Supporting Information

Rhodium-containing oxide-hydrides: covalently stabilized mixed-anion solids.

Lun Jin, and Michael A. Hayward*

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1. Preparation of $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Rh}_{0.5}\text{O}_4$ and $\text{LaSrCo}_{0.5}\text{Rh}_{0.5}\text{O}_4$.

Samples of $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Rh}_{0.5}\text{O}_4$ and $\text{LaSrCo}_{0.5}\text{Rh}_{0.5}\text{O}_4$ were prepared by a high-temperature ceramic method. Suitable stoichiometric ratios of La_2O_3 (99.999%, dried at 900 °C), SrCO_3 (99.994%), Rh_2O_3 (99.99%, dried at 800 °C), MnO_2 (99.997%) or Co_3O_4 (99.9985%) were ground together using an agate mortar and pestle, transferred into an alumina crucible, and then heated at a rate of 1 °C min⁻¹ to 1000 °C in air to decompose the carbonate. Samples were then reground, pressed and into 13 mm diameter pellets. Samples of $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Rh}_{0.5}\text{O}_4$ were heated for 3 periods of 48 hours at 1300 °C in air, with grinding between heating periods. Samples of $\text{LaSrCo}_{0.5}\text{Rh}_{0.5}\text{O}_4$ were heated for 3 periods of 48 hours at 1300 °C under flowing oxygen, with grinding between heating periods. It was observed that heating $\text{LaSrCo}_{0.5}\text{Rh}_{0.5}\text{O}_4$ samples in air led to the formation of perovskite impurity phases.

2. Structural characterisation of $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Rh}_{0.5}\text{O}_4$ and $\text{LaSrCo}_{0.5}\text{Rh}_{0.5}\text{O}_4$.

Neutron powder diffraction data collected from $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Rh}_{0.5}\text{O}_4$ and $\text{LaSrCo}_{0.5}\text{Rh}_{0.5}\text{O}_4$ could both be indexed on the basis of body-centred tetragonal unit cells with lattice parameters of $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Rh}_{0.5}\text{O}_4$: $a = 3.874$ Å, $c = 12.488$ Å; $\text{LaSrCo}_{0.5}\text{Rh}_{0.5}\text{O}_4$: $a = 3.879$ Å, $c = 12.519$ Å, consistent with the adoption of $n = 1$ Ruddlesden-Popper structures. Refinement of structural models of this type against the data gave good fits. There was no indication of any structural distortion or Rh/M (M = Co, Mn) cation order for either sample. Full details of the refinements against the neutron powder diffraction data are given in Table S1 and S2, with plots of the fitted data given in Figures S1 and S2. A detailed examination of the structural and magnetic behaviour of $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Rh}_{0.5}\text{O}_4$ and $\text{LaSrCo}_{0.5}\text{Rh}_{0.5}\text{O}_4$ will be described elsewhere.

Table S1. The structural parameters of $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Rh}_{0.5}\text{O}_4$ refined against neutron powder diffraction data collected at room temperature.

Atom	Wyckoff Position	<i>x</i>	<i>y</i>	<i>z</i>	Fraction	U ₁₁ (Å)	U ₂₂ (Å)	U ₃₃ (Å)
La/Sr(1)	4 <i>e</i>	0	0	0.35772(9)	0.25/0.75	0.0053(7)	0.0053(7)	0.0015(6)
Mn/Rh(1)	2 <i>a</i>	0	0	0	0.5/0.5	0.0167(46)	0.0167(46)	0.0582(88)
O(1)	4 <i>e</i>	0	0	0.1625(1)	1	0.0103(8)	0.01034(88)	0.0063(10)
O(2)	4 <i>c</i>	½	0	0	1	0.0045(15)	0.0061(15)	0.0152(10)

La_{0.5}Sr_{1.5}Mn_{0.5}Rh_{0.5}O₄ space group *I* 4/*m m m* (#139)
a = 3.8742(1) Å, *c* = 12.4863(3) Å, Volume = 187.42(1) Å³
Formula weight : 343.81 g mol⁻¹, *Z* = 2
Radiation source: Constant wavelength neutrons, λ = 1.5943(2)
χ² = 2.122; *wRp* = 3.31 %; *Rp* = 2.55 %.

Table S2. The structural parameters of $\text{LaSrCo}_{0.5}\text{Rh}_{0.5}\text{O}_4$ refined against neutron powder diffraction data collected at room temperature.

Atom	Wyckoff Position	x	y	z	Fraction	U ₁₁ (Å)	U ₂₂ (Å)	U ₃₃ (Å)
La/Sr(1)	4e	0	0	0.35937(9)	0.5/0.5	0.0037(5)	0.0037(5)	0.0018(7)
Co/Rh(1)	2a	0	0	0	0.5/0.5	0.0007(1)	0.0007(1)	0.0096(20)
O(1)	4e	0	0	0.1668(1)	1	0.0153(6)	0.0153(6)	0.0053(10)
O(2)	4c	½	0	0	1	0.0082(11)	0.0052(11)	0.0130(12)

LaSrCo_{0.5}Rh_{0.5}O₄ space group *I* 4/*m m m* (#139)
 $a = 3.8789(1) \text{ Å}$, $c = 12.5174(4) \text{ Å}$, Volume = 188.33(2) Å³
Formula weight : 371.45 g mol⁻¹, Z = 2
Radiation source: Constant wavelength neutrons, λ = 1.5943(2)
χ² = 3.071; wRp = 4.26 %; Rp = 3.28 %.

Figure S1. Observed, calculated and difference plots from the structural refinement of $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Rh}_{0.5}\text{O}_4$ against neutron powder diffraction data collected at room temperature.

Figure S2. Observed, calculated and difference plots from the structural refinement of $\text{LaSrCo}_{0.5}\text{Rh}_{0.5}\text{O}_4$ against neutron powder diffraction data collected at room temperature.

3. Chemical and structural characterisation of $\text{LaSrCo}_{0.5}\text{Rh}_{0.5}\text{O}_3\text{H}$.

Thermogravimetric data (Figure S3) collected during the reoxidation of the tetragonal phase which was the ultimate product of the reduction of $\text{LaSrCo}_{0.5}\text{Rh}_{0.5}\text{O}_4$ (after removal of CaO/CaH_2) revealed a mass gain of 4.35% indicating a composition of $\text{LaSrCo}_{0.5}\text{Rh}_{0.5}\text{O}_3$ if the sample is only considered as an anion-deficient oxide. Neutron powder diffraction data collected from this reduced phase could be indexed using a body-centred tetragonal cell with dimensions which are approximately similar to those of $\text{LaSrCo}_{0.5}\text{Rh}_{0.5}\text{O}_4$. However, refinement of a structural model based on the structure of $\text{LaSrCo}_{0.5}\text{Rh}_{0.5}\text{O}_4$ did not account for the data well until the occupancies of the anion sites were allowed to refine. This led to a sharp decrease in the occupancy of the O(2) 'equatorial' anion site to a value of 0.18. This value would give the phase a non-sensible composition ($\text{LaSrCo}_{0.5}\text{Rh}_{0.5}\text{O}_{2.36}$) and in combination with the TGA data suggests the phase is an oxy-hydride (^1H has a neutron scattering length of -3.73 fm).² To resolve this issue a disordered mixture of oxide and hydride ions were placed on the O/H(2) anion site within the refinement and the fraction allowed to vary. This rapidly refined to give a 1:1 mixture of O^{2-} and H^- indicating the overall composition of the phase to be $\text{LaSrCo}_{0.5}\text{Rh}_{0.5}\text{O}_3\text{H}$, consistent with the oxygen content determined by TGA data. Close inspection of the diffraction data revealed a small number of weak reflections which can be attributed to a small amount of La_2O_3 in the sample, so this was added to the structural model as a second phase. The refinement converged rapidly to give a good statistical fit ($\chi^2 = 1.764$). Full details of the refined structure are given in Table S3, with selected bond lengths in Table S4. A plot of the observed and calculated data is shown in Figure S4. The displacement parameters of the atoms within the Co-Rh-O-H plane (Table S3) are rather large suggesting the phase may be distorted into a lower symmetry structure – a common feature of many perovskite derived structures. However attempts to fit the data to a series of distorted structures did not improve the numerical or visual fit to the data, so this feature of the refined structure was assigned to local disorder.

Figure S3. Thermogravimetric data collected during the oxidation of $\text{LaSrCo}_{0.5}\text{Rh}_{0.5}\text{O}_3\text{H}$ under oxygen.

Table S3. Structural parameters from the refinement of $\text{LaSrCo}_{0.5}\text{Rh}_{0.5}\text{O}_3\text{H}$ against neutron powder diffraction data collected at 298 K.

	<i>x</i>	<i>y</i>	<i>z</i>	Fraction	<i>U</i> ₁₁ (Å ²)	<i>U</i> ₂₂ (Å ²)	<i>U</i> ₃₃ (Å ²)
La/Sr	0	0	0.3568(1)	0.5/0.5	0.013(1)	0.013(1)	0.007(1)
Co/Rh	0	0	0	0.5/0.5	0.024(2)	0.024(2)	0.021(4)
O(1)	0	0	0.1683(2)	1	0.018(1)	0.018(1)	0.015(2)
O/H(2)	0	½	0	0.50(1)/0.50(1)	0.043(8)	0.012(4)	0.011(1)
$\text{LaSrCo}_{0.5}\text{Rh}_{0.5}\text{O}_3\text{H}$: space group <i>I4/mmm</i> (#139) Formula weight: 356.46 g mol ⁻¹ , <i>Z</i> = 2 mass fraction = 95.5(1)% $a = 3.7175(2)$ Å, $c = 13.0926(8)$ Å, Volume = 180.94(3) Å ³							
La_2O_3 : space group <i>P</i> $\bar{3}m1$ (#164) Formula weight: 325.82 g mol ⁻¹ , <i>Z</i> = 4 mass fraction = 4.5(1)% $a = 3.944(1)$ Å, $c = 6.147(2)$ Å, Volume = 82.85(4) Å ³							
Radiation source: Constant wavelength neutrons, $\lambda = 1.5943$ Å $\chi^2 = 1.764$; <i>wRp</i> = 3.58 %; <i>Rp</i> = 2.74 %.							

Table S4. Selected bond lengths from the refined structure of $\text{LaSrCo}_{0.5}\text{Rh}_{0.5}\text{O}_3\text{H}$

Cation	Anion	length (Å)
La/Sr	O(1) × 1	2.468(3)
	O(1) × 4	2.649(1)
	O/H(2) × 4	2.650(1)
Co/Rh	O(1) × 2	2.203(3)
	O/H(2) × 4	1.859(1)

Figure S4. Observed calculated and difference plots from the structural refinement of $\text{LaSrCo}_{0.5}\text{Rh}_{0.5}\text{O}_3\text{H}$ against neutron powder diffraction data collected at room temperature. Lower tick marks indicate peak positions of $\text{LaSrCo}_{0.5}\text{Rh}_{0.5}\text{O}_3\text{H}$, upper tick marks indicate peak positions of the La_2O_3 secondary phase.

4. Chemical and structural characterisation of $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Rh}_{0.5}\text{O}_3\text{H}$.

Thermogravimetric data (Figure S5) collected during the reoxidation of the tetragonal phase which was the ultimate product of the reduction of $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Rh}_{0.5}\text{O}_4$ (after removal of CaO/CaH_2) revealed a mass gain of 5.40% indicating a composition of $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Rh}_{0.5}\text{O}_{2.84}$ if the sample is only considered as an anion-deficient oxide. A model based on the structure of $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Rh}_{0.5}\text{O}_4$ was refined against neutron diffraction data collected from this reduced phase, and again it only fit the data well when the occupancy of the O(2) anion site was allowed to vary, yielding a model of composition $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Rh}_{0.5}\text{O}_{2.40}$. Following the logic described above this again was seen as an indication that the reduced phase is an oxy-hydride, so a mixture of oxide and hydride ions were placed on the O/H(2) anion site within the refinement and the fraction allowed to vary. This rapidly refined to give a 1:1 mixture of O^{2-} and H^- indicating the overall composition of the phase to be $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Rh}_{0.5}\text{O}_3\text{H}$, approximately consistent with the oxygen content determined by TGA data. The refinement converged rapidly to give a good statistical fit ($\chi^2 = 4.951$). Full details of the refined structure are given in Table S5, with selected bond lengths in Table S6. A plot of the observed and calculated data is shown in Figure S6. Again the displacement parameters of the atoms within the Mn-Rh-O-H plane (Table S5) are rather large; however attempts to fit the data to a series of distorted structures did not improve the numerical or visual fit to the data, so this feature of the refined structure was again assigned to local disorder.

Figure S5. Thermogravimetric data collected during the oxidation of $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Rh}_{0.5}\text{O}_3\text{H}$ under oxygen.

Table S5. Structural parameters from the refinement of $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Rh}_{0.5}\text{O}_3\text{H}$ against neutron powder diffraction data collected at 298 K.

	<i>x</i>	<i>y</i>	<i>z</i>	Fraction	<i>U</i> ₁₁ (Å ²)	<i>U</i> ₂₂ (Å ²)	<i>U</i> ₃₃ (Å ²)
La/Sr	0	0	0.35409(4)	0.25/0.75	0.0266(6)	0.0266(6)	0.0201(6)
Mn/Rh	0	0	0	0.5/0.5	0.043(3)	0.043(3)	0.036(2)
O(1)	0	0	0.16591(7)	1	0.0219(7)	0.0219(7)	0.037(1)
O/H(2)	0	½	0	0.51(1)/0.49(1)	0.082(1)	0.0082(3)	0.0323(5)
$\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Rh}_{0.5}\text{O}_3\text{H}$: space group <i>I4/mmm</i> (#139) Formula weight: 328.82 g mol ⁻¹ , <i>Z</i> = 2 <i>a</i> = 3.7302(1) Å, <i>c</i> = 13.1425(4) Å, Volume = 182.87(1) Å ³							
Radiation source: time-of-flight neutron Temperature: 298 K $\chi^2 = 4.951$; <i>wRp</i> = 2.28 %; <i>Rp</i> = 1.66 %.							

Table S6. Selected bond lengths from the refined structure of $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Rh}_{0.5}\text{O}_3\text{H}$

Cation	Anion	length (Å)
La/Sr	O(1) × 1	2.473(1)
	O(1) × 4	2.651(1)
	O/H(2) × 4	2.675(1)
Mn/Rh	O(1) × 2	2.180(1)
	O/H(2) × 4	1.865(1)

Figure S6. Observed calculated and difference plots from the structural refinement of $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Rh}_{0.5}\text{O}_3\text{H}$ against time-of-flight neutron powder diffraction data collected at room temperature.

5. Magnetic characterization of $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Rh}_{0.5}\text{O}_3\text{H}$ and $\text{LaSrCo}_{0.5}\text{Rh}_{0.5}\text{O}_3\text{H}$.

Procedure used to measure the magnetization of samples containing ferromagnetic impurity phases:

The magnetization of both $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Rh}_{0.5}\text{O}_3\text{H}$ and $\text{LaSrCo}_{0.5}\text{Rh}_{0.5}\text{O}_3\text{H}$ is observed to become a linear with respect to the applied magnetic field in fields greater than 2 T (as shown in Figure S7 and S8) indicating that the magnetisation of the ferromagnetic impurity phases has saturated for $H > 2\text{T}$. Thus the paramagnetic susceptibility of a bulk samples can be measured in the presence of the ferromagnetic impurities by measuring the gradient of magnetization-field isotherms in applied fields larger than 2 T. As shown in Figure S7 and S8.

To this end the magnetization of samples was measured in a series of 5 fields between 3 T and 5 T. The magnetization vs. field data were fitted to a linear function, the gradient of which is the paramagnetic susceptibility of the bulk sample and the intercept is the saturated ferromagnetic moment of the sample. Data points with large errors were excluded from fits. All fits had at least 4 data points. This procedure was repeated at 5 K intervals between 5 K and 300 K to measure the temperature dependent susceptibility of samples.

Figure S7. Magnetisation of a $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Rh}_{0.5}\text{O}_3\text{H}$ sample measured as a function of applied field at 300 K. A linear fit to high-field region ($H > 30000$ Oe) yields a gradient which is the paramagnetic susceptibility of the sample, and an intercept which is the saturated ferromagnetic moment of the sample.

Figure S8. Magnetisation of a $\text{LaSrCo}_{0.5}\text{Rh}_{0.5}\text{O}_3\text{H}$ sample measured as a function of applied field at 300 K. A linear fit to high-field region ($H > 30000$ Oe) yields a gradient which is the paramagnetic susceptibility of the sample, and an intercept which is the saturated ferromagnetic moment of the sample.