SUPPORTING INFORMATION

RENiO$_3$ single crystals ($RE = Nd, Sm, Gd, Dy, Y, Ho, Er, Lu$) grown from molten salts under 2000 bar oxygen-gas pressure

Y. Maximilian Klein,*a Mirosław Kozłowski,b Anthony Linden,c Philippe Lacorre,d Marisa Medarde*a and Dariusz J. Gawryluk*aa

a. Laboratory for Multiscale Materials Experiments, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland.
E-mail: maximilian.klein@psi.ch, dariusz.gawryluk@psi.ch, marisa.medarde@psi.ch
b. Łukasiewicz Research Network - Tele & Radio Research Institute, 11 Ratuszowa Street, 03-450 Warsaw, Poland
c. Department of Chemistry, University of Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland
d. Institut des Molécules et Matériaux du Mans (IMMM) - UMR 6283 CNRS, Le Mans Université, Avenue Olivier Messiaen, 72085 Le Mans, France

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Starting rare earth oxides. Y$_2$O$_3$, La$_2$O$_3$, Ho$_2$O$_3$ (99.999%, Sigma Aldrich); Nd$_2$O$_3$ and Lu$_2$O$_3$ (99.999%, Chempur); $^{154}$Sm$_2$O$_3$ (98.30%, Oak Ridge National Laboratory); $^{160}$Gd$_2$O$_3$ (98.12%, Oak Ridge National Laboratory); $^{162}$Dy$_2$O$_3$ (96.17%, Oak Ridge National Laboratory); and Er$_2$O$_3$ (99.99+, Sigma Aldrich); Tm$_2$O$_3$ (99.99%, Sigma Aldrich); Yb$_2$O$_3$ (99.998%, Alfa Aesar). For Sm, Gd and Dy the use isotopically substituted oxide precursors is due to the low neutron capture cross sections of the chosen RE isotopes, a fact that can ease future neutron scattering experiments.

**Powder X-ray diffraction.** Because of their small size and regular habit, the as-prepared (i.e., uncrushed) RENiO$_3$ microcrystals (RE = Nd, Sm, and Gd) could be used in Laboratory Powder X-Ray Diffraction (PXRD) measurements for phase identification, to assess phase purity, and for structural analysis. The patterns, complemented by those of polycrystalline LaNiO$_3$, PrNiO$_3$ and EuNiO$_3$, were collected at the Paul Scherrer Institute at room temperature (RT) using a Bruker AXS D8 Advance diffractometer equipped with Ni-filtered Cu K$_\alpha$ radiation and a 1D LynxEye PSD detector. The presence of the RENiO$_3$ phases as the main product was confirmed in all PXRD patterns, which displayed the extremely sharp Bragg reflections characteristic of highly crystalline specimens. Tiny (<1%) amounts of flux and/or impurity phases (mostly Ni$_{1-x}$Li$_x$O, NiO and oxychloride phases of formula REClO, SG P4/nmm, $a \approx 4.0$ Å, $c \approx 6.7$ Å$^1$, see SI Fig. S3) were identified in some of the preparations. The refinement of the crystal structure was conducted using the Rietveld method$^2$ as implemented in the package FullProf Suite$^{3,4}$. The instrument resolution function was refined from a NAC (Na$_2$Al$_2$Ca$_3$F$_{14}$) standard, the profile of the Bragg reflections was modelled with a Thompson-Cox-Hastings pseudo-Voigt function and the preferred orientations, if present, were described with a March-Dollase Multiaxial function.

**Single crystal X-ray diffraction.** A few crystals with sizes between ~10 and ~40 μm were mounted on Kapton MicroMounts (MiTeGen LLC) for quality check using Laboratory Single Crystal X-ray diffraction (SCXRD). The measurements, conducted at room temperature, were performed at the Chemistry Department of the University of Zurich, Switzerland using a Rigaku Oxford Diffraction SuperNova Diffractometer$^5$. The device was equipped with a CCD area-detector and a micro-focus X-ray source delivering Mo K$_\alpha$ radiation. Data collections for ab-initio structure determination were only performed for the best, untwinned exemplars, and data reduction was performed with the CrystAlisPro$^5$ package. The intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction using spherical harmonics$^5$ was applied. The crystal structures were solved ab-initio with Superflip$^6$ and refined on $F^2$ using full-matrix least-squares procedures, as implemented in the program CRYSTALS$^7$. The CIF files (enclosed) can be also obtained from the Cambridge Crystallographic Data Centre (CCDC) using the deposition numbers 2077640 (Gd), 2077641 (Dy), 2077728 (Ho), 2077642 (Y) and 2077729 (Er).

**Field-Emission Scanning Electron Microscopy (FE-SEM) coupled with Energy-Dispersive X-ray Spectroscopy (EDX).** FE-SEM images were acquired with a JEOL JSM-7600F microscope operating with 15 keV incident electron beam energy, and equipped with a SE (Secondary Electron) detector. The device, located at the Tele & Radio Research Institute in Warsaw, Poland, was equipped with an Energy Dispersive X-ray Spectroscopy (EDX) system (X-
Max<sup>u</sup> 150 Silicon Drift Detector, Oxford Instruments) coupled with SEM, that we used for quantitative analyses of the nickelate crystal’s chemical composition.

**SQUID magnetometry.** DC magnetization measurements $M$ were performed in a superconducting quantum interference device magnetometer (MPMS-XL 7T, Quantum Design) between 2 and 300 K. The samples were mounted in gelatin capsules fixed on transparent drinking straws, and cooled in zero field down to 2K. The magnetization was then measured in a magnetic field $B = \mu_0 H = 5000 \text{ Oe (0.5T)}$ while heating. The signal from the empty sample holders, measured separately under the same conditions, was found to be negligible compared with the sample’s magnetization. The magnetic susceptibility $\chi_{DC} = M/B$ was then calculated for all samples. The values of the antiferromagnetic transitions (Ni and RE sublattice) mentioned in the text and in Table S2 correspond to the local maxima of the $\chi_{DC}$ versus temperature curves. For RE = Gd, Dy, Ho and Er, where the nickel signal is masked by the huge RE contribution, the $T_N$ values in Table S2 correspond to the local maxima in the $C_p(T)$ curves. For LuNiO$_3$, the tiny peak at ~56 K is due to some O$_2$ contamination in the MPMS chamber. For all nickelates, the paramagnetic region ($T_N < T < 300K$) was modelled with a Curie-Weiss law as described in the section “Effective paramagnetic moments and Curie-Weiss temperatures” on the paper. For YNiO$_3$ and LuNiO$_3$, with non-magnetic RE cations and hence much smaller $\chi_{DC}$, a second Curie-Weiss law was added to the fits in order to model the paramagnetic impurity contributions ($1/\chi_{imp} = T - \theta_{imp} / C_{imp}$). For YNiO$_3$, we obtained $\theta_{imp} = -100(4)$ K and $C_{imp} = 0.130(5)$ emu K mol$^{-1}$. For LuNiO$_3$, $\theta_{imp} = -33.9(4)$ K and $C_{imp} = 0.124(1)$ emu K mol$^{-1}$.

**Heat Capacity ($C_p$).** $C_p$ measurements were performed in a Physical Properties Measurement System (PPMS, 9T, Quantum Design) at zero magnetic field using the relaxation method between 10 and 250K. About 20 mg of RENiO$_3$ crystals with RE = Gd, Dy, Ho and Er were fixed with Apiezon-N grease to the sapphire holder of the calorimeter. The samples were then cooled down to 10K, and the heat capacity measured by heating. The signal from the N-Apiezon grease and the calorimeter, previously measured under the same conditions, was substracted from the data to obtain the sample’s $C_p$. The entropy change $\Delta S$ associated to the antiferromagnetic order of the Ni sublattice was calculated after subtracting the phonon contribution, modeled by a 6<sup>th</sup> order polynome (red lines in Figure 8 of the main paper). The coefficients were optimized to describe the background far from the $C_p$ anomaly, i.e., outside a ~50 degree-broad region below the inflexion point after $C_p(T)$ maxima.

**Differential scanning calorimetry (DSC).** The DSC experiments were carried on with a Netzsch DSC 204F1 thermal analysis instrument. Measurements were performed on heating to 670 K and cooling to RT with a rate of 5 K/min, using about 30 mg of sample encapsulated in standard aluminium crucibles. An argon stream was used during the whole experiment as protective gas. Prior to the sample measurement, a baseline, using two empty crucibles, was determined. The data were acquired during a heating-cooling cycle, aimed to check the presence of hysteresis on the metal-insulator transition temperature. The $T_{MIT}$ values shown in Figure 6 (and as red squares in Figure 1) of the main text correspond with the point where the second derivative of the DSC signal becomes zero.
Figure S1. Phase identification in YbNiO$_3$ and TmNiO$_3$ growth attempts. (a-b) Laboratory powder X-ray diffraction. (c-d) Differential Scanning Calorimetry. Both techniques signal the presence of the RENiO$_3$ phases with lattice parameters and metal-to-insulator temperature $T_{MIT}$ in excellent agreement with those reported in the literature for powder samples (red markers in Figures 1 and 4 of the main paper). The figure also illustrates the evolution of the RENiO$_3$ weight fraction with the number of annealings. YbNiO$_3$: 1 annealing, TmNiO$_3$: 2 annealings.
Figure S2. Optical microscope images of selected RENiO$_3$ crystals

Figure S3. Habit and elemental analysis of the REClO impurity phase crystals. (a) Scanning Electron Microscopy (RE = Nd). (b) Optical microscopy (RE = Nd). (c) Energy-Dispersive X-ray Spectroscopy (RE = Sm). (a) and (b) illustrate the different habit of the RENiO$_3$ and REClO crystals. The elemental composition of a SmClO crystal (c) is shown in the accompanying table.
|   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|
|i) NdNiO$_3$              |   |   |   |   |   |   |   |
| Maximum                  | 66.36 | 21.78 | 23.82 |   |   |   |   |
| Minimum                  | 54.39 | 16.21 | 17.38 |   |   |   |   |
| Average                  | 61.29 | 18.56 | 20.16 |   |   |   |   |
| Median                   | 60.42 | 18.86 | 20.49 |   |   |   |   |
| Standard Deviation       | 3.83  | 1.86  | 2.03  |   |   |   |   |
| Number of points:        | 18    |   |   |   |   |   |   |

| j) SmNiO$_3$              |   |   |   |   |   |   |   |
| Maximum                  | 19.66 | 17.96 | 68.12 |   |   |   |   |
| Minimum                  | 16.55 | 15.32 | 62.37 |   |   |   |   |
| Average                  | 18.11 | 16.71 | 65.18 |   |   |   |   |
| Median                   | 18.19 | 16.81 | 64.98 |   |   |   |   |
| Standard Deviation       | 1.10  | 0.86  | 1.95  |   |   |   |   |
| Number of points:        | 10    |   |   |   |   |   |   |

| k) GdNiO$_3$              |   |   |   |   |   |   |   |
| Maximum                  | 24.14 | 22.54 | 69.81 |   |   |   |   |
| Minimum                  | 15.58 | 14.62 | 53.31 |   |   |   |   |
| Average                  | 19.67 | 18.25 | 62.07 |   |   |   |   |
| Median                   | 19.70 | 18.57 | 61.74 |   |   |   |   |
| Standard Deviation       | 2.01  | 1.81  | 3.81  |   |   |   |   |
| Number of points:        | 25    |   |   |   |   |   |   |

| l) DyNiO$_3$              |   |   |   |   |   |   |   |
| Maximum                  | 22.92 | 22.67 | 70.94 |   |   |   |   |
| Minimum                  | 14.77 | 14.29 | 54.41 |   |   |   |   |
| Average                  | 18.33 | 17.52 | 64.15 |   |   |   |   |
| Median                   | 17.81 | 16.82 | 65.57 |   |   |   |   |
| Standard Deviation       | 2.53  | 2.54  | 5.06  |   |   |   |   |
| Number of points:        | 13    |   |   |   |   |   |   |

| m) YNiO$_3$               |   |   |   |   |   |   |   |
| Maximum                  | 24.05 | 22.53 | 67.54 |   |   |   |   |
| Minimum                  | 18.20 | 14.26 | 53.41 |   |   |   |   |
| Average                  | 21.14 | 18.16 | 60.70 |   |   |   |   |
| Median                   | 21.28 | 18.01 | 60.63 |   |   |   |   |
| Standard Deviation       | 1.42  | 2.01  | 3.30  |   |   |   |   |
| Number of points:        | 20    |   |   |   |   |   |   |

| n) ErNiO$_3$              |   |   |   |   |   |   |   |
| Maximum                  | 23.38 | 23.14 | 68.2  |   |   |   |   |
| Minimum                  | 16.38 | 15.41 | 52.48 |   |   |   |   |
| Average                  | 20.8  | 19.64 | 59.56 |   |   |   |   |
| Median                   | 20.99 | 20.11 | 58.74 |   |   |   |   |
| Standard Deviation       | 2.23  | 2.13  | 4.35  |   |   |   |   |
| Number of points:        | 21    |   |   |   |   |   |   |
Figure S4. Elemental analysis of RENiO$_3$ crystals. (a-h) SEM images, EDX elemental maps (RE, Ni and O) and representative EDX spectra for the RENiO$_3$ crystals with RE = Nd, Sm, Gd, Dy, Y, Er, Ho and Lu. (i-p) Elemental composition statistics (in atomic percentage) for the RENiO$_3$ crystals with RE = Nd, Sm, Gd, Dy, Y, Er, Ho and Lu.

Figure S5. SmClO recrystallization. The figure shows the shape of a crystal after the initial growth, and after a recrystallization attempt conducted under the same conditions as in the initial growth.
Figure S6. Rietveld fits. The powder diffraction data were recorded at RT using Cu $K\alpha$ radiation using uncrushed RENiO$_3$ single crystals (RE = Nd, Sm, Gd, Dy, Ho, Y, Er and Lu) and powders (RE= La, Pr, Eu). Red crosses: observed data. Black lines: calculated pattern. Grey lines: observed - calculated pattern. The vertical ticks indicate the positions of the Bragg reflections. The peak at $2\theta \sim 36$ degrees in (c) corresponds to an unknown impurity. The second row of ticks in (j) corresponds to Lu$_2$O$_3$ (10.4(5)% in weight).
Figure S7. RT crystal structure of RENiO$_3$ (RE = Gd, Dy, Ho, Y and Er) with atomic displacement ellipsoids (50% probability), as determined from laboratory single-crystal X-ray diffraction (Mo K$_\alpha$) using the SG Pbnm. The corresponding CIF files (enclosed) can be also obtained from the Cambridge Crystallographic Data Centre (CCDC) using the deposition numbers 2077640 (Gd), 2077641 (Dy), 2077728 (Ho), 2077642 (Y), and 2077729 (Er).
### Table S1. Structural parameters and reliability factors of RENiO$_3$ perovskites obtained from Rietveld refinements of laboratory X-ray diffraction data (Cu K$_{\alpha}$) at RT. For the nickelates with RE = Nd, Sm, Eu, Gd, Dy the refinements were carried out in the space group $Pbnm$, and for those with RE = Ho, Y, Er and Lu, in the space group $P2_1/n$. The average Ni-O-Ni superexchange angles $<\text{Ni}-\text{O}-\text{Ni}>$, tilt angles $\phi = (180 - <\text{Ni}-\text{O}-\text{Ni}>)/2$, Ni-O distances $d_{\text{Ni-O}}$ (coordination VI) and RE-O distances $d_{\text{RE-O}}$ (coordination VIII) are also provided.

| RE   | Nd  | Sm  | Eu  | Gd  | Dy  | Ho  | Y   | Er  | Lu  |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| a(Å) | 5.38957(8) | 5.3261(1) | 5.29177(7) | 5.26103(9) | 5.2073(2) | 5.18273(6) | 5.17993(6) | 5.16258(6) | 5.1114(1) |
| b(Å) | 5.38063(8) | 5.4351(1) | 5.46349(7) | 5.4879(1) | 5.5037(2) | 5.50958(7) | 5.51463(6) | 5.51064(6) | 5.4991(1) |
| c(Å) | 7.6111(1) | 7.5647(2) | 7.5364(1) | 7.5113(1) | 7.4457(3) | 7.42195(9) | 7.41750(8) | 7.39936(8) | 7.3406(1) |
| $\beta$(°) | 90 | 90 | 90 | 90 | 90 | 90.0844(3) | 90.0752(3) | 90.1006(3) | 90.1569(6) |
| V(Å$^3$) | 220.716(5) | 218.979(8) | 217.890(5) | 216.866(7) | 213.93(1) | 211.931(4) | 211.884(4) | 210.505(4) | 206.330(7) |
| $B_{\text{ov}}$ | 0.55(2) | 1.03(3) | 1.97(3) | 1.54(4) | 1.97(3) | 1.47(4) | 2.06(2) | 1.9(3) |
| Ni1 | x | 0.9933(5) | 0.9887(5) | 0.9861(3) | 0.9849(3) | 0.9819(4) | 0.9777(3) | 0.9852(3) | 0.9797(2) |
| Ni2 | y | 0.0350(1) | 0.0512(2) | 0.0572(1) | 0.0622(2) | 0.0682(2) | 0.0730(2) | 0.0724(1) | 0.0768(2) |
| O1  | z | 0.2550(4) | 0.2382(3) | 0.2513(4) | 0.2535(5) |
| O2  | x | 0.721(3) | 0.706(2) | 0.707(1) | 0.689(1) | 0.702(2) | 0.718(2) | 0.666(2) | 0.707(2) | 0.709(4) |
|     | y | 0.282(3) | 0.294(2) | 0.289(1) | 0.294(1) | 0.30(2) | 0.324(2) | 0.331(2) | 0.323(2) | 0.288(5) |
|     | z | 0.036(2) | 0.039(1) | 0.044(9) | 0.044(8) | 0.048(1) | 0.031(2) | 0.031(1) | 0.057(2) | 0.053(3) |
| O3  | x | 0.288(3) | 0.228(2) | 0.289(1) | 0.294(1) | 0.30(2) | 0.324(2) | 0.331(2) | 0.323(2) | 0.288(5) |
|     | y | 0.224(3) | 0.221(2) | 0.226(2) | 0.203(5) |
|     | z | 1.059(2) | 0.930(1) | 0.961(2) | 0.942(3) |

| $<\text{Ni}-\text{O}-\text{Ni}>$(°) | 158.8(5) | 154.8(3) | 152.7(2) | 151.7(2) | 149.1(3) | 154.4(6) | 148.7(4) | 148.0(5) | 145.9(9) |
| $<\phi>$ (°) | 10.6(3) | 12.6(2) | 13.7(1) | 14.2(1) | 15.5(2) | 12.8(3) | 15.7(2) | 16.0(3) | 17.1(5) |
| $<d_{\text{Ni-O}}>$(Å) | 1.937(5) | 1.946(4) | 1.951(3) | 1.953(2) | 1.954(3) | 1.927(6) | 1.9535(4) | 1.9515(5) | 1.950(9) |
| $<d_{\text{RE-O}}>$(Å) | 2.528(5) | 2.480(3) | 2.457(3) | 2.447(2) | 2.409(3) | 2.467(5) | 2.421(3) | 2.398(4) | 2.361(7) |
Table S2. Néel $T_N$ and Metal-Insulator $T_{MIT}$ transition temperatures for rare earth nickelate single crystals, as obtained from magnetic susceptibility, specific heat and DSC measurements.

| RE  | Pr ($T_N = T_{MIT}$) | Nd ($T_N = T_{MIT}$) | Sm | Eu | Gd | Dy | Ho | Y | Er | Lu |
|-----|----------------------|----------------------|----|----|----|----|----|---|----|----|
| $T_N$ (K) |                         |                      |    |    |    |    |    |   |    |    |
| $\chi$ heating | 130.1                  | 196.2                | 218.2 | 204.2 | -   | -   | 152.7 | - | 126.3 |
| $C_p$ heating | 186.6                  | 156.9                | 149.6 | 144.8 |
| $T_{MIT}$ (K) |                         |                      |    |    |    |    |    |   |    |    |
| DSC heating | 402.7                  | 466.3                | 511.2 | 564.4 | 574.8 | 579.3 | 583.3 | 594.7 |
| DSC cooling | 399.0                  | 460.5                | 508.1 | 559.9 | 570.1 | 574.3 | 578.0 | 588.7 |

Table S3. Curie constants $C = C_{RE} + C_{Ni}$ ground state (GS) terms, nominal ($\mu_{eff}^{Nominal}$) and experimental ($\mu_{eff}^{Experimental}$), RE$^{3+}$ effective paramagnetic moments, and Curie-Weiss temperatures ($\theta$) for RENiO$_3$ single crystals (RE = Nd, Sm, Gd, Dy, Ho, Er) and powders (RE = Pr, Eu) obtained from the Curie fits of the $1/\chi^{DC}$ ($T$) curves assuming the simultaneous presence of Ni$^{3+}$ LS with spin-only moment ($\mu_{eff} = 1.732 \mu_B$, $C_{Ni} = 0.375$ emu K mol$^{-1}$). The Goodness of the Fit (Chi$^2$) is also provided for each nickelate.

| RE  | Pr | Nd | Sm | Eu | Gd | Dy | Ho | Y | Er |
|-----|----|----|----|----|----|----|----|---|----|
| $C$ (emu K mol$^{-1}$) | 1.981(3) | 2.179(1) | 4.430(1) | 4.140(4) | 10.363(9) | 18.21(3) | 15.36(6) | 12.15(2) |
| GS Term | $^3H_4$ | $^4I_{1/2}$ | $^6H_{5/2}$ | $^7F_0$ | $^8S_{7/2}$ | $^6H_{15/2}$ | $^5I_{8}$ | $^4I_{15/2}$ |
| $\mu_{eff}^{Nominal}$ ($\mu_B$) | 3.58 | 3.62 | 0.84 | 0 | 7.94 | 10.63 | 10.60 | 9.59 |
| $\mu_{eff}^{Experimental}$ ($\mu_B$) | 3.583(3) | 3.798(1) | 5.695(1) | 5.487(3) | 8.938(4) | 11.94(1) | 10.95(2) | 9.704(8) |
| $\theta$ (K) | -76.2(4) | -102.8(2) | -1036(3) | -371.5(7) | -12.8(3) | -10.1(5) | -35(1) | -20.2(5) |
| Chi$^2$ | SI4. REFERENCES |
1. Meyer, G.; Schleid, T., Oxychlorides under Reducing Conditions - Single-Crystals of NdOCl and GdOCl. Zeitschrift Fur Anorganische Und Allgemeine Chemie 1986, 533 (2), 181-185.
2. Rietveld, H. M., A profile refinement method for nuclear and magnetic structures. J Appl Crystallogr 1969, 2 (2), 65-71.
3. Rodríguez-Carvajal, J., Recent advances in magnetic structure determination by neutron powder diffraction. Physica B: Condensed Matter 1993, 192 (1), 55-69.
4. Roisnel, T.; Rodríquez-Carvajal, J., WinPLOTR: A Windows Tool for Powder Diffraction Pattern Analysis. Materials Science Forum 2001, 378-381, 118-123.
5. Diffraction, R. O., CrysAlisPro Software System, Rigaku Corporation, Wroclaw, Poland, 2020.
6. Palatinus, L.; Chapuis, G., SUPERFLIP - a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions. J Appl Crystallogr 2007, 40 (4), 786-790.
7. Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J., CRYSTALS version 12: software for guided crystal structure analysis. *J Appl Crystallogr* **2003**, *36* (6), 1487.