Supplementary Materials

Crystal structure and coordination of B-cations in the Ruddlesden-Popper phases $Sr_{3-x}Pr_x(Fe_{1.25}Ni_{0.75})O_{7-\delta}$ ($0 \leq x \leq 0.4$)

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1. XRD studies

Room-temperature XRD patterns were recorded using a PIXCEL detector and variable slits with a 2 × 2 cm^2 illuminated area. The powder samples were evenly spread unto zero-background Si plates. In the structure refinements, 30–35 parameters were refined, and the 2θ range used covered ~120 theoretical reflections. The background was modeled by linear interpolation between ~20 specified background points. The peak widths were observed to show an anisotropic (i.e. *hkl* dependent) strain broadening. The extent and *hkl* dependence of this anisotropic strain broadening were furthermore found to vary with composition and between as-prepared and air-annealed samples. In general, the largest extent in variation was observed in the low x-values for as-prepared samples. This was taken into account in the refinements when refining S_{HKL} micro-strain parameters using the model by Stephens.[1] Corrections for surface roughness micro-absorption were made by refining the P_0 and C_p parameters for the model by Pitschke.[2] For the N_2-annealed samples, anisotropic atomic displacement parameters (ADPs) were refined for all metal atoms and a collective isotropic ADP refined for O1, O2, and O3. For the air-annealed samples, ADPs were refined for O3 and a collective isotropic ADP refined for O1 and O2.

The XRD refinement revealed the presence of small amounts of NiO in the air-annealed samples. This impurity was most probably present as Ni(s) in the corresponding N_2-annealed sample, but in too small or badly crystallized amounts, seen in the XRD pattern.

The problems associated with refining positions/occupancies of light elements together with heavier ones like Sr/Pr/Fe/Ni are well-known.

2. NPD Studies

The NPD patterns of the investigated x = 0 and 0.2, N_2(g)- and air-annealed samples are shown in Figure S1. Since the data are from two state-of-the-art instruments, the number of refined structural parameters is limited, low R- and χ^2 values, we have high trust in our results. The Rietveld refinements yield residual R_F factors of 4.2 or lower for all refinements. The refinements revealed the presence of minor impurity phases such as 2 wt% Pr_6O_{11}, and 1 wt% NiO for air-annealed Pr x = 0.2. The refined unit-cell and structural parameters are given in Table 1, and selected bond distances and angles in Table 2, in the main text.

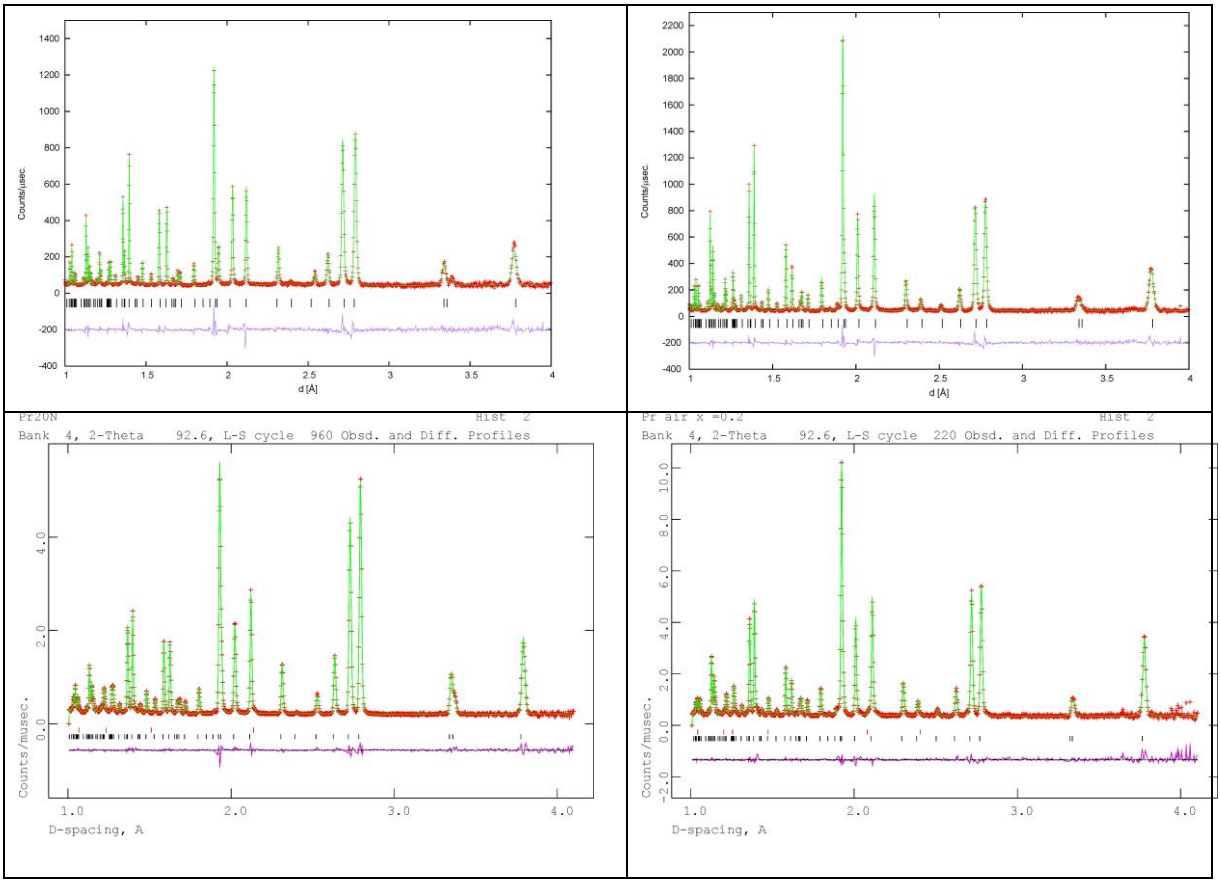

Figure S1. Measured, calculated, and differences in NPD patterns (147° bank): (a) *N_2-annealed $Sr_3Fe_{1.25}Ni_{0.75}O_{5.587(7)}$*, (b) air-annealed *$Sr_3Fe_{1.25}Ni_{0.75}O_{6.552(5)}$*, (c) *$N_2$-annealed* (tics; upper-magnetic structure, mid-NiO, *$Sr_{2.80}Pr_{0.20}Fe_{1.25}Ni_{0.75}O_{5.682(8)}$*) and (d) air-annealed (tics; upper-magnetic structure, mid-NiO, *$Sr_{2.80}Pr_{0.20}Fe_{1.25}Ni_{0.75}O_{6.640(6)}$*).

Table S1. Anisotropic thermal parameters (U_{ij}*100) (NPD-data) for N_2- and air-annealed $Sr_{3-x}Pr_xFe_{1.25}Ni_{0.75}O_{7-\delta}$ samples.

	x = 0.0					
	N_2-annealed			air-annealed		
Site	U_{11}	U_{22}	U_{33}	U_{11}	U_{22}	U_{33}
*A*1	2.39(5)	=U_{11}	0.78(5)	1.17(3)	=U_{11}	0.351(4)
*A*2	1.57(3)	=U_{11}	6.92(3)	0.60(2)	= U_{11}	0.49(3)
B	1.22(2)	= U_{11}	1.33(3)	0.23(1)	= U_{11}	0.85(3)
O1	3.5(2)	= U_{11}	0.74(2)	0.87(6)	= U_{11}	0.13(8)
O2	1.96(3)	= U_{11}	0.81(5)	1.01(2)	= U_{11}	0.55(4)
O3	3.42(6)	1.82(5)	2.80(6)	0.70(2)	0.66(2)	1.84(4)
	x = 0.2					
	N_2-annealed			air-annealed		
Site	U_{11}	U_{22}	U_{33}	U_{11}	U_{22}	U_{33}
*A*1	2.01(5)	= U_{11}	0.48(6)	1.21(5)	= U_{11}	0.32(6)
*A*2	1.37(3)	= U_{11}	0.93(4)	0.54(3)	= U_{11}	0.65(4)
B	1.09(2)	= U_{11}	0.78(4)	0.16(1)	= U_{11}	0.83(3)

O1	4.4(3)	= U_{11}	3.1(4)	0.97(7)	= U_{11}	0.97(6)
O2	1.87(3)	= U_{11}	0.75(5)	1.12(3)	= U_{11}	0.55(5)
O3	2.71(5)	1.51(5)	2.3(6)	0.77(3)	0.53(3)	1.82(5)

Table S2. Unit cell parameters and results from the refinement using XRD data for N_2-annealed $Sr_{3-x}Pr_xFe_{1.25}Ni_{0.75}O_{7-\delta}$ samples.

x	χ^2	R_F	*a*/Å	*c*/Å	*V*/Å^3
0.00	3.50	7.0	3.8394	20.3468	299.93
0.10	2.32	7.0	3.8474	20.2687	300.03
0.20	1.99	8.8	3.8584	20.1818	300.45
0.30	1.55	5.0	3.8675	20.1276	301.06
0.40	1.35	5.1	3.8797	20.0175	301.30

Table S3. Unit cell parameters, NiO content (mass %) and results from the refinement using XRD data for air-annealed $Sr_{3-x}Pr_xFe_{1.25}Ni_{0.75}O_{7-\delta}$ samples.

x	χ^2	R_F	NiO/mass %	*a*/Å	*c*/Å	*V*/Å^3
0.00	3.86	7.5	-	3.8433	20.1059	296.98
0.10	2.64	6.4	0.22	3.8437	20.0809	296.68
0.20	2.58	7.2	0.10	3.8438	20.0621	296.41
0.30	1.93	7.0	0.19	3.8441	20.0635	296.48
0.40	1.62	6.5	-	3.8435	20.0538	296.24

Table S4 Atomic coordinates (z-value) from the refinement using XRD data for N_2-annealed $Sr_{3-x}Pr_xFe_{1.25}Ni_{0.75}O_{7-\delta}$ samples.

x	*A*2	*B*	O2	O3
0.00	0.6832(1)	0.1009(2)	0.1925(7)	0.0885(7)
0.10	0.6828(1)	0.1015(2)	0.1930(8)	0.0874(8)
0.20	0.6823(1)	0.1012(2)	0.1954(7)	0.0821(8)
0.30	0.6819(1)	0.1009(2)	0.1940(6)	0.0806(4)
0.40	0.6812(1)	0.1005(1)	0.1958(4)	0.0818(3)

Table S5 Atomic coordinates (z-value) from the refinement using XRD data for air-annealed $Sr_{3-x}Pr_xFe_{1.25}Ni_{0.75}O_{7-\delta}$ samples.

x	*A*2	*B*	O2	O3
0.00	0.6815(1)	0.1000(2)	0.1935(6)	0.0903(4)
0.10	0.6816(1)	0.0992(1)	0.1925(5)	0.0909(5)
0.20	0.6818(1)	0.0993(2)	0.1928(6)	0.0913(6)
0.30	0.6818(1)	0.0989(1)	0.1941(5)	0.0905(5)
0.40	0.6820(1)	0.0985(1)	0.1939(5)	0.0914(4)

Table S6 A-O bond lengths (Å) from the refinement using XRD data for N_2-annealed $Sr_{3-x}Pr_xFe_{1.25}Ni_{0.75}O_{7-\delta}$ samples.

x	*A*1-O3, 8x	*A*1–O1, 4x	*A*2-O3, 4x	*A*2-O2, 4x	*A*2-O2, 1x
0.00	2.632(9)	2.7150	2.720(9)	2.722(1)	2.53(1)

0.10	2.617(10)	2.7209	2.729(10)	2.729(1)	2.52(1)
0.20	2.544(10)	2.7272	2.796(10)	2.740(1)	2.47(1)
0.30	2.523(5)	2.7345	2.810(7)	2.745(1)	2.50(1)
0.40	2.538(4)	2.7430	2.779(5)	2.758(1)	2.46(1)

Table S7 A-O bond lengths (Å) from the refinement using XRD data for air-annealed $Sr_{3-x}Pr_xFe_{1.25}Ni_{0.75}O_{7-\delta}$ samples.

x	*A*1-O3, 8x	*A*1–O1, 4x	*A*2-O3, 4x	*A*2-O2, 4x	*A*2-O2, 1x
0.00	2.644(8)	2.7176	2.655(8)	2.728(1)	2.51(1)
0.10	2.651(5)	2.7178	2.648(8)	2.727(1)	2.53(1)
0.20	2.654(8)	2.7180	2.646(8)	2.727(1)	2.52(1)
0.30	2.644(8)	2.7179	2.654(8)	2.729(1)	2.49(1)
0.40	2.655(5)	2.7175	2.645(5)	2.728(1)	2.49(1)

Table S8 B-O bond lengths (Å) and angles (in degrees) from the refinement using XRD data for N_2-annealed $Sr_{3-x}Pr_xFe_{1.25}Ni_{0.75}O_{7-\delta}$ samples.

x	*B*-O3, 4*x*	*B* –O2, 1*x*	*B*- O1, 1*x*	O3-*B*-O3
0.00	1.936(2)	1.87(1)	2.052(4)	165.10
0.10	1.945(2)	1.86(1)	2.058(5)	163.16
0.20	1.967(3)	1.90(1)	2.046(4)	157.30
0.30	1.976(2)	1.87(1)	2.030(3)	156.13
0.40	1.976(1)	1.91(1)	2.012(3)	158.09

Table S9 B-O bond lengths (Å) and angles (in degrees) from the refinement using XRD data for air-annealed $Sr_{3-x}Pr_xFe_{1.25}Ni_{0.75}O_{7-\delta}$ samples.

x	*B*-O3, 4*x*	*B* –O2, 1*x*	*B*-O1, 1*x*	O3-*B*-O3
0.00	1.931(11)	1.88(1)	2.010(3)	168.48
0.10	1.929(8)	1.87(1)	1.994(3)	170.04
0.20	1.929(11)	1.88(1)	1.993(1)	170.45
0.30	1.929(8)	1.91(1)	1.985(3)	169.95
0.40	1.927(8)	1.91(1)	1.974(3)	171.56

Table S10 Bond valence sums based on the crystal structures refined from XRD data for N_2-annealed $Sr_{3-x}Pr_xFe_{1.25}Ni_{0.75}O_{7-\delta}$ samples.

x	*A*1	*A*2	*B*
0.00	1.52	1.90	2.62
0.10	1.79	1.87	2.84
0.20	1.81	1.77	2.33
0.30	2.43	1.71	2.76
0.40	2.51	1.77	2.84

Table S11 Bond valence sums based on the crystal structures refined from XRD data for air-annealed $Sr_{3-x}Pr_xFe_{1.25}Ni_{0.75}O_{7-\delta}$ samples.

x	*A*1	*A*2	*B*
0.00	1.99	2.05	3.30
0.10	2.07	2.05	3.50
0.20	2.03	2.07	3.45
0.30	2.19	2.07	3.55
0.40	2.14	2.10	3.58

Table S12 Oxygen content of $Sr_{3-x}Pr_xFe_{1.25}Ni_{0.75}O_{7-\delta}$ calculated from the occupancies of oxygen atomic positions using XRD, NPD (*in italics*), and TG data for N_2- and air-annealed samples. Δδ is the difference in oxygen content per formula unit between N_2- and air-annealed samples.

	N_2 - annealed			Air - annealed		Change in oxygen content upon annealing in air	
x	O3	O1	O	O1	O	Δδ	ΔTG
0.00	0.73(3), *0.813(3)*	0.17(5), *0.335(5)*	5.1(1), *5.587(7)*	0.14(5), 0.552(6)	6.13(5), *6.552(5)*	1.0(1), *1.03(1)*	0.80
0.10*	0.85(3)	0.07(6)	5.5(1)	0.44(4)	6.44(4)	1.0(1)	0.75
0.20	0.74(3), 0.*852(2)*	0.20(5), 0.*274(4)*	5.2(1), *5.6(1)*	0.38(5), *0.66(4)*	6.38(5), *6.64(4)*	1.2(1), *1.0(1)*	0.70
0.30	0.90(2)	0.03(2)	5.6(1)	0.66(4)	6.66(4)	1.1(1)	0.82
0.40	0.98(2)	0.02(3)	5.9(1)	0.68(4)	6.68(4)	0.8(1)	-

*5.46 according to TG

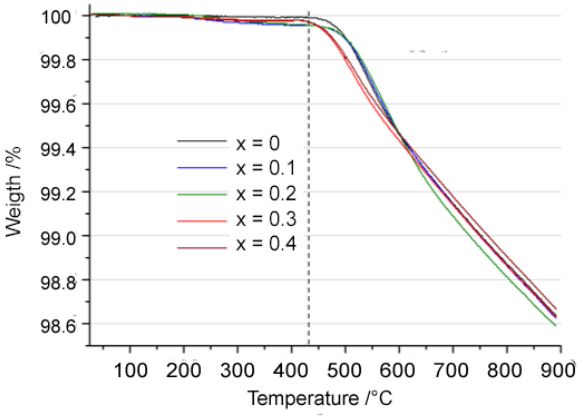

Figure S2. TG curves for air-annealed $Sr_{3-x}Pr_xFe_{1.25}Ni_{0.75}O_{7-\delta}$.

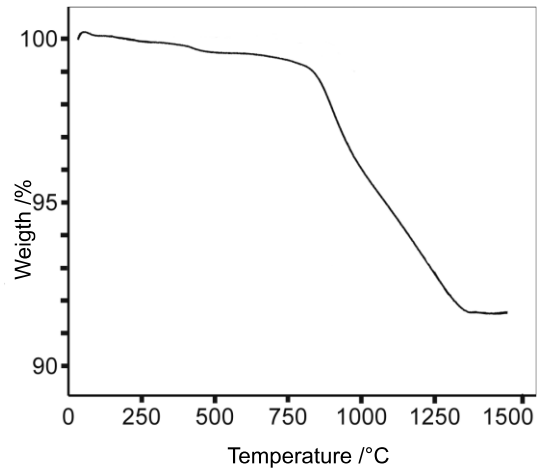

Figure S3. TG curves for $Sr_{3-x}Pr_xFe_{1.25}Ni_{0.75}O_{7-\partial}$ x = 0.1 recorded in 4% H_2/Ar atmosphere and using a heating rate 5 °C·min^{-1}.

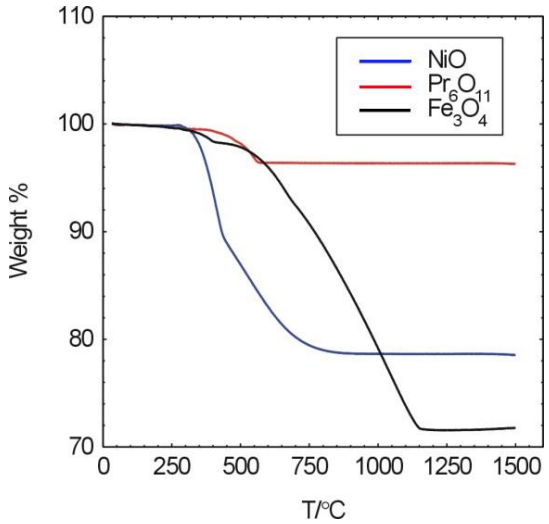

Figure S4. TG curves for pure oxides recorded in 4% H_2/Ar atmosphere and using a heating rate of 10 °C·min^{-1}, based on supplementary information in Reference [14].

References

14. Samain, L., Amshoff, P., Biendicho, J.J., Tietz, F., Mahmoud, A., Hermann, R.P., Istomin, S.Y. Grins, J., Svensson, G., *J. Solid State Chem.* **2015,** 227, 45–55, DOI: 10.1016/j.jssc.2015.03.018