Electronic Supplementary Information
Electronic modifications in (Ba,La)(Fe,Zn,Y)O$_{3-\delta}$ unveiled by Oxygen *K*-edge X-Ray Raman Scattering

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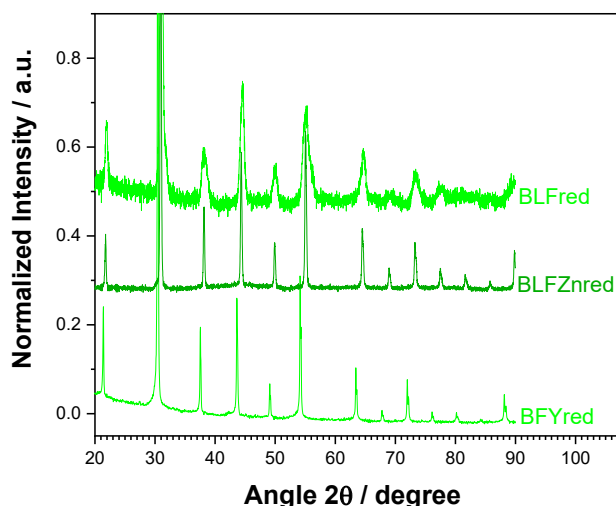
1- Diffractograms of reduced samples

Figure SI 1 X-ray diffractograms of reduced samples, data for BLFred and BLFZnred taken from Ref. [1].

In the XRD in Fig. SI 1b of Ref. 1, the sample labelled "BFYred" accidentally had a different cation composition (BLFZn), the correct diffractogram is now included here (please note that the sample labelled BFYred in XANES/EXAFS spectra in ref. 1 had the correct composition, cf. presence of Y K-edge).

2- *q* dependence of the spectra: an example for BLFox

As mentioned in the main text, signals from analyzer crystals at different scattering angle were measured, covering a momentum transfer from 2.5 to 9.2 ± 0.4 Å^{-1}. The data analysis refers just to the data at high q because of the data quality and S/N ratio. In fact, while *s* and *p* orbitals contribution are better characterized at low and medium *q*, for the *d* orbitals the data at high q are more suitable. For completeness, the q dependence for BLFox is reported in **Figure SI 2**.
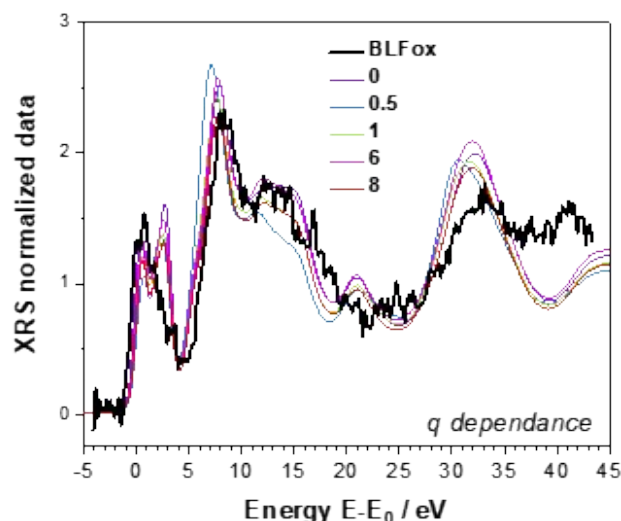
Figure SI 2 Spectra simulated at different *q*-values for BLFox. *Dilatorb* and *screening* values are set to 0.

3- Method validation

In order to validate the method discussed in the section **Calculation scheme** the O *K*-edge simulations obtained from the DFT optimized structure of $BaZrO_3$ and BFYox and the one calculated by using *screening* and/or *dilatorb* have been compared with each other and with the experimental signals. The results are shown in **Figure SI 3**.

The calculations are done using the FDMNES code as described in the main text. The starting structures are $BaZrO_3$ or $BaFeO_3$, both with Pm-3m space group, calculated with the experimental lattice parameter and covering a cluster radius of 8 Å around the absorber atom. When running the calculation, it is possible to include the option of calculating a matrix of *screening* and *dilatorb* values. The DFT calculation reported in **Figure SI 3** are done according the method reported in Ref.[2].
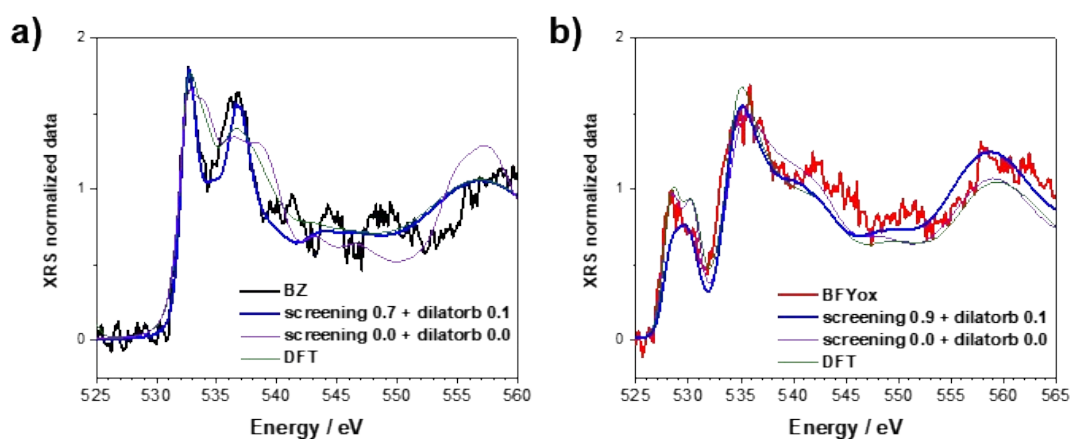

Figure SI 3 O *K*-edge of $BaZrO_3$ (a) and BFYox (b). Comparison of the simulations starting from the DFT optimized structure, and FDMNES with *screening* and *dilatorb*.

Figure SI 3a demonstrates that even for $BaZrO_3$ with empty d orbitals the semiempirical parameter *screening* is required to properly reproduce the features of the O *K*-edge. This apparently reflects a general necessity for the modelling of perovskites with a B cation in formal 4+ oxidation state. Note that the value of *screening*=0.7 is larger than 0.6 for BLFox in **Figure 4a**, in line with the larger ionic radius (less polarizing character) of Zr^{4+} compared to Fe^{4+}. Since the *screening* parameter is a correction over the calculation, a comparison within a series of differently doped oxidized samples is expected to be meaningful. However, a comparison of

absolute *screening* values between oxidized (formal Fe^{4+}) and reduced samples (Fe^{3+}) may not be appropriate. These materials strongly differ in their bonding and electronic structure (*cf.* strong difference of O *K*-edge pre- and main peaks) and thus different amounts of correction over the basic calculation level may be required.

4- The case of BFY20red

4.1 Simulation of the O *K*-edge using *screening* and *dilatorb*

Figure SI 4 shows the attempts to simulate the O *K*-edge using different *screening* values. As mentioned in the main text, this methodology fails when more important structural modification are occurring in the system.
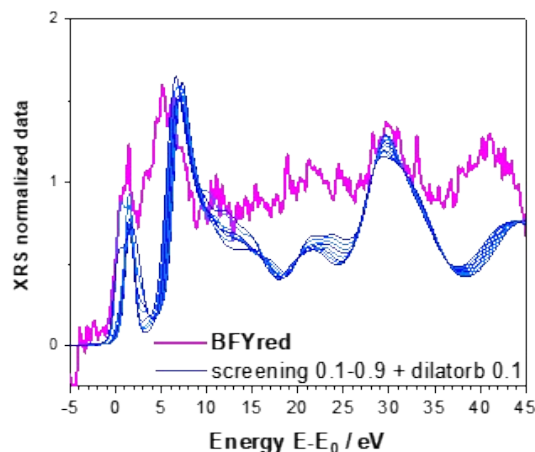

Figure SI 4 O *K*-edge simulation of BFYred applying different values of *screening* and *dilatorb*.

4.2 Methodology eventually used to simulate the O *K*-edge

As stated in the main text, to reproduce the structure that fits the experimental spectrum best, several different oxygen arrangements around the cations have been explored, including an oxygen vacancy in the first coordination sphere.

To keep the procedure as simple as possible, initially only O distortion around the iron was considered. To this aim, different configurations were considered (ideal, A, B, C, D in **Figure SI 5**). Each configuration was obtained by modifying the oxygen coordinates. In this respect the overall oxygen stoichiometry was kept constant (this will affect the jump height of the different simulations). As a first step, we have increased the degree of disorder by increasing the displacement with respect to the ideal crystallographic structure. This was systematically done site by site. Of course, this variation produced a variation in Fe/Y-O distances as well. Finally also the iron and yttrium were slightly moved around their atomic positions. The representative starting configurations, for which different simulations have been performed, are reported in the **Table SI 1**. The barium was kept at its ideal position.

The best simulation (**Figure SI 6**) is approached first by averaging several configurations obtained by slightly modifying the xyz coordinates of the configuration B. After that, a single best configuration was identified by stepwise modifying the coordinates (starting from the initial B coordinates) until it finally reproduced the "best averaged" spectrum. Its xyz coordinates are reported in **Table SI 1** as well.
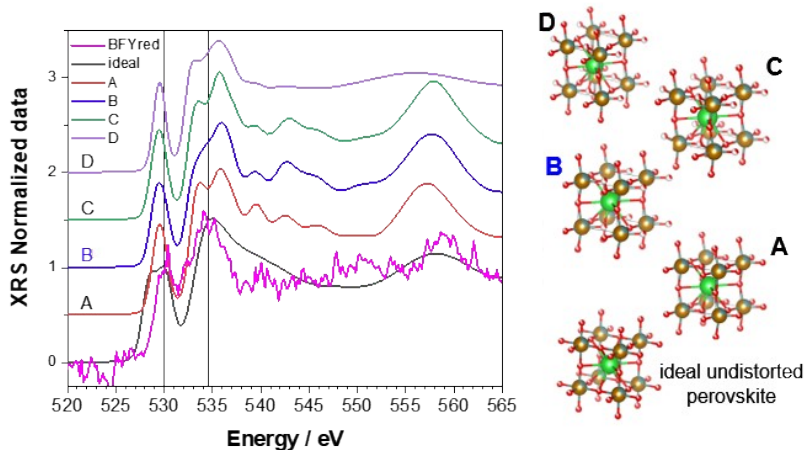
Figure SI 5 O *K*-edge simulations of BFYred using five different configurations: with iron in 6-fold coordination (ideal, D, C) and 5-fold (A, B). Configurations ideal, B, D are the same included in **Figure 5** of the main text.

Table SI 1 Atomic coordinates of the exemplary structures used for calculating the O *K*-edge of BFYred.

Atoms	Occupancy	Ideal positions (In SG#221)			Best			A			B			C			D		
		x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Fe	0.8	0.0	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
O	0.821	0.5	0.0	0.0	0.5	0.35	0.0	0.5	0.25	0.0	0.5	0.3	0.0	0.5	0.25	0.0	0.5	0.2	0.0
O	0.821	0.0	0.5	0.0	0.0	0.5	0.03	0.0	0.5	0.03	0.0	0.5	0.01	0.0	0.5	0.0	0.03	0.5	0.01
O	0.821	0.0	0.0	0.5	0.03	0.0	0.5	0.03	0.0	0.5	0.0	0.0	0.5	0.03	0.0	0.5	0.01	0.0	0.5
Y	0.2	0.	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ba	1.0	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

The configuration A and B are both distorted with the TMs in 5-fold coordination but different buckling angles of the B-O-B connections. This strongly affects the multiple scattering (XANES is very sensitive to it) as is evident in the shape of the two simulated spectra in **Figure SI 5**. The same applies for the configuration C,D which instead have a 6-fold coordination. Given the fact that the simulated spectrum of B is the most similar to the experimental data, this configuration was chosen as the starting one for the additional simulations in **Figure SI 6.**
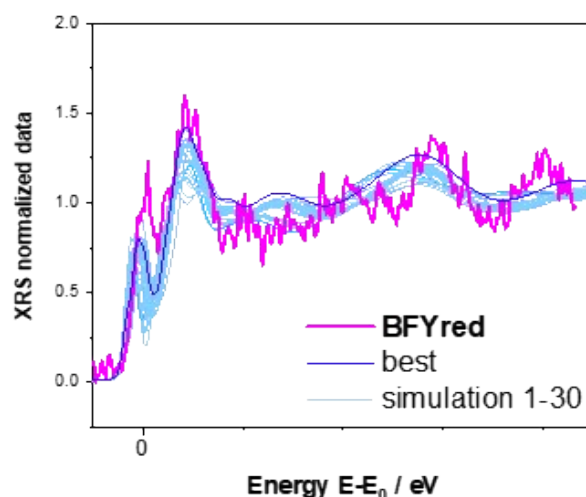
Figure SI 6 BFYred O *K*-edge: best (blue) is the average of 30 simulation (light blue) with iron in 5-fold coordination obtained by slightly modifying the configuration B.

5- Simulation of the Fe *K*-edge XANES using *screening* and *dilatorb*

In **Figure SI 7** an attempt to simulate the iron XANES of BLFox and BFY using *screening* and *dilatorb* is reported. While this method reasonably reproduces the height of the white line of BLFox, it fails in the case of BFY. This agrees with the fact that this correction scheme does not suffice in the case of important structural rearrangements. The iron local environment is, in fact, very disordered for the doped and reduced samples. Moreover, even for BLFox (small modification of the iron local environment) the oscillations after the white line are not well reproduced with only the semi-empirical parameters, therefore using two components, cf. **Section 3.2** of the main text, yields better simulations. For BLFox, it is possible to reproduce the height of the white line using a *screening* value of 0.7 (i.e. 0.3 charge is missing from the iron states) and a *dilatorb* value of 0.1. Therefore, the iron partly retains its charge, but there is some charge transfer to the neighboring O *2p* orbitals. This agrees well with the XANES data reported in Ref.[1] , where it was highlighted that Ba-rich oxidized compositions show an average effective oxidation state of iron lower than 4+.
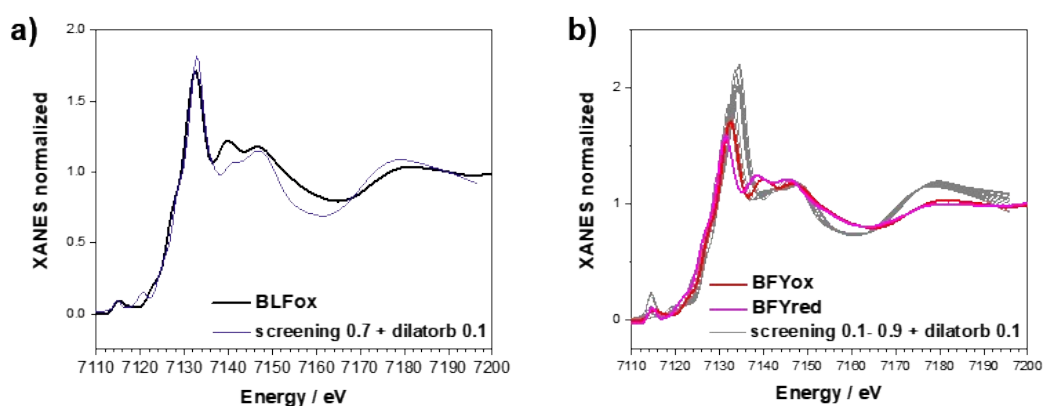

Figure SI 7 Fe *K*-edge simulation of (a) BLFox with *screening* 0.7, *dilatorb* 0.1 (b) BFYox and BFYred. In panel b, different *screening* values in the range 0.1-0.9 are applied, but they all fail to reproduce the height of the white line.

References
[1] G. Raimondi, F. Giannici, A. Longo, R. Merkle, A. Chiara, M.F. Hoedl, A. Martorana, J. Maier. *Chem. Mater.* 2020, **32**, 8502.

[2] M. F. Hoedl, D. Gryaznov, R. Merkle, E. A. Kotomin, J. Maier. *J Phys. Chem. C* 2020. **22**, 11780.