Electronic Supplementary Information for

"Oxidation states of the transition metal cations in the highly nonstoichiometric perovskite-type oxide $Ba_{0.1}Sr_{0.9}Co_{0.8}Fe_{0.2}O_{3-\delta}$"

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Experimental Details - Preparation of powder samples

For synthesis of the BSCF powder, the combustion route was employed,[S1] utilizing urea as fuel. The appropriate amounts of metal nitrates ($Ba(NO_3)_2$ [Merck, 99%], $Sr(NO_3)_2$ [Merck, 99%], $Fe(NO_3)_2$*9 H_2O [Merck, 99%] and $Co(NO_3)_3$*6 H_2O [Alfa Aesar, 97.0%]) were ground together; urea [Merck, 99.9%] was then added; and the mixture was ground again in an agate mortar till a purple gel was formed. The gel was heated to $T = 523$ K, after which the combustion takes place. The green powder was subsequently calcined at $T = 1273$ K for 24h. Phase purity was confirmed by X-Ray Diffraction measurements.

Experimental Details - XAS

The XAS experiments were performed at beamline C (storage ring DORIS, HASYLAB@DESY, Hamburg, Germany). The storage ring operates at 4.5 GeV with a maximum current of 140 mA. Measurements at the Fe and Co K-edges were carried out in transmission XAS geometry with ionisation chambers as detectors. The Si (111) double crystal monochromator is equipped with an optical angle encoder (Renishaw plc.) for higher accuracy and reproducibility of the energy scale. For filtering higher harmonics the monochromator was detuned to 70 % of the maximum intensity by using a D-MOSTAB (digital monochromator stabilization system). Energy calibration of the monochromator was done by measuring a Co reference foil and setting the first inflection point to the literature value of 7709 eV.

The measurements were split up into two parts. First, cobalt and iron reference samples with well known oxidation states (CoO, Co_3O_4, FeO, Fe_2O_3 and $SrFeO_{2.86}$) were measured; second, the BSCF samples were measured under *in situ* conditions in a special developed XAS furnace[S2] at temperatures between 783 and 918 K and oxygen partial pressures between 50 and 2×10^4 Pa. In all cases only the XANES region of the spectra was measured with a high energy resolution ($\Delta E = 0.25$ eV). Each data point was collected for 1 s and several scans were averaged to improve statistical quality. The spectrum of a Co foil was measured simultaneously as a reference for alignment of the energy scale. The calibration curves obtained from the standards are shown in Fig. S1. Edge positions were defined as the energy at half the step height of the normalised curves.

For Fe we obtain (3.66 ± 0.15) eV / unit oxidation state. The difference between our calibration curve and that determined by Blasco *et al.* [S3] comes about because they used the energy at a (not specified) point of inflection. If we use the same procedure as Blasco *et al.*, i.e., use a point of inflection, then we obtain for our standards (1.90 ± 0.19) eV / unit oxidation state. In other words, we obtain a similar value, but with a much larger relative error. Thus, our method has the benefit of being more sensitive (3.66 vs. 1.90 eV / unit oxidation state) and with a lower relative error (4% vs. 10%). No data are available for Co.

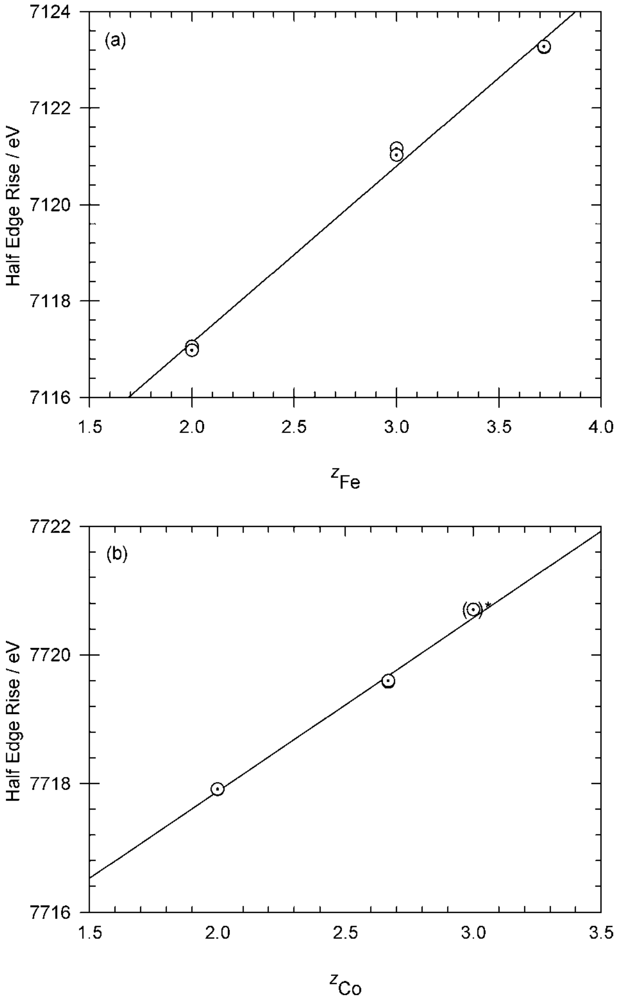

Fig. S1: Calibration curves for (a) Fe, determined from FeO, Fe_2O_3 and $SrFeO_{2.86}$ and for (b) Co, determined from CoO, Co_3O_4 and $LaCoO_3$ (taken from the Literature[S4] and indicated in the figure by an asterisk). Edge positions were defined as the energy at half the step height of the normalised curves.

The measured samples were well ground powders. For getting the required powder amount for the sample holder, the samples were diluted with boron nitride powder (Aldrich, purity: > 99 %). In each case 5 mg of BSCF1982 was mixed with 40 mg of BN and filled into the sample holder consisting of MACOR ceramics. In front of and behind the samples BN windows were used to hold the powder arrangement in place. Transport of the gases to the powder particles was ensured by holes in the sample holder.

Data was analysed with the program Athena[S5], according to the standard procedures.[S6] The raw data was smoothed with a 3-point adjacent averaging cycle with two iterations. The energy scale was aligned to the first inflection point of the Co reference spectrum with $E_0(\mathrm{Co}) = 7709$ eV. For normalization the pre-edge range of the spectra were fitted by a linear function and the post-edge range by a polynomial of third degree and subtracted from the spectra. Edge positions of the reference and BSCF spectra were defined as the energy at half the step height of the normalised curves. We did not use points of inflection, because determining points of inflection for the BSCF spectra was not a simple procedure on account of the lower signal to noise ratio of the high temperature *in situ* data. In contrast, the energy at half the step height of the normalised curves could be identified unambiguously.

Experimental Details - TG

Thermogravimetric measurements were conducted on a Setsys 16/18 thermobalance (Setaram, France).

The oxygen release experiments were carried out at constant $p\mathrm{O}_2$ and heating with a temperature ramp of 1 K min^{-1} from 723 to 973 K. To ensure that the heating ramp rate was sufficiently slow to be comparable to data from static experiments, a control experiment was conducted with a ramp rate of 0.5 K min^{-1}; these data showed no difference to the main experiment. Buoyancy correction was done by repeating the above described experiments with the same mass of Al_2O_3 instead of BSCF and subtracting the resulting mass change from TG-Data of the experiment.

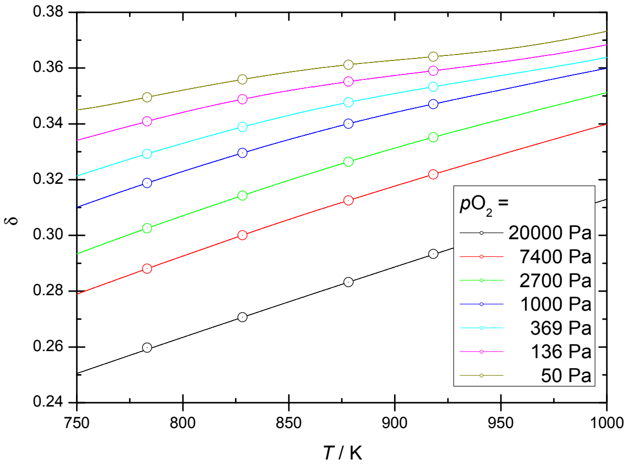

Fig. S2: Oxygen nonstoichiometry δ as a function of temperature *T* for different pO_2 obtained by heating with 1 K min^{-1}. The excerpted data points used for comparison to XAS data are marked with open circles.

In Fig. S2 we show δ as a function of *T* for different pO_2 with the data points extracted for comparison to the XAS-data highlighted. δ was calculated using the value for δ obtained from the total reduction as a reference point.

The total reduction was performed on 100 mg of BSCF1982 powder, previously calcined for 8h at 1273 K in air, with 5% Hydrogen (Messer, 99.9%) diluted in Nitrogen (99.999%) as reducing agent at a temperature of 1273 K. The reduction was performed in several steps: at first the chamber of the TG with the introduced sample was evacuated to evaporate any adsorbed water on the sample or the crucible. Then, the chamber was flushed with a mixture of 20% O_2 (Messer, 99.999%) in Nitrogen and the balance was tared. After flushing the chamber with Nitrogen to prevent the formation of explosive gas mixtures, the sample was heated with a ramp of 10 K min^{-1} in a flow of 5% Hydrogen diluted in Nitrogen to 1273 K. The temperature was kept for 2h to assure the completeness of the reduction reaction, which is observed as a plateau in the mass signal. The cooling was done with a ramp of 10 K min^{-1} in 5% Hydrogen in Nitrogen. After reaching room temperature, the gas flow was changed to Nitrogen to purge any residual Hydrogen from the chamber and thereafter the flow was changed to 20% Oxygen in Nitrogen.

As temperature and atmosphere was the same for the starting and the end point of the reduction process, no buoyancy correction was required. The above described program was done with the same mass of Al_2O_3 to obtain the overall drift of the balance which resulted in an error in δ of +/-0.003.

The absolute value of δ was determined assigning the mass loss to the released oxygen of the reaction

$$\left(2-\delta\right)\mathrm{H_2} + \mathrm{Ba_{0.1}Sr_{0.9}Co_{0.8}Fe_{0.2}O_{3-\delta}} \rightarrow 0.1\mathrm{BaO} + 0.9\mathrm{SrO} + 0.8\mathrm{Co} + 0.2\mathrm{Fe} + \left(2-\delta\right)\mathrm{H_2O}$$

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S2. D. Samuelis, Ph. D. thesis, RWTH Aachen University, 2008.

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S5. B. Ravel, M. Newville, *J. Synchrotron Rad.*, 2005, **12**, 537.

S6 D. C. Koningsberger, R. Prins, in *X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES*, Wiley-Interscience, New York, 1988.