Three - coordinate metal centres in extended transition metal oxides

Amy Bowman,[†] Mathieu Allix,[†] Denis Pelloquin[‡] and Matthew J. Rosseinsky^{*†}.

[†]Department of Chemistry, University of Liverpool, Liverpool, L69 7ZD, U.K and [‡]Laboratoire CRISMAT-ENSICAEN, UMR6508, 6 Bd du Maréchal Juin, 14050 Caen Cedex, France.

Synthesis

Sr₃LaFe_{1.5}Co_{1.5}O_{10.1} (I)

La₂O₃ (Alfa Aesar, 99.999%), SrCO₃ (Alfa Aesar, 99.994%), Fe₂O₃ (Alfa Aesar, 99.998%) and Co₃O₄ (Alfa Aesar, 99.9985%) were ground together in the required molar ratios, pelleted and fired at 1100°C for 14h, 1400°C for 20h and after regrinding a further 12h.

H₂ reduction (II)

Sr₃LaFe_{1.5}Co_{1.5}O_{10.1} was heated under flowing 5% H₂/N₂ for 14h at 450°C (to form **II**).

CaH₂ reduction (III)

Caution: synthetic procedure results in the generation of over-pressures of hydrogen in sealed tubes. Wear eye protection and handle with extreme care.

Sr₃LaFe_{1.5}Co_{1.5}O_{10.1} (1g) was ground together with CaH₂ (90-95%, Aldrich) in a 1:3 molar ratio (to form **III**) in a He filled glovebox. A pyrex tube (12mm diameter x 25.5cm length) was charged with the mixtures and sealed under vacuum. The ampoule was heated at 450 °C for 24h. The sample was washed with 0.1M NH₄Cl/MeOH (3 x 75mL) and rinsed with MeOH (2 x 50mL) to remove any remaining CaH₂ and the CaO formed.

Samples were initially characterised with Co K α ₁ radiation using a Panalytical X'Pert diffractometer equipped with an X'Celerator detector.

Table S1. Cell parameters for samples I, II and III.

	a/Å	c/Å	V/Å ³
Sr ₃ LaFe _{1.5} Co _{1.5} O _{10.1} I	3.8386(2)	27.850(2)	410.36(5)
Sr ₃ LaFe _{1.5} Co _{1.5} O _{8.25} II	3.8558(4)	29.134(3)	433.2(1)
Sr ₃ LaFe _{1.5} Co _{1.5} O _{7.5} III	3.816(1)	29.30(1)	426.7(3)

TGA

Thermogravimetric data were collected using a Seiko SII TG/DTA 6300 instrument. The starting material **I** LaSr₃Fe_{1.5}Co_{1.5}O_{10.1} was heated under 5% H₂/N₂ on the TGA at a rate of 5°Cmin⁻¹. The reduced materials **II** and **III** were heated under an O₂ flow at a rate of 15°Cmin⁻¹ to 800°C and then cooled to room temperature at the same rate.

Figure S1. (a) Reduction of $\text{Sr}_3\text{LaFe}_{1.5}\text{Co}_{1.5}\text{O}_{10+\delta}$ under 5% H_2/N_2 . The plateau at $\sim 500\text{-}800^\circ\text{C}$ corresponds to composition $\text{Sr}_3\text{LaFe}_{1.5}\text{Co}_{1.5}\text{O}_{8.25}$ (average o.s. +2.5). The compound was not completely reduced in flowing O_2 at 1100°C (XRD showed SrO , SrLaFeO_4 , La_2O_3 , Fe and Co). (b) Oxidation of III $\text{Sr}_3\text{LaFe}_{1.5}\text{Co}_{1.5}\text{O}_{10-y}$ (reduced by CaH_2) – $y=2.5$ (mean metal oxidation state +2) (c) Oxidation of II $\text{Sr}_3\text{LaFe}_{1.5}\text{Co}_{1.5}\text{O}_{10-y}$ (reduced with H_2)- $y=1.75$ (mean metal oxidation state +2.5)

In-situ XRD

Data were recorded on a capillary containing **I** and CaH_2 on station 9.1 of the Daresbury SRS.

Figure S2. The reaction between $\text{Sr}_3\text{LaFe}_{1.5}\text{Co}_{1.5}\text{O}_{10.1}$ and 3 molar equivalents of CaH_2 monitored in situ by X-ray diffraction. The capillary was heated at $1.5^\circ\text{Cmin}^{-1}$.

X-ray absorption spectroscopy

X-ray absorption data were collected on station 7.1 at the SRS in $\sim 0.5\text{eV}$ steps across the Co and Fe K edges. The samples used were the Co oxidation state standards, NdSrCoO_4 (+3) and La_2CoO_4 (+2), the Fe oxidation state standards, LaFeO_3 (+3) and FeSO_4 (+2), $\text{Sr}_3\text{LaFe}_{1.5}\text{Co}_{1.5}\text{O}_{10.1}$ and $\text{Sr}_3\text{LaFe}_{1.5}\text{Co}_{1.5}\text{O}_{10-y}$ **III** (Figure S3(a) Fe (b) Co edges, Table S2).

Figure S3. X-ray absorption spectra at (a) Fe K and (b) Co K edges

Table S2. Fe K and Co K XAS edges. The edge position was determined by measuring the position of the first-derivative maximum. The edge is marked as broad when the maximum covers >0.5eV.

	Fe edge (1 st derivative) (eV)	Co edge (1 st derivative) (eV)
FeSO ₄ +2	~7119 v. broad	
LaFeO ₃ +3	7123.2	
Sr ₃ LaFe _{1.5} Co _{1.5} O _{10.1} I	7124.15	7720.38
Sr ₃ LaFe _{1.5} Co _{1.5} O _{7.5} III	7122.73	7713.8 broad

Transmission electron microscopy (TEM)

Samples for transmission electron microscopy were prepared by crushing the powder in *n*-butanol and the small crystallites in suspension were deposited onto a holey carbon film, supported by a copper grid. The electron diffraction (ED) study was carried out with a JEOL 2000FX electron microscope. Energy dispersive spectroscopy (EDS) analyses were systematically carried out during the ED study, the JEOL 2000FX being equipped with EDAX analyser. High-resolution electron microscopy (HREM) was performed with a TOPCON 002B microscope operating at 200kV and having a point resolution of 1.8Å. The HREM theoretical images were calculated using the JEMS program¹ and the multi-slice module, varying the focus values and crystal thickness and using the atomic positions obtained from the neutron powder refinement.

Sr₃LaFe_{1.5}Co_{1.5}O_{7.5}

The sample was well crystallised. The reconstruction of the reciprocal space was carried out by tilting around the *c** axis. It showed a quadratic lattice with *a* ≈ 3.8Å and *c* ≈ 29Å. The general condition *h*+*k*+*l*=2*n* was observed while no extra conditions limiting the reflections could be seen, which is compatible with the *I4/mmm* space group symmetry.

Numerous crystals of **I** and **III** were selected in the batch in order to determine the actual cationic composition. EDS analysis of the starting material **I** is in good agreement with the LaSr₃Fe_{1.5}Co_{1.5} formula as no deviation was observed from this composition, according to the precision of the technique. Moreover, the reduced samples **III** did not show any variation either.

HREM – Sr₃LaFe_{1.5}Co_{1.5}O_{7.5} **III**

The stacking mode after the reduction with CaH₂ was checked using HREM techniques. One characteristic HREM image recorded along to the main [100]_p direction is shown in Figure 2. These image contrasts have been recorded with focus close to the Scherzer value for which the low electron density rows are displayed as bright dots. A regular structure built from seven layers is clearly observed near the crystal edge: the two lightened layers as bright dots spaced by *a*_p along [010] direction and shifted by *a*_p/2 along *c* axis can be correlated to two successive [AO] RS-type layers. These blocks, 2.7 Å thick, are spaced by thicker blocks, ~11.5 Å, of five layers (chessboard of bright and grey dots) along the *c* axis. Such image contrasts are characteristic of an intergrowth between a triple perovskite block and one rock salt layer related to the *n* = 3 term of the RP series^{2, 3} (see structural model, Figure 1(a)).

In the thicker part of the crystal, some bright dots (white arrows Figure 2) can be observed in the middle of the perovskite block especially at the level of intermediate [Fe_{0.5}Co_{0.5}O_x] layer. Taking into account the experimental defocus value and their intensity compared to those observed in the [La/SrO]RS-type layers, we can claim that these dots are mainly correlated to the large number of vacancies expected in the BO_x layers.

Image contrasts have been simulated from refined atomic positions and occupation sites (see powder neutron diffraction section). The corresponding image (inset

in Figure 2) fits well with the experimental one and validates the model especially the unusual $[100]_p$ oriented triangular coordination $[\text{O}_2(\text{Fe}_{0.5}\text{Co}_{0.5})-\text{O}-(\text{Fe}_{0.5}\text{Co}_{0.5})\text{O}_2]$ identified in the middle of the triple perovskite block (Figure 1(c))

Powder neutron diffraction

$\text{Sr}_3\text{LaFe}_{1.5}\text{Co}_{1.5}\text{O}_{7.5}$ **III** was sealed in a He-filled vanadium can. Variable temperature neutron diffraction data were collected on the D20 instrument (take off angle 120° - high resolution, $\lambda = 1.88\text{\AA}$). At room temperature **III** is antiferromagnetic. The sample was heated in the furnace to 170°C at a rate of $1.5^\circ\text{Cmin}^{-1}$. At this temperature all the magnetic peaks had disappeared. Figure S4 shows the Rietveld fit to the data collected at 170°C . The Rietveld refinement ($\chi^2 = 1.06$) compares well with the model-independent LeBail fit ($\chi^2 = 1.05$). The extensive refined disorder in the oxygens in the *ab* plane coordinating to Fe/Co1 does produce some anisotropy in the displacement parameters on the metal site. The anisotropic displacement parameters for Fe/Co1 are two times larger in the *ab* plane (0.043(6)) than along *c* (0.021(9)), however the esd is large and the difference is only $\sim 2\sigma$. Displacement of Fe/Co1 from the (0,0,0) position to for example (x,y,0) did not produce a stable Rietveld refinement.

The interpretation of the Fe/Co2 coordination environment given in the text and Figure 1(c) as five coordinate is not the only possible interpretation of the refined scattering density – the mean coordination number of 5 could be an average of locally four-coordinate (rectangular; 2x Co2-O1, 1xCo2-O2, 1xCo2-O3) and six-coordinate. The bond valence sums in the three possible cases are shown below, and provide some support for the idea that five coordination is preferred in this case, given that the six coordinate site would require Fe^{+3} to be present, at variance with the XAS results. This problem can only be fully resolved with a dedicated diffuse scattering study. It should be noted that the depiction of the relative location of the anion vacancies at neighbouring Fe/Co2 sites within a trilayer in Figure 1(c) is not constrained by symmetry, and three other relative locations of the anion vacancies in the basal plane are possible within the average $I4/mmm$ symmetry.

Coordination number	4	5	6
BVS with Fe^{2+} parameters	1.77	2.38	3
BVS with Co^{2+} parameters	1.58	2.12	2.67

The discussion in the text focuses on the 68% of Fe/Co1 sites that have no O5 neighbour at (0,1/2,0) i.e the original equatorial anion position in the starting material. As the O4 site is 5.5% occupied and 6.25% occupancy corresponds to one O4 position per metal site, 12% of the Fe/Co1 sites have no O4 neighbour and one O5 neighbour (i.e 3 coordinate but with O5 rather than O4 in the coordination sphere in the basal plane), and 20% of the Fe/Co1 sites have both O4 and O5 neighbours. Due to the extensive positional disorder associated with O4, it is possible to identify two chemically sensible O4-Fe/Co1-O5 bond angles in the equatorial plane of $148(1)^\circ$ and $121(1)^\circ$, but the structure may be relaxed considerably away from this average picture at the small number of metal sites in question.

Figure S4. Observed (red crosses), calculated (green line) and difference plot for $\text{Sr}_3\text{LaFe}_{1.5}\text{Co}_{1.5}\text{O}_{7.5}$ **III**. Data collected at 170°C (above the Néel temperature). The positions of the reflections are shown with black tick marks.

Table S3. Structural parameters for $\text{Sr}_3\text{LaFe}_{1.5}\text{Co}_{1.5}\text{O}_{7.5}$ **III**.

$\text{Sr}_3\text{LaFe}_{1.5}\text{Co}_{1.5}\text{O}_{7.5(1)}$ III	
D20 170°C	
space group	I 4/m m m
a , Å	3.8242(1)
c , Å	29.327(1)
V , Å ³	428.88(4)
La/Sr1 (0,0,z)	z 0.5758(3)
La/Sr2 (0,0,z)	z 0.7029(2)
Fe/Co1 (0,0,0)	
Fe/Co2 (0,0,z)	z 0.1431(3)
O1 (0,½,z)	z 0.1373(3)
O2 (0,0,z)	z 0.0609(2)
O3 (0,0,z)	z 0.2137(3)
O4 (x,y,0)	x 0.264(9)
	y 0.44(1)
O5 (½,0,0)	
wRp	0.0377
Rp	0.0298
χ^2	1.06

Table S4. Atomic displacement parameters for Sr₃LaFe_{1.5}Co_{1.5}O_{7.5} III.

	Fractional occupancy	U _{iso} /U _{aniso} (Å ²)		
		U _{iso} /U ₁₁	U ₂₂	U ₃₃
La/Sr1	1	0.021(1)		
La/Sr2	1	0.021(1)		
Fe/Co1	1	0.043(6)	0.043(6)	0.021(9)
Fe/Co2	1	0.015(3)	0.015(3)	0.018(4)
O1	0.76(1)	0.056(4)	0.007(3)	0.013(5)
O2	1	0.061(4)	0.061(4)	0.028(7)
O3	0.96(2)	0.015(2)		
O4	0.054(5)	0.015(2)		
O5	0.08(1)	0.015(2)		

Titration

The average transition metal oxidation state in **II** was determined by iodometric titration carried out under argon. The samples (20-60mg) were dissolved in 0.1M HCl (100mL) using an ultrasound bath. For the iodometric titrations an excess of KI was added. The I₂ formed was then titrated with Na₂S₂O₃ solution using starch as an indicator. The average of 3 measurements is quoted in each case.

Iodometric titration **II** Sr₃LaFe_{1.5}Co_{1.5}O_{8.28}

References

- (1) Stadelmann, P. *JEMS*, 3.0406W2006; CIME-EPFL: Switzerland, 1999-2006.
- (2) Barrier, N.; Pelloquin, D.; Nguyen, N.; Giot, M.; Bouree, F.; Raveau, B., *Chemistry of Materials* **2005**, 17, (26), 6619.
- (3) Pelloquin, D.; Hadermann, J.; Giot, M.; Caignaert, V.; Michel, C.; Hervieu, M.; Raveau, B., *Chemistry of Materials* **2004**, 16, (9), 1715.