Hole and electron doping of the 4d transition-metal oxyhydride $\text{LaSr}_3\text{NiRuO}_4\text{H}_4$.

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1. Synthesis of $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_8$ ($0.5 < x < 1.5$).

Samples of $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_8$ ($0.5 < x < 1.5$) were synthesized by a high-temperature ceramic method. Suitable stoichiometric ratios of La_2O_3 (99.999%, dried at 900°C), SrCO_3 (99.994%), RuO_2 (99.99%, dried at 800°C) and NiO (99.998%) were ground together using an agate mortar and pestle, transferred into an alumina crucible, and then heated at a rate of $1\text{ }^\circ\text{C min}^{-1}$ to 1000°C in air to decompose the carbonate. Samples were then reground, pressed into pellets and then heated for 3 periods of 48 hours at 1200°C in air, with grinding between heating periods.

2. Structural Characterization of $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_8$ ($0.5 < x < 1.5$).

Synchrotron X-ray powder diffraction data collected from $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_8$ ($0.5 < x < 1.5$) samples at 300 K, using beamline I11 at the Diamond Light Source, can be indexed using a body-centred tetragonal unit cells with lattice parameters listed in Table S1. Structural models, based on the reported structure of $\text{LaSr}_3\text{NiRuO}_8$ (space group $I4/mmm$) were constructed for all samples and refined against the data, yielding good fits.

x	a (Å)	c (Å)	Volume (Å ³)
0.5	3.8866(2)	12.5610(1)	189.741(3)
0.6	3.8870(2)	12.5732(1)	189.972(3)
0.7	3.8882(3)	12.5944(1)	190.411(4)
0.8	3.8877(2)	12.6005(1)	190.453(4)
0.9	3.8911(1)	12.6273(1)	191.190(2)
1.0	3.8912(1)	12.6315(1)	191.261(2)
1.1	3.8926(1)	12.6401(1)	191.530(2)
1.2	3.8905(1)	12.6346(1)	191.242(2)
1.3	3.8911(1)	12.6339(1)	191.293(2)
1.4	3.8932(1)	12.6351(1)	191.510(1)
1.5	3.8923(1)	12.6275(1)	191.314(2)

Table S1. Lattice parameters extracted from fits to synchrotron X-ray powder diffraction data collected from $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_8$ ($0.5 < x < 1.5$) samples.

3. Synthesis of $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$ ($0.5 < x \leq 1.5$).

Samples of $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$ ($0.5 < x < 1.5$) were prepared by grinding approximately 0.5 g of the corresponding $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_8$ ($0.5 \leq x \leq 1.5$) phase with 0.13 g of CaH_2 , using an agate mortar and pestle in an argon filled glovebox. The resulting mixtures were then sealed in silica ampoules under vacuum and heated for 2 periods of 7 days at the temperatures indicated: $x = 0.5$, $T = 410^\circ\text{C}$; $x = 0.6$, $T = 420^\circ\text{C}$; $x = 0.7$, $T = 430^\circ\text{C}$; $0.8 \leq x \leq 1.0$, $T = 450^\circ\text{C}$; $x = 1.1$, $T = 460^\circ\text{C}$; $1.2 \leq x \leq 1.5$, $T = 470^\circ\text{C}$, with samples reground between heating periods. Once reactions were deemed complete, reaction mixtures were washed with 6×25 ml of 0.1 M solution of NH_4Cl in methanol, under nitrogen, to remove the CaO formed as a by-product of the reaction and any unreacted CaH_2 . Samples were then washed with 3×25 ml of clean methanol to dissolve NH_4Cl residues and then dried under vacuum.

4. Structural Characterization of $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$ ($0.5 < x < 1.5$).

Synchrotron X-ray powder diffraction data collected from $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$ ($0.5 < x < 1.5$) at 300 K using beamline I11 at the Diamond Light Source, can be indexed using body-centred tetragonal unit cells with values similar to those observed for $\text{LaSr}_3\text{NiRuO}_4\text{H}_4$.^[2d] Structural models, based on the reported structure of $\text{LaSr}_3\text{NiRuO}_4\text{H}_4$ (space group $I4/mmm$) were constructed for all samples and refined against the data, yielding good fits. Lattice parameters extracted from these refinements are listed in Table S2 and shown graphically in Figure S1. It can be seen from these data that the a -lattice parameter is essentially independent of composition, while the c -lattice parameter evolves smoothly as a function of composition for all samples except “ $\text{La}_{1.5}\text{Sr}_{2.5}\text{NiRuO}_4\text{H}_4$ ”, indicating that the topochemical reaction does not follow the sample pathway for the $x = 1.5$ sample and the isostructural phase range of $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$ is restricted to the range $0.5 < x < 1.4$.

x	a (Å)	c (Å)
0.5	3.6202(5)	13.262(2)
0.6	3.6215(5)	13.272(2)
0.7	3.6227(5)	13.290(2)
0.8	3.6247(5)	13.299(2)
0.9	3.6250(5)	13.324(2)
1.0	3.6215(5)	13.315(2)
1.1	3.6244(5)	13.322(2)
1.2	3.6232(5)	13.339(2)
1.3	3.6201(5)	13.342(2)
1.4	3.6256(5)	13.351(2)
1.5	3.639(1)	13.271(6)

Table S2. Lattice parameters extracted from fits to synchrotron X-ray powder diffraction data collected from $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$ ($0.5 < x < 1.5$) samples.

Figure S1. Plot of lattice parameters as a function of composition for $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$ ($0.5 < x < 1.5$) samples.

5. Thermogravimetric characterization of $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$ ($0.5 < x < 1.4$).

Thermogravimetric data were collected using a Mettler-Toledo MX1 thermogravimetric microbalance. Samples of $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$ were heated under flowing oxygen to temperatures between 800 °C ($x = 0.5$) and 1000°C ($x = 1.5$) to reoxidize them back to the corresponding $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_8$ phases, and then allowed to cool. A measurement of the mass gain on oxidation was performed after the sample was cooled to avoid any buoyancy effects. The oxidized samples were recovered and X-ray powder diffraction data collected to confirm that complete oxidation had occurred.

Figure S2 shows the thermogravimetric data for the $x = 0.5$, 1 and 1.5 samples. Full details of the mass gains for all the samples is detailed in Table S3. It can be seen that all the observed mass gains, with the exception of the $x = 0.9$ sample, are consistent with the stated $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$ compositions.

$\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$ x	Calculated mass gain for conversion of $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$ to $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_8$	Observed mass gain.
0.5	9.92%	9.90(3)%
0.6	9.84%	9.85(3)%
0.7	9.76%	9.76(2)%
0.8	9.68%	9.67(3)%
0.9	9.60%	9.13(3)%
1.0	9.52%	9.49(3)%
1.1	9.44%	9.45(3)%
1.2	9.37%	9.36(3)%
1.3	9.29%	9.30(2)%
1.4	9.22%	9.19(3)%

Table S3. Calculated and observed mass gains for the oxidation of $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$ to $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_8$.

Figure S2. Thermogravimetric data collected during the reoxidation of $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$ samples to the corresponding $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_8$ phases.

6. Iodometric characterization of $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$ ($0.5 < x < 1.4$).

A series of iodometric back titrations were performed to establish the oxidation states of Ni and Ru in the $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$ phases, and thus confirm the hydride content of the phases. A back titration was required because the Ni and Ru cations were reduced ($\text{Ni}^{1+/2+}$, $\text{Ru}^{1+/2+}$) relative to their final oxidation states in acid solution (Ni^{2+} , Ru^{2+}).

Initially a known amount of I_2 was prepared by combining a carefully weighed quantity of KIO_3 with an excess of KI in a 1:5 mixture of distilled water:HCl. Carefully weighed aliquots of $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$ samples (~20mg) were then dissolved in the acidified iodine solution and stirred under argon to ensure complete dissolution. The remaining iodine in the solution was then titrated with a previously standardized solution of $\text{Na}_2\text{S}_2\text{O}_3$ and the combined Ni + Ru oxidation state determined. The process was then repeated three times for each of the samples.

Table S4 lists the calculated combined (Ni + Ru) oxidation states of the $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$ samples based on the stated compositions, and the values determined by titration. The measured values agree with the calculated values within error, confirming the state compositions. The $x = 0.9$ sample was not titrated as TGA measurements (Table S3) show the anion exchange reaction was incomplete.

$\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$ x	Calculated sum of the Ni and Ru oxidation states.	Measured sum of the Ni and Ru oxidation states from titration.
0.5	3.50	3.51(2)
0.6	3.40	3.40(2)
0.7	3.30	3.31(2)
0.8	3.20	3.20(2)
1.0	3.00	3.01(1)
1.1	2.90	2.89(2)
1.2	2.80	2.81(3)
1.3	2.70	2.69(3)
1.4	2.60	2.59(3)

Table S4. Calculated and observed oxidation state sums for Ni and Ru in $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$ samples.

7. Magnetic characterization of $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$ ($0.5 < x < 1.4$).

Procedure used to measure the magnetization of samples containing elemental nickel:

The magnetization of elemental nickel is observed to saturate in applied magnetic fields of more than 2 T. Thus the paramagnetic susceptibility of a bulk sample can be measured in the presence of elemental nickel impurities by measuring the gradient of magnetization-field isotherms in applied fields larger than 2 T. As shown in Figure S3.

To this end the magnetization of $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$ ($0.5 < x < 1.4$) samples was measured in a series of 7 fields between 2 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 5 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 S3. Magnetisation of a $\text{LaSr}_3\text{NiRuO}_4\text{H}_4$ sample measured as a function of applied field at 300 K. A linear fit to high-field region ($H > 20000$ 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 S4. Plots of the reciprocal of the paramagnetic susceptibility of hole-doped $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$ samples as a function of temperature.

Figure S5. Plots of the reciprocal of the paramagnetic susceptibility of electron-doped $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$ samples as a function of temperature.