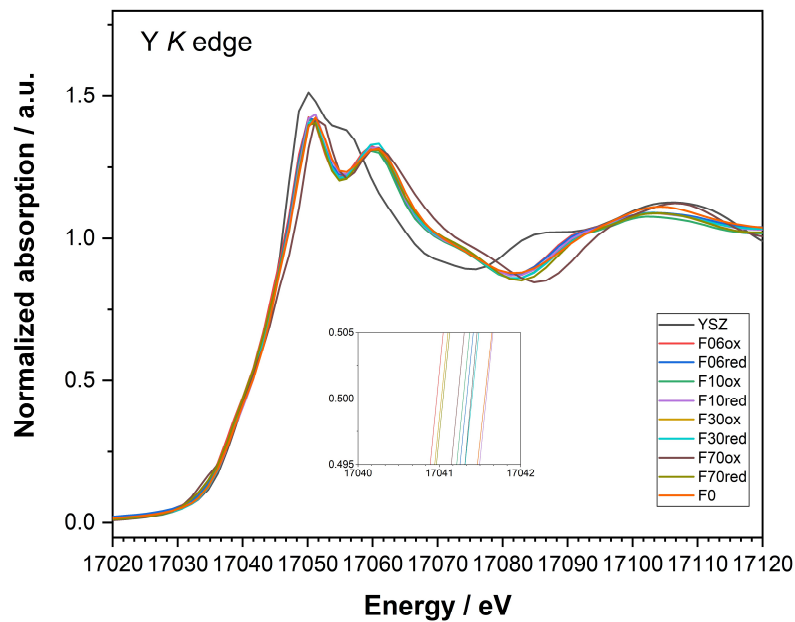


Figure 3 Y K edge XANES of all the measured samples.

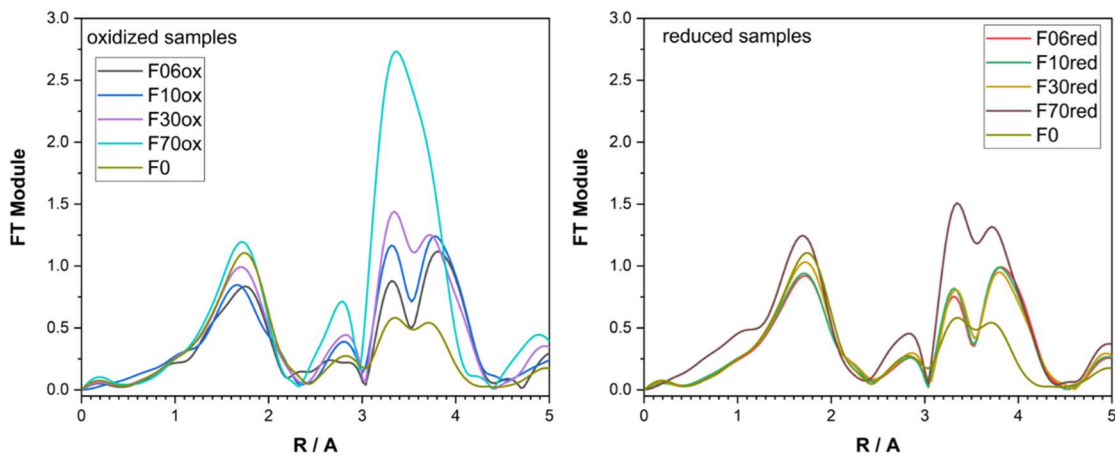


Figure 4 Y K edge FTs of all the measured samples: oxidized (left) and reduced (right).

Zr K-edge

In Fig.5 e Fig.6 the XANES and the FTs of all the oxidized and reduced samples are reported.

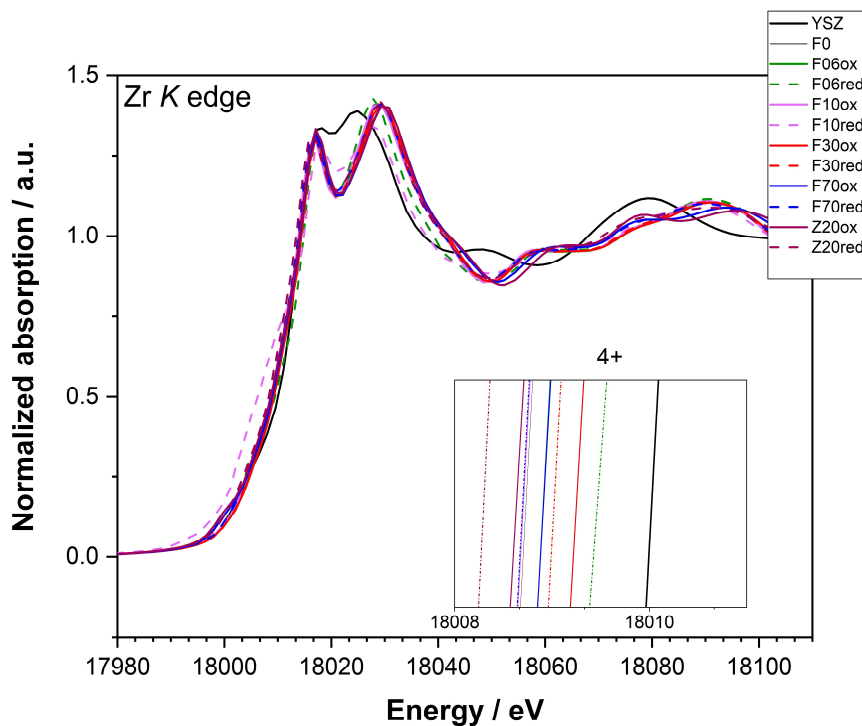


Figure 5 Zr K edge XANES of all the measured samples.

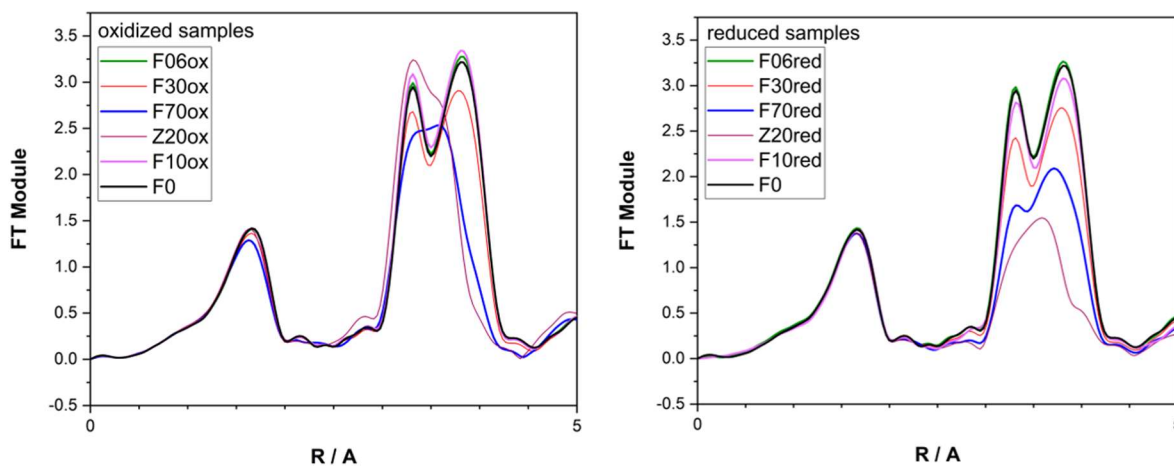


Figure 6 Zr K edge FTs of all the measured samples: oxidized (left) and reduced (right).

Conclusion

The bigger differences appear at the Fe *K* edge and are a function of the iron content. A quantitative fitting of the experimental results will give insights regarding the changes of the iron local environment and the full trends in the studied composition. The combination of the latter with the data at the O *K* edge will allow us to have a comprehensive understanding of the role of the mixed valent dopant in the $\text{BaZr}_{0.88-x}\text{Y}_{0.12}\text{Fe}_x\text{O}_{3-\delta}$ solid solution and how this is correlated to proton uptake and TM-O interaction.

References

- [1] G.Raimondi, F.Giannici, A.Longo, R.Merkle, A.Chicara, MF.Hoedl, A.Martorana, J.Maier. *Chem. Mater.* 2020, 32, 19, 8502-8511.
- [2] Report MA-4681.