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wissel, kerstin; malik, ali muhammad; vasala, sami; Plana-Ruiz, sergi; Kolb, ute; Slater, Peter; da silva, ivana; Alff, lambert; clemens, oliver

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Topochemical reduction of $\text{La}_2\text{NiO}_3\text{F}_2$: the first Ni-based Ruddlesden-Popper $n = 1$ T'-type structure and the impact of reduction on magnetic ordering

Kerstin Wissel^a, Ali Muhammad Malik^{a,b}, Sami Vasala^a, Sergi Plana-Ruiz^{c,d}, Ute Kolb^{c,e}, Peter R. Slater^f, Ivan da Silva^g, Lambert Alff^h, Jochen Rohrer^b, Oliver Clemens^{a,i,*}

^a Institut für Materialwissenschaft, Fachgebiet Materialdesign durch Synthese, Technische Universität Darmstadt, Alarich-Weiss-Straße 2, 64287 Darmstadt, Germany

^b Institut für Materialwissenschaft, Fachgebiet Materialmodellierung, Technische Universität Darmstadt, Otto-Berndt-Straße 3, 64287 Darmstadt, Germany

^c Institut für Angewandte Geowissenschaften, Technische Universität Darmstadt, Fachgebiet Elektronenkristallographie, Schnittsphanstraße 9, 64287 Darmstadt, Germany

^d LENS-MIND, Departament d'Enginyeria Electrònica i Biomèdica, Universitat de Barcelona, Martí i Franquès 1, 08028 Barcelona, Catalonia

^e Institut für Anorganische Chemie und Analytische Chemie, Centre for High Resolution Electron Microscopy, Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14, Mainz, 55128, Germany

^f School of Chemistry, University of Birmingham, Birmingham B15 2TT, United Kingdom

^g ISIS Facility, Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0QX, United Kingdom

^h Technische Universität Darmstadt, Institut für Materialwissenschaft, Fachgebiet Dünne Schichten, Alarich-Weiss-Straße 2, 64287 Darmstadt, Germany

ⁱ Institute for Nanotechnology, Karlsruhe Institute of Technology, Herrmann-von-Helmholtz-Platz 1, 73644 Eggenstein-Leopoldshafen, Germany

* Corresponding Author

Fax: +49 6151 16 20965

E-Mail: oliver.clemens@md.tu-darmstadt.de

Abstract

Within this study, we show that a broad range of reduced phases $\text{La}_2\text{NiO}_3\text{F}_{2-\Delta}$ can be derived from Ruddlesden-Popper-type $\text{La}_2\text{NiO}_3\text{F}_2$ using a reductive topochemical defluorination method based on reactions between the oxyfluoride and sodium hydride. The selective extraction of fluoride results in strong structural changes, and the nuclear and magnetic structures of the obtained phases have been determined. Due to the high anion content in $\text{La}_2\text{NiO}_3\text{F}_2$, the formation of Ni^{+} containing compounds has been observed under reduction. For the first time, this has led to the formation of the highest reduced end member with T'-type structure with an approximate composition of $\text{La}_2\text{NiO}_3\text{F}$ in the $n = 1$ Ruddlesden-Popper-type series containing only Ni^{+} as the B-cation. This compound can be described as stacking of alternating (La/O₂/La) fluorite-type layers with $\text{La}_{n-1}(\text{NiO}_2)_n$ infinite layer structural blocks. The underlying reaction mechanism has been investigated by means of X-ray and neutron diffraction, elemental analysis and magnetic measurements. Further, to gain a deeper understanding of structural distortions, DFT-based calculations were performed, providing information about structural rearrangements upon defluorination and magnetic interactions. It is highlighted that the presence of even small amounts of d^9 configured Ni^{+} cations leads to strong structural changes in $\text{La}_2\text{NiO}_3\text{F}_{1.93}$, introducing long range antiferromagnetic ordering between the adjacent perovskite building blocks by increasing the Ni-X-X-Ni super-superexchange interactions as compared to stoichiometric $\text{La}_2\text{NiO}_3\text{F}_2$.

1 Introduction

Topochemical modifications of transition metal oxides, especially of perovskites or related Ruddlesden-Popper (RP) type compounds, allow the synthesis of metastable phases that are inaccessible by conventional high-temperature reactions.¹ This gives the ability to control the oxidation state of the transition metal, which is critical for the development of new materials with defined intrinsic properties. For multinary oxides containing more than one cation species, the control of the transition metal oxidation state can be achieved via aliovalent substitution of another cation or via manipulation of the anion sublattice. These latter manipulations can cover a wide range from anion exchange, over intercalation to extraction. In this respect, low-temperature fluorination methods using gaseous or solid-state reagents (e.g. F₂ gas, NH₄F, metal fluorides (CuF₂, AgF₂, AgF etc.), XeF₂, fluorinated polymers (PTFE, PVDF)) and electrochemical reactions can be used for the stabilization of oxide and fluoride anions within one structure.²⁻⁵ Depending on the reaction method the fluorination can be oxidizing (fluoride is intercalated into vacant or interstitial sites), non-oxidative (substitution of one oxide by one fluoride and additional intercalation of one fluoride, e.g. in Sr₂TiO₃F₂^{6,7}) or even reducing (substitution of one oxide by one fluoride, e.g. in SrFeO₂F⁸). Other powerful approaches for the manipulation of the anion sublattice are topochemical reduction methods using metal hydrides leading to anion deintercalation, which can be also accompanied by hydride intercalation.⁹

As indicated above, compounds with the perovskite structure ABO₃ and the RP (also called K₂NiF₄ or T for n = 1) structure A_{n+1}B_nO_{3n+1} (Figure 1 left) have been investigated widely. The perovskite-related Ruddlesden-Popper structure can be described as n ABO₃ perovskite building blocks being separated by AO rock salt layers. Additional anions can be intercalated into vacant interstitial sites, which are located where the rock salt and the perovskite building blocks interpenetrate each other.

Prominent examples for topochemical reactions can be found in cuprates derived from the RP-type La₂CuO₄ (n = 1) and its higher order members (n = 2, 3) leading to the observation of high-temperature superconductivity.¹⁰⁻¹⁷ On these compounds, numerous studies on the influence of cation substitution, oxygen over-stoichiometry and fluoride incorporation have been performed. After the discovery of superconductivity in cuprates, nickelates have been also considered promising candidates for superconductivity due the isoelectronic configuration of Cu³⁺/Cu²⁺ and Ni²⁺/Ni⁺ (d⁹/d⁸)¹⁸⁻²⁰. Theoretical studies predict that superconductivity can only be evoked in nickelates with Ni²⁺/Ni⁺ in a square-planar coordination forming infinite NiO₂ layers.¹⁸ Interestingly, all known nickelates having infinite NiO₂ square-planar layers are members of the T'-type Ln_{n+1}Ni_nO_{2n+2} (Ln = La, Nd, Pr; n = 2, 3, ∞) homologous series.²¹⁻²⁷ For example, the deoxygenation of La₃Ni₂O₇ and La₄Ni₃O₁₀ leads to the formation of La₃Ni₂O₆ and La₄Ni₃O₈, respectively. These T' structures can be described as stacking of alternating (La/O₂/La) fluorite-type layers and La_{n-1}(NiO₂)_n infinite layer structural blocks. So far, only the so-called double (n=2) and triple (n=3) layer T'-type nickelates have been reported.^{24, 25}

In analogy to La₃Ni₂O₆ and La₄Ni₃O₈ (Table 1, which illustrates the Ni oxidation states and anion site occupations in lanthanum nickelates and lanthanum nickel oxyfluorides and their reduced compounds), it could be assumed that a reduction of La₂NiO₄ (n=1) to La₂NiO_{4-d} would lead to the formation of the single (n=1) layer T'-type structure (Figure 1 right). For this compound, the formation of significant

amounts of monovalent Ni species would result in a considerable number of vacancies. Despite the great research interest into low-valent nickelates in the field of high-temperature superconductors in the recent years, this T'-type structure has not been reported for the $n = 1$ member of the RP series $\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$ so far. This might be related to the fact that T' compounds with large anion deficiency on the interstitial sites are not known, with a structural origin possibly lying in the resulting low coordination numbers of the A-site cation. For strongly reduced phases with the $\text{RP}_{n=1}$ structure type, e.g. $\text{LaSrNiO}_{3.1}$ ²⁸, anion vacancies on the equatorial site have been observed, which results in chains of square-planar coordinated cations instead of layers.

Figure 1: (left) schematic drawing of the $n = 1$ Ruddlesden-Popper-type (K_2NiF_4 -type or T-type) structure with composition $\text{A}_2\text{BX}_{12}^{\text{eq}}\text{X}_2^{\text{ap}}\text{X}_3^{\text{int}}$; (right) schematic drawing of the $n = 1$ T'-type structure with composition $\text{A}_2\text{BX}_{12}^{\text{eq}}\square_2^{\text{ap}}\text{X}_3^{\text{int}}$. Equatorial (eq.), apical (ap.) and interstitial (int.) anion sites are shown with different colors. In the stoichiometric T'-type compounds, the interstitial anion site is not occupied.

In order to avoid such an anion deficiency, while still be able to reduce the compound and stabilize the T'-type structure, a topochemical modification leading to the introduction of additional anions into the parent compound might be a suitable approach. In this context, the polymer-based low-temperature fluorination of $\text{La}_2\text{NiO}_{4+d}$ to $\text{La}_2\text{NiO}_3\text{F}_2$ using polyvinylidene fluoride (PVDF) as fluorination reagent was already shown to facilitate the incorporation of more anions via a coupled substitution/insertion process, in which 1 O^{2-} is replaced by 2 F^- under maintenance of the Ni^{2+} oxidation state.²⁹

A subsequent reductive metal hydride-based defluorination might further allow for the synthesis of a single ($n=1$) layer T' type nickel oxyfluoride with a composition of $\text{La}_2\text{NiO}_3\text{F}$. This defluorination strategy was suggested by our group recently.^{30, 31} It was shown that sodium hydride (NaH) is a good candidate for the selective extraction of fluoride species from $\text{Sr}_2\text{TiO}_3\text{F}_2$ and $\text{Sr}_3\text{Ti}_2\text{O}_5\text{F}_4$ due to the high stability of the reaction product NaF.³⁰

The introduction of additional anions while maintaining a Ni^{2+} oxidation state (five anions per formula unit in $\text{La}_2\text{NiO}_3\text{F}_2$ instead of four anions per formula unit in La_2NiO_4) might be crucial to obtain the $n = 1$ T'-type structure. For $\text{La}_2\text{NiO}_3\text{F}_2$, one F^- anion could be removed before an anion deficiency on the interstitial site (less than four anions per formula unit) would have to be generated (Table 1). Further, by reducing $\text{La}_2\text{NiO}_3\text{F}_2$ to $\text{La}_2\text{NiO}_3\text{F}$, a Ni valence as low as +1 might be achieved. In contrast, only higher Ni valences of +1.5 and +1.33 could be achieved for previously studied $\text{La}_3\text{Ni}_2\text{O}_6$ and $\text{La}_4\text{Ni}_3\text{O}_8$.²⁴⁻²⁷

Table 1: Comparison between $n = 1, 2, 3, \infty$ Ruddlesden-Popper-type and reduced T' -type lanthanum nickelates and $n = 1$ Ruddlesden-Popper-type and reduced T' -type lanthanum nickel oxyfluorides. Also given are the Ni oxidation states and occupations of anion sites of the different compounds.

	Ruddlesden-Popper structure of oxide	T' structure of reduced oxide	Ruddlesden-Popper structure of oxyfluoride	T' structure of reduced oxyfluoride
n = 1	$La_2Ni^{2+}O_2^{eq}O_2^{ap}\square_2^{int}$	$La_2Ni^{(2-2d)+}O_2^{eq}\square_2^{ap}O_{2-d}^{int}$	$La_2Ni^{2+}O_2^{eq}O^{ap}F^{ap}F^{int}\square^{int}$	$La_2Ni^{+}O_2^{eq}\square_2^{ap}O^{int}F^{int}$
n = 2	$La_3Ni_2^{2.5+}O_4^{eq}O_3^{ap}\square_2^{int}$	$La_3Ni_2^{1.5+}O_4^{eq}\square_3^{ap}O_2^{int}$		
n = 3	$La_4Ni_3^{2.67+}O_6^{eq}O_4^{ap}\square_2^{int}$	$La_4Ni_3^{1.33+}O_6^{eq}\square_4^{ap}O_2^{int}$		
n = ∞	$LaNi^{3+}O_3$	$LaNi^{+}O_2$		

The layered structure of RP-type compounds $A_{n+1}B_nO_{3n+1}$ leads to highly anisotropic magnetic exchange interactions with overall low effective magnetic moments.³²⁻³⁴ A decreased dimensionality (low n) corresponds to decreasing strength of magnetic interactions in the c direction via the rock salt building blocks. In particular for $n = 1$, quasi-two dimensional B-O-B networks are formed which are separated by the non-magnetic rock-salt layers. The in-plane (within the ab -plane) exchange interactions are mediated via B-O-B bonds, while the intra-bilayer (out-of-plane along the c axis) exchange takes place via B-X-X-B (X being oxide or fluoride ions). The interactions can be ferromagnetic or antiferromagnetic depending on whether the dominating interaction is double exchange or superexchange, respectively. The introduction of additional anions into the interstitial site, further, increases the distances between adjacent layers, reducing the exchange interactions significantly since they take place over longer distances and/or possibly over a larger number of anions (e.g. B-X-X-X-B). With respect to the type of anion, interactions via oxide ions are known to be stronger as compared to fluoride ions.³⁵

In this article, we report on the preparation of low-valent nickel compounds via hydride based reduction of $La_2NiO_3F_2$ using sodium hydride. The reaction mechanism was studied via a combination of methods (X-ray and neutron powder diffraction, elemental analysis and magnetic measurements). Further, the nuclear and magnetic structures of the obtained phases were derived. Quantum chemical calculations help to provide insights into the reaction mechanism, structural rearrangement processes and their impact on the magnetic interactions. By this, a broad range of new fluoride extracted compounds was found, in which the reduction induces unusual strengthening of antiferromagnetic ordering between the perovskite-type layers for $RP_{n=1}$ compounds.

2 Experimental

2.1 Synthesis of La_2NiO_{4+d} and $La_2NiO_3F_2$

The precursor oxide La_2NiO_{4+d} was synthesized by a solid-state reaction of previously dried (700 °C, 4h, Ar) high purity La_2O_3 (Alfa Aesar, 99.9%) and NiO (Alfa Aesar, 99%). The starting materials were mixed in stoichiometric amounts using a planetary ball mill (ZrO_2 grinding jar and balls, 250 RPM, 30 min) and heated to 1200 °C for 12 h in air with an intermediate regrinding step. The oxyfluoride $La_2NiO_3F_2$ was prepared by chemical fluorination of La_2NiO_{4+d} using the fluorination agent polyvinylidene fluoride $(CH_2CF_2)_n$ (PVDF, Sigma-Aldrich). The as prepared precursor oxide was mixed with PVDF with 2.5 % excess and heated to 370 °C for 24h under air.

2.2 Topochemical reductions of $\text{La}_2\text{NiO}_3\text{F}_2$

The reductions of $\text{La}_2\text{NiO}_3\text{F}_2$ were performed using NaH (dry, 95 %, Sigma-Aldrich) as reducing agent. The oxyfluoride was intimately ground with NaH using mortar and pestle in an Ar-filled glovebox according to equation 1:

Since side reactions are known to occur for Ni containing compounds (e.g., formation of metallic Ni)²², an increased range of NaH equivalents was studied, $0.25 \leq x \leq 2$ ($\Delta x = 0.25$). Additionally, one reduction was performed using a large excess of NaH ($x = 2.5$). The different mixtures were subsequently placed into corundum crucibles, sealed in stainless steel vacuum tight reactors equipped with an oil bubbler to avoid build-up of overpressure, and heated to 300 °C for 48 h. After the reaction, the reactor was opened inside an Ar-filled glovebox and the sample was removed.

2.3 Re-oxidation and re-fluorination of reduction reaction products

Reacted phase mixtures $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{NaH}$ with $x = 0.5, 1$ and 1.5 were intentionally re-oxidized by heating them to 350 °C for 4 h in air.

The re-fluorination experiments on $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{NaH}$ with $x = 1$ and 1.5 were performed using flowing F_2 (10 % in N_2) at temperatures between 50 and 300 °C for durations of 15 min.

2.4 X-ray and neutron diffraction experiments

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance in Bragg-Brentano geometry with $\text{Cu K}\alpha$ radiation and a VANTEC detector. For phase quantification of the reacted samples of $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{NaH}$ ($0.25 \leq x \leq 2.5$), the samples were measured in a 2θ -range between 20° and 70° using a fixed divergence slit for ~ 4 h. The high quality data for the Rietveld refinements of $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{NaH}$ with $x = 0.25, 0.5, 1$ and 1.5 were recorded using a variable divergence slit of 6 mm with measurement times of ~ 17.5 h in the angular range of 20–130°. All samples were measured inside low background airtight specimen holders (Bruker A100B36/B37), which were sealed inside an Ar-filled glovebox.

Time of flight (TOF) powder neutron powder diffraction (NPD) data³⁶ were recorded on the GEM diffractometer at the ISIS pulsed spallation source (Rutherford Appleton Laboratory, UK)^{37, 38}. ~1.5 g of $\text{La}_2\text{NiO}_3\text{F}_2$ or the reacted samples of $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{NaH}$ with $x = 0.25, 0.5, 1$ and 1.5 were loaded into 6 mm diameter thin-walled, air-tight sealed cylindrical vanadium sample cans. For the measurements of $\text{La}_2\text{NiO}_3\text{F}_2$, data were collected at ambient temperature, 100 K, 55 K and 10 K for 170 μAh proton beam current to the ISIS target (corresponding to ~ 1 hours of beam time). The reacted samples of $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{NaH}$ with $x = 0.25, 0.5, 1$ and 1.5 were measured at ambient temperature, 100 K and 10 K for 510 to 850 μAh proton beam current (corresponding to ~ 3 to 5 hours of beam time). The time-of-flight data were normalized to the incident spectrum and corrected for detector efficiency by reference to a V:Nb standard using the Mantid suite of diffraction utilities³⁹.

Analysis of diffraction data was performed using the Rietveld method with the program TOPAS V. 5.0^{40, 41} using the whole XRD data 2θ -range as well as the data recorded on all diffraction banks of the TOF

neutron powder diffractometer. The instrumental intensity distribution of the XRD and NPD instruments were determined empirically from a sort of fundamental parameters set ⁴² using a reference scan of LaB₆ (NIST 660a) and silicon (NIST SRM640c), respectively. The microstructural parameters (crystallite size and strain broadening) were refined to adjust the peak shapes. Thermal displacement parameters were constrained to be the same for all atoms of all phases to minimize quantification errors and correlation with occupancy parameters. Note that quantification errors are of the order of 1-2 wt-% at least for the phase quantities given in the article; numerical errors obtained from the refinement are known for not representing a reasonable interval of trust, and so error bars of the numerical errors are omitted for the graphical representations of phase quantities.

For the determination of the magnetic structure, the magnitude and the orientation of magnetic moments, refinements were performed on GEM bank 3 data only.

For the determination of amorphous phase content, the reduced samples were mixed in a defined weight ratio with the standard LaB₆ (Sigma-Aldrich, 99 %) and XRD patterns were recorded. The calculation of the respective amorphous fraction was performed using the internal standard method as implemented in TOPAS V. 5.0.

2.5 Elemental analysis

Elemental analysis was performed on a VarioEL III CHN (Elementar). Samples were heated in Sn boats under oxygen and the evolving gases were gas chromatographically separated and analyzed quantitatively with a thermal conductivity detector. The hydride content was determined as the mean of four measurements.

2.6 Transmission electron microscopy characterization

Samples of La₂NiO₃F₂ and the reduction reaction products La₂NiO₃F₂ + x NaH with x = 0.25 and 1.5 were prepared by placing a drop of a dispersion of the respective powder in n-hexane on a carbon coated copper grid. A FEI Tecnai F30 S-TWIN transmission electron microscope (TEM) equipped with a field emission gun and operated at 300 kV was used. For fast and automated diffraction tomography (Fast-ADT) experiments ^{43, 44}; a 10-μm condenser aperture, spot size 6 and gun lens 8 were set to produce a quasi-parallel beam of 200-nm in size. For the identification of Ni-containing particles, energy dispersive X-ray (EDX) spectroscopy measurements were conducted with a 50-μm condenser aperture, spot size 6 and gun lens 1 to increase the electron dose and have a reliable amount of counts on the EDX detector (EDAX EDAM III). STEM images were collected using a Fischione high-angle annular dark field (HAADF) detector. Electron diffraction patterns were acquired with an UltraScan4000 CCD camera provided by Gatan (16-bit, 4096 x 4096 pixels). Hardware binning 2 and exposure time of 1 seconds were used to acquire non-saturated diffraction reflections. Fast-ADT datasets were acquired with an automated acquisition module developed for FEI and JEOL microscopes, which allows the acquisition of electron diffraction tomographies in around 10 minutes for conventional CCD cameras and fixed tilt step of 1°. Precession electron diffraction (PED) ⁴⁵ was coupled to the Fast-ADT data collection to minimize the dynamical effects and improve the reflection intensity integration quality. ⁴⁶ PED was generated by means of the DigiStar system developed by NanoMegas SPRL and it was kept to 1°.

Three-dimensional processing of the Fast-ADT data was done by the eADT software package.⁴⁷ Sir2014⁴⁸ was used for ab initio structure solution and Jana2006⁴⁹ was later used for crystal structure refinement. Intensity extraction for dynamical refinement was done by PETS2⁵⁰. EDX peak identification and quantification was carried out by the ES Vision software.

2.7 Magnetic measurements

Magnetic characterization was performed with a Quantum Design MPMS-3 Squid VSM. Powder samples were placed and sealed in gelatin capsules and mounted in a straw. Zero-field cooled (ZFC) and field-cooled (FC) curves were measured in the temperature region from 5 to 300 K in the applied field $\mu_0 H = 1$ T. Field-dependent measurements were performed at 10, 100 and 300 K. The magnetic field was scanned from 5 to -5 T.

2.8 DFT+U calculations

The DFT calculations were performed using Vienna ab-initio simulation package (VASP)^{51, 52} by employing projector augmented wave (PAW)^{53, 54} method for pseudopotential and plane wave expansion of wave function. The Perdew–Burke–Ernzerh (PBE)⁵⁵ form of generalized gradient approximation (GGA) for exchange-correlation functional along with the +U correction as proposed by Dudarev, et al.⁵⁶ was used to account for strong localization of the d-orbitals of transition metal (Ni) ions, which is not well described in standard GGA. The difference of U and J parameters known as U_{eff} bears importance for the currently utilized +U model. The $U_{\text{eff}} = U - J$ for all compounds was selected to be 6 eV, lying within a suitable U range for nickelate compounds^{18, 57}. The parameter J was fixed at 0 eV for all the calculations. The energy cut-off for the plane wave basis set was chosen to be 600 eV. The reciprocal space was sampled by a Monkhorst-Pack type⁵⁸ Γ -centered k-mesh of 2x4x5. During structural optimization, the forces were converged within 0.01 eV/Å for each atom. All degrees of freedom without symmetry constraint were allowed during structural relaxations, unless mentioned otherwise. The energy criterion for convergence of the electronic self-consistency was set to 1×10^{-6} eV. The utilized pseudopotentials treated 7, 11, 10, and 6 electrons as part of the valence band of F, La, Ni, and O atoms respectively.

3 Results and discussion

3.1 Topochemical reduction of $\text{La}_2\text{NiO}_3\text{F}_2$

3.1.1 Analysis of reduction mechanism

The topochemical fluorination of $\text{La}_2\text{NiO}_{4+d}$ to $\text{La}_2\text{NiO}_3\text{F}_2$ ($a = 12.8473(2)$ Å, $b = 5.79922(8)$ Å, $c = 5.49222(10)$ Å, $V_{\text{f.u.}} = 204.60(1)$ Å³) leads to a symmetry lowering from $I4/mmm$ to $Cccm$. The structural distortion is caused by a channel-like ordering of oxide ions on the interlayer sites leading to an expansion of the lattice perpendicular to the stacking direction, accompanied by a strong tilting of the NiO_4F_2 octahedra.²⁹ This unusual anion ordering might have interesting effects on the structure of the defluorinated phases. Depending on the used synthesis batch of the parent oxide $\text{La}_2\text{NiO}_{4+d}$, either phase pure samples are formed or additionally a small amount of $\text{La}_{0.5}\text{Zr}_{0.5}\text{O}_{1.75}$ (~ 1 wt%) is found. Presumably, the impurity phase is formed due to the use of a ZrO_2 grinding jar and balls during the ball

milling process. The phase fraction of this impurity phase, if found in $\text{La}_2\text{NiO}_{4+d}$ and $\text{La}_2\text{NiO}_3\text{F}_2$, remains constant in the defluorinated products.

For the topochemical reduction of $\text{La}_2\text{NiO}_3\text{F}_2$, various mixtures of $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{ NaH}$ were reacted and investigated by means of X-ray diffraction (Figure 2). Neglecting decomposition during the reaction, the reaction equation of the desired reduction takes place according to equation 2 (for $x \leq 1$).

Figure 2: X-ray diffraction patterns of $\text{La}_2\text{NiO}_3\text{F}_2$ and the products obtained after reaction of $\text{La}_2\text{NiO}_3\text{F}_2$ with $x \text{ NaH}$ ($0.25 \leq x \leq 2.5$). For the Rietveld refinements of the patterns shown together with an assignment of reflections to $\text{La}_2\text{NiO}_3\text{F}_2$ and the reduced phases monoclinic $\text{La}_2\text{NiO}_3\text{F}_{2-a}$, orthorhombic #1 $\text{La}_2\text{NiO}_3\text{F}_{2-b}$, orthorhombic #2 $\text{La}_2\text{NiO}_3\text{F}_{2-c}$ and tetragonal $\text{La}_2\text{NiO}_3\text{F}_{2-d}$ the reader is referred to Figure S 1 in the Electronic Supplementary.

Depending on the amount x of added NaH , phase mixtures of phases with different fluoride contents and strongly different structures are formed, visually evident from the strong shifts and splitting of reflections in comparison to $\text{La}_2\text{NiO}_3\text{F}_2$. By studying the broad range of compositions, the following four phases (given in the order of appearance for increasing x) were identified: monoclinic $\text{La}_2\text{NiO}_3\text{F}_{2-a}$, orthorhombic #1 $\text{La}_2\text{NiO}_3\text{F}_{2-b}$, orthorhombic #2 $\text{La}_2\text{NiO}_3\text{F}_{2-c}$ and tetragonal $\text{La}_2\text{NiO}_3\text{F}_{2-d}$. The metastability

of $\text{La}_2\text{NiO}_3\text{F}_2$ and the necessity to reduce reaction temperatures can be considered as possible limitations to obtain phase pure samples. In particular, the reaction chemistry must be carefully balanced between the energetic stability of the reaction products, kinetic limitations to reach the energetically most stable reaction products and the metastability of the educt. Rietveld analysis of XRD data was performed for all compositions studied; the crystal structures of the above given phases were analyzed by coupled analysis of X-ray and neutron powder diffraction data (see section 3.1.2.1; the refined patterns of the reacted mixtures $\text{La}_2\text{NiO}_3\text{F}_2 + 0.25 \text{ NaH}$, $\text{La}_2\text{NiO}_3\text{F}_2 + 0.5 \text{ NaH}$ and $\text{La}_2\text{NiO}_3\text{F}_2 + 1.5 \text{ NaH}$, from which the used structural models of the four phases were deducted, are shown in Figure 4, Figure 7 and Figure 8). Each phase has a distinctive set of lattice parameters with a nearly constant volume per formula unit (Figure 3 a) within their range of existence. A detailed list of refined lattice parameters, unit cell volumes and phase fractions is given in Table S 1. Compared to $\text{La}_2\text{NiO}_3\text{F}_2$, the volumes of the orthorhombic phases $\text{La}_2\text{NiO}_3\text{F}_{2-b}$ and $\text{La}_2\text{NiO}_3\text{F}_{2-c}$ decrease significantly with increasing defluorination. The monoclinic phase $\text{La}_2\text{NiO}_3\text{F}_{2-a}$ has an increased volume and the tetragonal phase $\text{La}_2\text{NiO}_3\text{F}_{2-d}$ shows a slightly decreased volume although strong changes of lattice parameters are found.

The evolution of the weight fractions of obtained phases as a function of x is given in Figure 3 b). For $x = 0.25$, the majority of the samples consists of the monoclinic phase, with the orthorhombic #1 phase being present in addition. While the phase fraction of the monoclinic phase is continuously decreasing for values $0.25 \leq x \leq 0.75$, the orthorhombic #1 phase becomes the main phase for increasing x . For $x \geq 1$, the phase fraction of the orthorhombic #1 phase is reduced and additionally a second orthorhombic #2 phase and a tetragonal phase are formed. The phase fractions of these phases increase in the following before they decrease drastically. This strong decrease for $x \geq 1.75$ suggests a substantial decomposition of the former RP-type phases (the possibility of decomposition due to water and a resulting HF release can be ruled out since the samples were prepared, stored and characterized under Ar atmosphere ($< 0.1 \text{ ppm H}_2\text{O}$)). This also becomes evident with respect to the formation of decomposition products (LaOF , NiO , La_2O_3) (Figure 3 c), as well as on comparing the amount of formed NaF to the hypothetical amount of a product containing only crystalline phases (Figure 3 d). A strong increase of LaOF and the considerable divergence between the weight fraction of measured and calculated NaF (assuming a complete reaction of used NaH to NaF since no unreacted NaH or NaOH are present) starts already at $x = 1$. In contrast, the formation of La_2O_3 can only be observed for $1.75 \leq x$. For $x = 2.5$, besides La_2O_3 , only $\sim 7 \text{ wt\%}$ of the orthorhombic phase #2 is found. The presence of crystalline Ni (or NiO) which should be formed during decomposition could not be confirmed by means of diffraction (except for $x = 1.75$ and 2, where a very small phase fraction of NiO is observed) possibly since it may form amorphous or nanocrystalline clusters. Indication for the formation of an amorphous Ni containing phase is given in reaction products with large excess NaH ($x = 2.5$), in which, even though no crystalline Ni phase can be found at all, a very broad bump is found between $43 - 46^\circ 2\theta$ (see Figure S 2 in Electronic Supplementary). This angular range coincides with the range, in which the scattering of amorphous Ni has been reported.⁵⁹ The highest-intense (111) reflection of crystalline Ni would be expected at $\sim 44^\circ 2\theta$.⁶⁰ However, magnetic measurements give clear indication for the existence of ferromagnetic Ni (see section 3.1.3.1), especially with regards to the antiferromagnetic ordering found for the reduced compounds. The partial decomposition on reduction can be confirmed further by determining the amorphous weight fractions (Figure 3 e) within the reaction products using the method

of an internal standard. For $0.25 \leq x \leq 1.5$, a continuous increase of the amorphous weight fractions is found (it is emphasized that the outlier of $x = 1$ could be reproduced within 3 attempts). Remarkably, for $1.75 \leq x \leq 2.5$, the amorphous phase fractions decrease again, indicating a re-crystallization on the formation of the final decomposition product La_2O_3 .

From the broad range of samples measured, a set of competing reactions as well as decomposition reactions (equation 3-5) can be formulated, which explain the reaction products and variety of phases found, highlighting the most plausible reaction mechanism:

Decomposition reactions: $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{NaH} \rightarrow 2 \text{LaOF} + \text{Ni} + x \text{NaOH} + \frac{1-x}{2} \text{O}_2$ (equation 3)

Partial fluoride-oxide exchange: $\text{La}_2\text{NiO}_3\text{F}_{2-x} + y \text{La}_2\text{O}_3 \rightarrow \text{La}_2\text{NiO}_{3+y}\text{F}_{2-x-y} + 2y \text{LaOF}$ ($x+y = \Delta$) (equation 5)

Since no NaOH was observed, a reaction according to equation 3 seems unlikely. This phase could also not be observed in our previous study on the reduction of $\text{Sr}_2\text{TiO}_3\text{F}_2$ ³⁰ and $\text{Sr}_3\text{Ti}_2\text{O}_5\text{F}_4$ ³¹, which do not show significant amorphization.

LaOF is found for $x \leq 1.75$, while La_2O_3 (equation 4) is only present for $x \geq 1.75$. This fact might be explained by a partial fluoride-oxide exchange between $\text{La}_2\text{NiO}_3\text{F}_{2-\Delta}$ and La_2O_3 according to equation 5, which could be facilitated for the fluoride richer RP phases at low values of x . Taking this into account (together with the fact that more than one RP type phase is present especially for high values of x), it is clear that a detailed determination of the anion composition, i.e. the O/F ratio, of the reduced phases is not possible. However, the neutron diffraction studies allow for the approximate determination of an anion content of each phase. Nevertheless, the consistency of the structural changes together with the quantification of the reaction products renders the above described defluorination mechanism the most likely scenario.

The occupation factors of the different anions sites of the reduced phases (as obtained from the couple Rietveld analysis, see section 3.1.2) allow for an estimation of the composition of each individual phase. Weighted by the relative phase fraction of the phases derived from $\text{La}_2\text{NiO}_3\text{F}_2$ (not taking decomposition and side products, fluoride-hydride substitution (see below) or amorphization into account) an approximate overall value of Δ with Δ being the fluoride extracted from $\text{La}_2\text{NiO}_3\text{F}_{2-\Delta}$ can be determined for a specific x (Figure 3 f). While for values $0.25 \leq x \leq 0.75$, a steady increase in Δ can be observed, Δ adopts values between ~ 0.81 and 0.94 for higher x . This seems to be reasonable since a theoretical extraction of more than one fluoride ion from $\text{La}_2\text{NiO}_3\text{F}_2$ would correspond to the formation of metallic nickel (or an average nickel oxidation state below +1, respectively) within the reduced compound, which is chemically implausible. It might be, further, possible to extract more fluoride if a (partial) fluoride-hydride substitution takes place. Elemental analysis indicates, however, that this occurs only to a small extent ($\text{La}_2\text{NiO}_3\text{F}_{2-\Delta}\text{H}_{0.12(2)}$ for $x = 0.25$ and 0.5 ; $\text{La}_2\text{NiO}_3\text{F}_{2-\Delta}\text{H}_{0.17(2)}$ for $x = 1$; $\text{La}_2\text{NiO}_3\text{F}_{2-\Delta}\text{H}_{0.21(4)}$ for $x = 1.5$). The hydride contents are significantly lower as compared to the reduction of $\text{Sr}_2\text{TiO}_3\text{F}_2 + x \text{NaH}$, where average composition of $\text{Sr}_2\text{TiO}_3\text{FH}_{0.48(1)}$ and $\text{Sr}_2\text{TiO}_3\text{H}_{1.48(10)}$ were found for $x = 1$ and $x = 2$, respectively.

³⁰ From the diffraction analysis, it was not possible to assign the residual hydride ions to one of the phases or to the amorphous phase fraction.

Figure 3: (a) Unit cell volumes per formula unit of $\text{La}_2\text{NiO}_3\text{F}_2$ and reduction reaction products $\text{La}_2\text{NiO}_3\text{F}_{2-a}$, $\text{La}_2\text{NiO}_3\text{F}_{2-b}$, $\text{La}_2\text{NiO}_3\text{F}_{2-c}$ and $\text{La}_2\text{NiO}_3\text{F}_{2-d}$ as a function of x ; (b) weight fraction of $\text{La}_2\text{NiO}_3\text{F}_2$ and reduction reaction products $\text{La}_2\text{NiO}_3\text{F}_{2-a}$, $\text{La}_2\text{NiO}_3\text{F}_{2-b}$, $\text{La}_2\text{NiO}_3\text{F}_{2-c}$ and $\text{La}_2\text{NiO}_3\text{F}_{2-d}$ not including amorphous weight fractions as a function of x ; (c) weight fraction of decomposition products in reduction reaction products $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{NaH}$ ($0.25 \leq x \leq 2.5$) not including amorphous weight fractions as a function of x ; (d) weight fraction of NaF in reduction reaction products $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{NaH}$ ($0.25 \leq x \leq 2.5$) not including amorphous weight fractions as a function of x , together with theoretically expected values calculated assuming full conversion to NaF from the amount of NaH added; (e) amorphous weight fractions in reduction reaction products $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{NaH}$ ($0.25 \leq x \leq 2.5$) fractions as a function of x (f) value of extracted fluoride Δ in $\text{La}_2\text{NiO}_3\text{F}_{2-\Delta}$ (calculated using the relative weight fractions of phases derived from $\text{La}_2\text{NiO}_3\text{F}_2$ and occupation factors as obtained from coupled Rietveld analysis into account) as a function of x .

Further support of the proposed reaction mechanism can be obtained by re-oxidation and re-fluorination experiments of the reduced samples. After the exposure of the reduction reaction products $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{NaH}$ with $x = 0.5, 1$ and 1.5 to air at elevated temperatures, phase mixtures with several re-oxidized phases are found (Figure S 3). Phases with similar lattice parameters were found when the parent oxide

$\text{La}_2\text{NiO}_{4+d}$ was fluorinated with varying non-stoichiometric amounts of PVDF to $\text{La}_2\text{NiO}_{3+y/2}\text{F}_{2-y}$ ⁶¹; this, together with the fact that $\text{La}_2\text{NiO}_3\text{F}_2$ cannot be reformed on re-oxidation supports the extraction of fluoride ions on the topochemical reduction, in agreement with the formation of NaF. Further, the re-fluorination of the reduction reaction products $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{NaH}$ with $x = 1$ and 1.5 were attempted using F_2 gas at various temperatures (Figure S 4). A re-fluorination could only be obtained within a narrow temperature range; for this reaction, progressive decomposition occurs in parallel. Instead of the synthesis of desired $\text{La}_2\text{NiO}_3\text{F}_2$, $\text{La}_2\text{NiO}_3\text{F}_{2+x}$ with a considerably increased c lattice parameter was found due to difficulties in controlling the extent of fluorination when using F_2 gas. Nevertheless, the successful fluorination demonstrates the reversibility of the reduction process and confirms the reaction mechanism.

3.1.2 Structural characterization of reduction products

3.1.2.1 Coupled Rietveld analyses of reduction reaction products

For the determination of the nuclear structures of the four reduced phases, coupled Rietveld analyses of room-temperature XRD and NPD data were performed on reacted samples of $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{NaH}$ with $x = 0.25, 0.5, 1$ and 1.5 . The refinements of the patterns of $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{NaH}$ with $x = 0.25, 0.5$ and 1.5 are given in Figure 4, Figure 7 and Figure 8, respectively (the refinements of $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{NaH}$ with $x = 1$ are given in Figure S 5). Due to the presence of two to three reduced phases (beside side and decomposition products) within each sample, a structural model of a particular phase was deduced from the measurement showing the highest phase fraction of this phase. The obtained model was then used in the refinement of the other samples with lower phase fractions of the phase. While doing so, no significant changes in structural parameters (lattice parameters, atom positions, site occupations etc.) of the phase and stable convergence of the refinements were observed. Although structural characterization had to be performed on phase mixtures, the large d -spacing range covered with the measurement in combination with the changes of resolution of the diffraction detector banks, and sufficient peak separation of the phases allow the determination of a concise picture of the structural changes which occur on the reductive fluoride extraction from $\text{La}_2\text{NiO}_3\text{F}_2$.

Facilitated by the high phase fraction of monoclinic $\text{La}_2\text{NiO}_3\text{F}_{2-a}$ (~ 73 wt%) within the sample, its structural model was derived from the measurement of $\text{La}_2\text{NiO}_3\text{F}_2 + 0.25 \text{NaH}$ (Figure 4). Indexing could be performed with a base-centered $\sqrt{2} \times \sqrt{2} \times 1$ supercell of the tetragonal aristotype RP-type structure. Different structural models were tested, and a close structural relationship between orthorhombic $\text{La}_2\text{NiO}_3\text{F}_2$ (space group: $Cccm$) and the monoclinic reduced phase $\text{La}_2\text{NiO}_3\text{F}_{2-a}$ was observed. Here it is found that reduction of the symmetry from the orthorhombic space group $Cccm$ towards a monoclinic distortion with C centering is only possible for the *translationengleiche* subgroups $C12/m1$ or $C12/c1$, with superior fits obtained for the model with $C12/c1$ symmetry (for comparison, refined patterns with space group $C12/m1$ can be found in Figure S 6). The corresponding symmetry tree and the refined structural parameters are given in Figure 5 and Table 2, respectively.

Figure 4: Coupled Rietveld analysis of $\text{La}_2\text{NiO}_3\text{F}_2 + 0.25 \text{ NaH}$ of GEM bank 1-6 NPD and XRD data measured at room temperature (RT), from which the structural model of monoclinic $\text{La}_2\text{NiO}_3\text{F}_{2-a}$ (approximate composition: $\text{La}_2\text{NiO}_3\text{F}_{1.93}$) was derived. The structural model for $\text{La}_2\text{NiO}_3\text{F}_{2-b}$ was derived from the coupled Rietveld analysis of $\text{La}_2\text{NiO}_3\text{F}_2 + 0.5 \text{ NaH}$.

eq
ap
int

Tetragonal
I4/mmm (139)

$a_1 = 4.02 \text{ \AA}$
 $c_1 = 12.94 \text{ \AA}$

$\downarrow$
 $a_2 = c_1$
 $b_2 = a_1 - b_1$
 $c_2 = a_1 + b_1$

Orthorhombic
Fmmm (69)

$a_2 = 12.94 \text{ \AA}$
 $b_2 = 5.76 \text{ \AA}$
 $c_2 = 5.62 \text{ \AA}$

$\downarrow$
 $a_3 = a_2$
 $b_3 = b_2$
 $c_3 = c_2$

Orthorhombic
Cccm (66)

$a_3 = 12.94 \text{ \AA}$
 $b_3 = 5.76 \text{ \AA}$
 $c_3 = 5.62 \text{ \AA}$

$\downarrow$
 $a_4 = a_3$
 $b_4 = b_3$
 $c_4 = c_3$

Monoclinic
C12/c1 (15)

$a_4 = 12.94 \text{ \AA}$
 $b_4 = 5.76 \text{ \AA}$
 $c_4 = 5.62 \text{ \AA}$
 $\beta = 88.5^\circ$

La: 4e	Ni: 2a	X1 ^{eq} : 4c	X2 ^{ap} : 4e	X3 ^{int} : 4d
0	0	0	0	0
0	0	$\frac{1}{2}$	0	$\frac{1}{2}$
z	0	0	z	$\frac{1}{4}$
z = 0.61			z = 0.84	

La: 8g	Ni: 4a	X1 ^{eq} : 8c	X2 ^{ap} : 8g	X3 ^{int} : 8f
x	0	0	x	$\frac{1}{4}$
0	0	$\frac{1}{4}$	0	$\frac{1}{4}$
0	0	$\frac{1}{4}$	0	$\frac{1}{4}$
x = 0.61			x = 0.84	

La: 8l	Ni: 4e	X1 ^{eq} : 8g	X2 ^{ap} : 8l	X3 ^{int} a: 4a	X3 ^{int} b: 4b
x	$\frac{1}{4}$	x	x	0	0
y	$\frac{1}{4}$	0	y	0	$\frac{1}{2}$
0	0	$\frac{1}{4}$	0	$\frac{1}{4}$	$\frac{1}{4}$
x = 0.14		x = 0.25	x = 0.91		
y = 0.75			y = 0.75		

La: 8f	Ni: 4c	X1 ^{eq} : 8f	X ^{ap} 2: 8f	X3 ^{int} a: 4e	X3 ^{int} b: 4e
x	$\frac{1}{4}$	x	x	0	0
y	$\frac{1}{4}$	y	y	y	y
z	0	z	z	$\frac{1}{4}$	$\frac{1}{4}$
x = 0.14		x = 0.25	x = 0.91	y = 0	y = 0.5
y = 0.75		y = 0	y = 0.75		
z = 0		z = 0.75	z = 0		

Figure 5: Symmetry tree for the symmetry reduction from the aristotype $RP_{n=1}$ with $I4/mmm$ symmetry to $Cccm$ of $La_2NiO_3F_2$ to $C12/c1$ of $La_2NiO_3F_{2-a}$. Equatorial (eq), apical (ap), and interstitial (int) sites of the anions X (O^{2-} or F^-) are indicated (see also structural data reported in Table 2).

Table 2: Structural parameters of monoclinic $La_2NiO_3F_{2-a}$ (approximate composition: $La_2NiO_3F_{1.93}$) from coupled analysis of X-ray and neutron diffraction data of $La_2NiO_3F_2 + 0.25 NaH$.

	Wyckoff site	x	y	z	Occupancy	Thermal displacement [$\text{\AA}^2$]
La1	8f	0.1123(7)	0.7483(3)	-0.0236(2)	1	0.88(1)
Ni1	4c	1/4	1/4	0	1	0.88(1)
O1 at X1 ^{eq}	8f	0.2704(1)	-0.0317(3)	0.7771(3)	1	0.88(1)
F2 at X2 ^{ap}	8f	0.9118(1)	0.8445(2)	-0.0330(3)	0.964(3)	0.88(1)
X3a ^{int}	4e	0	0	1/4	0	0.88(1)
O2 at X3b ^{int}	4e	0	0.5177(5)	1/4	1	0.88(1)
a [$\text{\AA}$]	12.9413(4)		b [$\text{\AA}$]	5.7608(2)		
c [$\text{\AA}$]	5.6186(2)		β [$^\circ$]	88.509(2)		
R_{wp}(XRD+NPD) [%]	3.40	GOF(XRD+NPD)	1.66	R_{bragg} [%]	1.73 (XRD)	
					3.70 (NPD, bank3)	
Space group	C12/c1					

Oxide and fluoride ions are indistinguishable by neutron and X-ray diffraction due to the nearly identical scattering lengths and atomic form factors. Nevertheless, the neutron diffraction data can be used to investigate the structure and composition of the anion sublattice in more detail by analysis of the occupation factors of anion sites. The symmetry reduction from $I4/mmm$ to $C12/c1$ leads to a splitting of the interlayer anion site into two 4e crystallographic sites (Figure 5). Similar to what was found for $\text{La}_2\text{NiO}_3\text{F}_2$ ²⁹, only one of those sites is fully occupied resulting in a channel-like half-filling of the interstitial sites. When also refining the occupations of the equatorial and apical anion sites, a small but considerable decrease in the occupancy of the apical anion site is observed, while the equatorial anion site remains fully occupied. From this, an overall composition of approximately $\text{La}_2\text{NiX}_{4.93}$ or of $\text{La}_2\text{NiO}_3\text{F}_{1.93}$ (assuming that only fluoride is extracted in the reduction process) can be derived. Further, this indicates that the fluoride is, as in $\text{La}_2\text{NiO}_3\text{F}_2$, occupying the apical anion site. Major structural rearrangements of the oxide and fluoride ions between different anion sites upon the reduction with low amounts of NaH can, therefore, be excluded. This can be confirmed by bond-valence-sum calculations where, similar to calculations made on $\text{La}_2\text{NiO}_3\text{F}_2$ ²⁹, more stable configurations are found when fluoride is occupying the apical site. In comparison to the orthorhombic parent phase $\text{La}_2\text{NiO}_3\text{F}_2$, the slight reduction results in a change of the b/c ratio towards unity accompanied by the monoclinic distortion. For orthorhombic $\text{La}_2\text{NiO}_3\text{F}_2$, the distortion originates from a considerable tilting of the NiO_4F_2 octahedra along the b axis.²⁹ The additional degrees of freedom of the monoclinic compound enable also a tilting of the octahedra along the c axis. This tilting leads to an increase of the distance of $\text{F}^{\text{ap}}\text{-F}^{\text{ap}}$ ($d(\text{X}2^{\text{ap}}\text{-X}2^{\text{ap}}(\text{La}_2\text{NiO}_3\text{F}_2) = 2.88 \text{ \AA}$, $d(\text{X}2^{\text{ap}}\text{-X}2^{\text{ap}}(\text{La}_2\text{NiO}_3\text{F}_{2-a}) = 2.93 \text{ \AA}$) between two neighboring perovskite building blocks. As it will be shown in section 3.1.2.2, this structural behavior on small extraction of fluoride ions can be well confirmed from DFT based calculations on compounds with composition $\text{La}_2\text{NiO}_3\text{F}_{1.75}$ and will be explained there in detail. The crystal structure of $\text{La}_2\text{NiO}_3\text{F}_{2-a}$ is shown in Figure 6 a).

Figure 6: Crystal structure of monoclinic $\text{La}_2\text{NiO}_3\text{F}_{2-a}$ (approximate composition: $\text{La}_2\text{NiO}_3\text{F}_{1.93}$) (a), orthorhombic #1 $\text{La}_2\text{NiO}_3\text{F}_{2-b}$ (approximate composition: $\text{La}_2\text{NiO}_3\text{F}_{1.39}$) (b), orthorhombic #2 $\text{La}_2\text{NiO}_3\text{F}_{2-c}$ (approximate composition: $\text{La}_2\text{NiO}_3\text{F}_{1.08}$) (c) and tetragonal $\text{La}_2\text{NiO}_3\text{F}_{2-d}$ (approximate composition: $\text{La}_2\text{NiO}_3\text{F}$) (d). For mixed anion sites, a 0.5/0.5 O/F occupation was assumed.

In the sample $\text{La}_2\text{NiO}_3\text{F}_2 + 0.25 \text{ NaH}$, besides the main phase $\text{La}_2\text{NiO}_3\text{F}_{2-a}$, additionally the phase $\text{La}_2\text{NiO}_3\text{F}_{2-b}$ ($\sim 14 \text{ wt\%}$) is present. The structural model of $\text{La}_2\text{NiO}_3\text{F}_{2-b}$ was derived from the sample $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{ NaH}$ with $x = 0.5$ (Figure 7), since this sample has a higher phase fraction of this phase. The highest weight fractions of $\text{La}_2\text{NiO}_3\text{F}_{2-c}$ ($\sim 45 \text{ wt\%}$) and $\text{La}_2\text{NiO}_3\text{F}_{2-d}$ ($\sim 18 \text{ wt\%}$) were found in the sample $\text{La}_2\text{NiO}_3\text{F}_2 + 1.5 \text{ NaH}$ (Figure 8) and their structural models were derived from its measurement.

Figure 7: Coupled Rietveld analysis of $\text{La}_2\text{NiO}_3\text{F}_2 + 0.5 \text{ NaH}$ of GEM bank 1-6 NPD and XRD data measured at room temperature (RT), from which the structural model of orthorhombic #1 $\text{La}_2\text{NiO}_3\text{F}_{2-b}$ (approximate composition: $\text{La}_2\text{NiO}_3\text{F}_{1.39}$) was derived.

Figure 8: Coupled Rietveld analysis of $\text{La}_2\text{NiO}_3\text{F}_2 + 1.5 \text{ NaH}$ of GEM bank 1-6 NPD and XRD data measured at room temperature (RT), from which the structural model of orthorhombic #2 $\text{La}_2\text{NiO}_3\text{F}_{2-c}$ (approximate composition: $\text{La}_2\text{NiO}_3\text{F}_{1.08}$) and tetragonal $\text{La}_2\text{NiO}_3\text{F}_{2-d}$ (approximate composition: $\text{La}_2\text{NiO}_3\text{F}$) were derived.

For both $\text{La}_2\text{NiO}_3\text{F}_{2-b}$ and $\text{La}_2\text{NiO}_3\text{F}_{2-c}$, best fits could be achieved using structural models with space group $Cccm$. Higher symmetries such as $Fmmm$ or other orthorhombic space groups, which show different tilting patterns of the NiX_6 octahedra (e.g. $Cmce$ ⁶²), were tested in addition. These models can, however, not explain the superstructure reflection at e.g. $d \approx 5.1 \text{ \AA}$, which can be described using the $Cccm$ model. The structural parameters are given in Table 3 and Table 4.

Table 3: Structural parameters of orthorhombic #1 $\text{La}_2\text{NiO}_3\text{F}_{2-b}$ (approximate composition: $\text{La}_2\text{NiO}_3\text{F}_{1.39}$) from coupled analysis of X-ray and neutron diffraction data of $\text{La}_2\text{NiO}_3\text{F}_2 + 0.5 \text{ NaH}$.

	Wyckoff site	x	y	z	Occupancy	Thermal displacement [$\text{\AA}^2$]
La1	8l	0.1117(2)	0.7416(5)	0	1	0.73(1)
Ni1	4e	1/4	1/4	0	1	0.73(1)
O1 at X1 ^{eq}	8g	0.2430(4)	0	1/4	1	0.73(1)
O2/F1 at X2 ^{ap}	8l	0.9271(3)	0.8153(4)	0	1	0.73(1)
X3a ^{int}	4a	0	0	1/4	0	0.73(1)
F2 at X3b ^{int}	4b	0	1/2	1/4	0.386(9)	0.73(1)
a [$\text{\AA}$]	12.698(1)		b [$\text{\AA}$]	5.6484(5)		
c [$\text{\AA}$]	5.4675(5)					
R _{wp} (XRD+NPD)[%]	4.44	GOF(XRD+NPD)	2.36	R _{bragg} [%]	0.34 (XRD)	
					1.65 (NPD, bank3)	
Space group	Cccm					

Table 4: Structural parameters of orthorhombic #2 $\text{La}_2\text{NiO}_3\text{F}_{2-c}$ (approximate composition: $\text{La}_2\text{NiO}_3\text{F}_{1.08}$) from coupled analysis of X-ray and neutron diffraction data of $\text{La}_2\text{NiO}_3\text{F}_2 + 1.5 \text{ NaH}$.

	Wyckoff site	x	y	z	Occupancy	Thermal displacement [$\text{\AA}^2$]
La1	8l	0.1134(1)	0.7500(5)	0	1	0.44(1)
Ni1	4e	1/4	1/4	0	1	0.44(1)
O1 at X ^{eq}	8g	0.2558(3)	0	1/4	1	0.44(1)
O2/F1 at X2 ^{ap}	8l	0.9284(2)	0.7875(3)	0	1	0.44(1)
X3a ^{int}	4a	0	0	1/4	0	0.44(1)
F2 at X3b ^{int}	4b	0	1/2	1/4	0.077(5)	0.44(1)
a [$\text{\AA}$]	12.5309(3)		b [$\text{\AA}$]	5.5427(1)		
c [$\text{\AA}$]	5.4758(1)					
R _{wp} (XRD+NPD)[%]	4.31	GOF(XRD+NPD)	2.28	R _{bragg} [%]	1.35 (XRD)	
					2.46 (NPD, bank3)	
Space group	Cccm					

When refining the occupations of the equatorial, apical and interstitial sites of the orthorhombic phases, the occupation factor of the 4b interstitial site, which was fully occupied in $\text{La}_2\text{NiO}_3\text{F}_2$, decrease considerably resulting in a composition of $\text{La}_2\text{NiX}_{4.39}$ ($\text{La}_2\text{NiO}_3\text{F}_{1.39}$) for orthorhombic #1 $\text{La}_2\text{NiO}_3\text{F}_{2-b}$ and of $\text{La}_2\text{NiX}_{4.08}$ ($\text{La}_2\text{NiO}_3\text{F}_{1.08}$) for orthorhombic #2 $\text{La}_2\text{NiO}_3\text{F}_{2-c}$. For monoclinic $\text{La}_2\text{NiO}_3\text{F}_{2-a}$, it was found that vacancies are formed on the apical sites, i.e. where the fluoride ions were located in the parent phase $\text{La}_2\text{NiO}_3\text{F}_2$. In contrast, no indication was given for the presence of vacancies on the apical sites for the orthorhombic phases $\text{La}_2\text{NiO}_3\text{F}_{2-b}$ and $\text{La}_2\text{NiO}_3\text{F}_{2-c}$. This shows that at least a partial rearrangement of anions between the apical and interstitial sites can take place, which is also accompanied by a lowering of the tilting of the NiX_6 polyhedra. This lowering of the tilting leads to a decrease of the bond valance sums of the interstitial anion site, which renders the allocation of fluoride ions on it more plausible. This correlates with a change in the bond distances of Ni to the apical (X2^{ap})

and equatorial ($X1^{eq}$) anions, showing increased stretching of the octahedra for increased amounts of used NaH (Table 5 and Figure 6 b and c). This is in plausible agreement with the formation of Jahn-Teller active Ni^{+} and is also observed for DFT based calculations (see section 3.1.2.2). Further, when comparing the bond distances between apical ($X2^{ap}$) and interstitial anions ($X3^{intb}$) of $La_2NiO_3F_2$ and the reduced monoclinic and orthorhombic phases, it can be seen that the distances decrease considerably indicating that the tilting of the octahedra decreases for stronger reduced phases. These distances are relatively short, but it has to be taken into account that the occupancies of this interstitial site in these phases decrease significantly. This also shows that refinements can only serve to determine an average structure of the disordered state, in which local adaptations have to be expected. The unrealistic small distances between the apical ($X2^{ap}$) and the unoccupied interstitial anions ($X3^{inta}$) highlight, moreover, that this interstitial site cannot be occupied. The distances between two apical sites ($X2^{ap}$) of neighboring perovskite building blocks are also given.

Table 5: Bond distances of $La_2NiO_3F_2$, monoclinic $La_2NiO_3F_{2-a}$, orthorhombic #1 $La_2NiO_3F_{2-b}$, orthorhombic #2 $La_2NiO_3F_{2-c}$ and tetragonal $La_2NiO_3F_{2-d}$. $X1^{eq}$ refers to the equatorial, $X2^{ap}$ to the apical and $X3^{int}$ to the interstitial anion site. In the orthorhombic space group $Cccm$ of $La_2NiO_3F_2$, $La_2NiO_3F_{2-b}$ and $La_2NiO_3F_{2-c}$ and in the monoclinic space group $C12/c1$ of $La_2NiO_3F_{2-b}$ two interstitial anion sites $X3^{inta_{Cccm}}$ or $C12/c1$ and $X3^{intb_{Cccm}}$ or $C12/c1$ exist, of which only $X3^{intb_{Cccm}}$ or $C12/c1$ is (partially) occupied. The tetragonal space group $I4/mmm$ of $La_2NiO_3F_{2-d}$ has just one interstitial site $X3^{int_{I4/mmm}}$. $X2^{ap}$ of the $La_2NiO_3F_{2-d}$ is unoccupied.

	Bond distance [Å]				
	$La_2NiO_3F_2$	$La_2NiO_3F_{2-a}$ monoclinic	$La_2NiO_3F_{2-b}$ orthorhombic #1	$La_2NiO_3F_{2-c}$ orthorhombic #2	$La_2NiO_3F_{2-d}$ tetragonal
La1 – $X1^{eq}$	2.539(2) [2x] 2.813(2) [2x]	2.423(2) [1x] 2.621(2) [1x] 2.626(2) [1x] 3.145(2) [1x]	2.552(4) [2x] 2.721(4) [2x]	2.546(3) [2x] 2.642(3) [2x]	2.665(2) [4x]
La1 – $X2^{ap}$	2.356(2) [1x] 2.602(2) [1x] 2.809(1) [2x]	2.379(2) 2.577(2) 3.176(2) 3.450(2)	2.551(4) [1x] 2.809(1) [2x] 3.184(4) [1x]	2.617(3) [1x] 2.7953(6) [2x] 3.025(3) [1x]	
La1 – $X3b^{int_{Cccm}}$ or $C12/c1$ or La1 – $X3^{int_{I4/mmm}}$	2.4718(8) [2x]	2.486(2) 2.487(2)	2.396(2) [2x]	2.411(2) [2x]	2.417(1) [4x]
Ni1 – $X1^{eq}$	2.0076(2) [4x]	2.071(2) [2x] 2.019(2) [2x]	1.9673(3) [4x]	1.9492(1) [4x]	1.9962(1) [4x]
Ni1 – $X2^{ap}$	2.160(2) [2x]	2.152(3) [2x]	2.279(4) [2x]	2.245(3) [2x]	
$X2^{ap}$ – $X3a^{int_{Cccm}}$ or $C12/c1$ or $X2^{ap}$ – $X3^{int_{I4/mmm}}$	1.990(2) [2x] ($X3^{inta_{Cccm}}$ is unoccupied)	1.876(1) [1x] 2.174(2) [1x] ($X3^{inta_{C12/c1}}$ is unoccupied)	1.953(2) [2x] ($X3^{inta_{Cccm}}$ is unoccupied)	2.017(2) [2x] ($X3^{inta_{Cccm}}$ is unoccupied)	2.2921(1) [4x] ($X2^{ap}$ is unoccupied)
$X2^{ap}$ – $X3b^{int_{Cccm}}$ or $C12/c1$ or $X2^{ap}$ – $X3^{int_{I4/mmm}}$	2.657(2) [2x]	2.659(3) [1x] 2.733(2) [1x]	2.428(2) [2x]	2.284(2) [2x]	
$X2^{ap}$ – $X2^{ap}$	2.883(2) [1x] 3.536(2) [2x] 4.552(3) [1x]	2.933(2) [1x] 3.297(2) [1x] 3.963(2) [1x] 4.599(2) [1x]	2.790(5) [1x] 3.302(3) [1x] 4.014(4) [2x]	2.961(3) [1x] 3.274(2) [1x] 3.658(2) [2x]	3.6117(1) [4x] ($X2^{ap}$ is unoccupied)

On further increase of the amount of NaH, tetragonal $\text{La}_2\text{NiO}_3\text{F}_{2-d}$ (Figure 8) is formed. This phase was found to possess a completely different intensity pattern with strong changes in the relative reflection intensities compared to the T-related orthorhombic #1 and #2 phases $\text{La}_2\text{NiO}_3\text{F}_{2-b}$ and $\text{La}_2\text{NiO}_3\text{F}_{2-c}$ in the neutron diffraction pattern (see Figure S 7 in the Electronic Supplementary). This intensity pattern is indicative for the formation of a T' type compound (space group $I4/mmm$), where the apical site is empty and the interstitial site is filled and, thus, resulting in square planar coordination for the Ni cations (Figure 6 d). The structural parameters are listed in Table 6. DFT calculations (see section 3.1.2.2) support this observation, showing that this is the most stable structure for a composition of $\text{La}_2\text{NiO}_3\text{F}$. Such T' type RP phases have only been found for compounds containing high amounts of Jahn-Teller active cations, e.g. for the Nd_2CuO_4 ⁵², $\text{La}_3\text{Ni}_2\text{O}_6$ ²⁵, $\text{La}_4\text{Ni}_3\text{O}_8$ ²⁴, giving further support that a composition close to $\text{La}_2\text{NiO}_3\text{F}$ is obtained here.^{24, 25, 63}

Table 6: Structural parameters of $\text{La}_2\text{NiO}_3\text{F}_{2-d}$ (approximate composition: $\text{La}_2\text{NiO}_3\text{F}$) from coupled analysis of X-ray and neutron diffraction data of $\text{La}_2\text{NiO}_3\text{F}_2 + 1.5 \text{ NaH}$.

	Wyckoff site	x	y	z	Occupancy	Thermal displacement [Å²]
La1	4e	0	0	0.6411(2)	1	0.44(1)
Ni1	2a	0	0	0	1	0.44(1)
O1 at X ^{eq}	4c	0	1/2	0	1	0.44(1)
X2 ^{ap}	4e	0	0	0.84	0	0.44(1)
O2/F1 at X3a ^{int}	4d	0	1/2	1/4	1	0.44(1)
a [Å]	3.9925(2) (a*√2 = 5.6462(3))		c [Å]	12.5150(9)		
R_{wp}(XRD+NPD)[%]	4.31	GOF(XRD+NPD)	2.28	R_{bragg} [%]	0.77 (XRD)	
					1.85 (NPD, bank3)	
Space group	<i>I4/mmm</i>					

3.1.2.2 Transmission electron microscopy characterization

High-resolution-TEM imaging can be a powerful technique to investigate structural changes in phase mixtures. But this type of analysis is impeded by the fact that the crystals obtained are generally quite thick and can be composed of multiple domains of different the RP-type phases as well as decomposition and side products. Therefore, an alternative approach was used to confirm the structures observed via X-ray and neutron powder diffraction methods by independent means using the Fast-ADT technique. This relatively new tool is based on the sequential acquisition of electron diffraction patterns from preferably mono-domain crystals at different consecutives tilt angles, which are separated by a fixed tilt step. The 3D reconstruction of this diffraction space data allows the determination of crystal structures in a similar way as single crystal X-ray methods.

In order to reinforce the proposed structures of $\text{La}_2\text{NiO}_3\text{F}_2$ and the reduced phases derived from X-ray and neutron powder diffraction, Fast-ADT measurements were performed on $\text{La}_2\text{NiO}_3\text{F}_2$ and the reduction reaction products with 0.25 and 1.5 NaH. The selection of suitable crystals for the measurements had proven to be very difficult because they have to be reasonably thin in order to obtain good quality data sets. Although thinner particles (see Figure S 8 in Electronic Supplementary) were chosen for the acquisition of the Fast-ADT data, these crystals were still relatively thick even for electron

diffraction. Most of the analyzed particles contain twins, other domains or large amounts of the side product NaF and/or the decomposition product LaOF for higher NaH amounts, which hamper successful structure determination of some of the reported phases. Further, it cannot be excluded that a (partial) re-oxidation of the phases has taken place during the preparation of the samples; especially isolated particles should be more prone towards oxidation. However, the deduction of unit-cell and space group information was possible for all measurements. The obtained lattice parameters (within the accuracy of this method) and space group information (see Table S 2 in Electronic Supplementary) are in agreement with the results obtained from X-ray and neutron diffraction reported in the previous sections.

Using dynamical refinement approaches, it was possible to confirm the orthorhombic structure of the precursor material $\text{La}_2\text{NiO}_3\text{F}_2$ reported previously²⁹ and the monoclinic structure of $\text{La}_2\text{NiO}_3\text{F}_{2-\Delta}$ present within the reduction reaction product with $x = 0.25$ (see Table S 3 and Table S 4 in Electronic Supplementary). It was also attempted to refine the structures of the orthorhombic #1 and #2 phases as well as the tetragonal phase found in the products with $x = 0.25$ and $x = 1.5$. Although C-centered orthorhombic and tetragonal phases could be observed, accurate structural analyses of these phases were not possible. This is presumably due to an epitaxial growth of the decomposition product LaOF on the reduced RP-type phases along the c axis, which biases the obtained reflection intensities significantly. This epitaxy gives an indication of the decomposition mechanism of the metastable oxyfluoride phases, which will be discussed in a follow-up article. The phase fractions of LaOF increase, moreover, significantly for higher NaH contents (Figure 5 c). Therefore, it is not possible to confirm the structural models of the stronger reduced phase determined from coupled Rietveld analysis of X-ray and neutron diffraction data by means of electron diffraction methods.

It has to be pointed out that the combination of X-ray and neutron diffraction methods provides a more robust analysis of the anion sublattice, especially with respect to small details in anion occupancies found for $\text{La}_2\text{NiO}_3\text{F}_2$ and $\text{La}_2\text{NiO}_3\text{F}_{2-\Delta}$. Therefore, the observed structural changes were further supported by means of theoretical methods (see section 3.1.2.3).

3.1.2.3 DFT calculation: towards understanding the structural distortions in reduced phases

As shown in the previous section, obtaining a complete structural understanding of the anion chemistry of the compounds is difficult to achieve experimentally. Therefore, DFT calculations were performed to develop a deeper understanding of the most favorable structural relaxations of the anion sublattice on reductive defluorination of $\text{La}_2\text{NiO}_3\text{F}_2$. To do so, the orthorhombic structural model of $\text{La}_2\text{NiO}_3\text{F}_2$ ($Cccm$, as published in reference 29) was considered as a starting point. Then, one to four fluoride ions per unit cell were subsequently removed (corresponding to compositions of $\text{La}_2\text{NiO}_3\text{F}_{1.75}$ to $\text{La}_2\text{NiO}_3\text{F}$), and the structure was allowed to relax. In addition, various different relative orientations of the introduced vacancies were examined together with different distributions of oxide and fluoride ions at the apical and/or interstitial sites. The equatorial site was always occupied by oxide ions. In the following, the discussion is limited to the changes of the initial to the most stable relaxed structures of the reduced phases.

For calculations on compounds $\text{La}_2\text{NiO}_3\text{F}_{2-\Delta}$ with high values of Δ , it was found that the remaining anions show a very high mobility, although no molecular dynamics was chosen (i.e. a structure optimization at

0 K). This is exemplified for the defluorinated compound with composition $\text{La}_2\text{NiO}_3\text{F}$ (Figure 9). For this compound, a complete relaxation to the T' structure can be observed for suitable initial vacancy configurations, which results from the movement of apical fluoride ions to the interstitial site, leading to a fully unoccupied apical site and a fully occupied interstitial site (an occupation with 50 % F^- and 50 % O^{2-} is assumed). This is in agreement with the experimental observation of a tetragonal T'-type $\text{La}_2\text{NiO}_3\text{F}_{2-d}$ phase (see section 3.1.2). It was found that the principle relaxation of the lattice parameters on transition to the T'-type structure could also be reproduced: the b and c lattice parameters after relaxation are found to be of the order of 5.7 - 5.8 Å, which is close to the experimental value 5.65 Å, whereas the lattice parameter a decreases to 12.67 Å (12.52 Å experimentally). Further, it was found that a relaxation to the T' structure is independent of the initial anion configuration; both, $\text{La}_2\text{Ni}(\text{O}_2)^{\text{eq}}(\text{F})^{\text{ap}}(\text{O})^{\text{int}}$ and $\text{La}_2\text{Ni}(\text{O}_2)^{\text{eq}}(\text{O})^{\text{ap}}(\text{F})^{\text{int}}$ relax to T'-type $\text{La}_2\text{Ni}(\text{O}_2)^{\text{eq}}(\square)^{\text{ap}}(\text{OF})^{\text{int}}$. We would also like to emphasize, that a relaxation to a T'-type structure seems to be hindered, if the relative location of the vacancies towards each other are unfavorable (Figure 9). This might also explain why both, T and T'-type compounds can be observed for the defluorination of $\text{La}_2\text{NiO}_3\text{F}_2$. This behavior is in principle also found for intermediate compositions, such as $\text{La}_2\text{NiO}_3\text{F}_{1.25}$ and $\text{La}_2\text{NiO}_3\text{F}_{1.5}$.

Figure 9: Structural relaxation of different vacancy ordered starting models of $\text{La}_2\text{NiO}_3\text{F}$. The starting models were derived based on removing fluoride ions from the experimentally determined orthorhombic structure of $\text{La}_2\text{NiO}_3\text{F}_2$ ²⁹. Configuration 1 was found to relax to a T' type structure, whereas configuration 2 does not.

Removing only one fluoride ion from the unit cell of $\text{La}_2\text{NiO}_3\text{F}_2$ results in a composition of $\text{La}_2\text{NiO}_3\text{F}_{1.75}$. With respect to the subgroups of C_{ccm} , this corresponds to a monoclinic ordering variant (isomorphic subgroups which maintain the orthorhombic symmetry for a similar composition require a 3- to 5-fold increase of the unit cell size, which was computationally too costly to be considered). This deviation from the orthorhombic symmetry is also found in a partly relaxed structure (compare Figure 10 (right) i) and ii)), where the angle γ changes due to this artificial fluoride ion / vacancy ordering. On fully relaxing the structure by inducing further strain, it is found that the energetically most stable structure has a similar distortion and tilting pattern as the experimentally found structure of the monoclinic compound $\text{La}_2\text{NiO}_3\text{F}_{1.93}$ (compare Figure 10 (right) iii) and iv)), which is expressed by the deviation of the angle β from 90°. The structural distortion is complicated and can be explained as follows: the reductive defluorination results in a change of the electronic structure to a d^9 Jahn-Teller-active electron

configuration of the formed Ni^+ . This Ni^+ ion is located in the NiO_4F polyhedron, and, consequently, close to the anion vacancy. The polyhedron distorts towards square planar coordination by shifting the remaining F^- ion away from the apical site towards the position of the interstitial site. However, this shift is energetically costly due to the proximity to the fluoride ion of the polyhedron with identical tilting in the layer above. By inducing the tilting along the c -axis, the fluoride ion of the NiO_4F polyhedron can move further away from the central Ni -ion by an additional $\sim 0.12 \text{ \AA} = \Delta(d_{\text{Ni-F}}) = d_{\text{Ni-F, Figure 10 (right) iii)} - d_{\text{Ni-F, Figure 10 (right) ii)}$, while additionally increasing the distance to the next closest fluoride ion by $\sim 0.05 \text{ \AA}$. This has a strong energetic impact of -0.39 eV per unit cell (u. c.).

Figure 10: Scheme of the DFT-based calculations performed to determine the most stable structure for chemically reduced $\text{La}_2\text{NiO}_3\text{F}_{1.93}$ by performing calculations on strained and non-strained $\text{La}_2\text{NiO}_3\text{F}_2$ (left) and $\text{La}_2\text{NiO}_3\text{F}_{1.75}$ (right). *: "Overall" refers to the combination of cell metrics and inner symmetry of the atoms. The viewing directions of the left (upper) and right (lower) representations corresponding to one relaxed structure are along the b axis and c axis, respectively.

The electronic origin of the monoclinic distortion can also be verified by comparing with results of a similar calculation strategy for the structure of $\text{La}_2\text{NiO}_3\text{F}_2$. Even after inducing a monoclinic strain to $\text{La}_2\text{NiO}_3\text{F}_2$, a relaxation back to the orthorhombic symmetry with negligible orthorhombic distortion ($\beta = 89.94^\circ$) and energy difference (0.00 eV per unit cell) can be observed (Figure 10 (left)). This indicates the absence of a structural driving force for lowering the symmetry in stoichiometric, well-ordered $\text{La}_2\text{NiO}_3\text{F}_2$, highlighting the strong impact of small compositional changes in materials containing elements with d^9 electron configuration.

3.1.3 Magnetic characterization of $\text{La}_2\text{NiO}_3\text{F}_2$ and its reduction products

3.1.3.1 SQUID measurements

In our previous work ²⁹, it was shown that $\text{La}_2\text{NiO}_3\text{F}_2$ orders magnetically below 49 K, where the low magnitude of the magnetic moment indicates an antiferromagnetic ordering.

The reduction reaction products $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{ NaH}$ with $x = 0.25, 0.5, 1$ and 1.5 were characterized by ZFC/FC measurements in the temperature range from 5 to 300 K (Figure 11 a). No divergence in

magnetization between ZFC and FC measurements was observed. The overall magnetization increases strongly for samples where higher amounts of NaH were used in the reduction. This provides an indication for a magnetic contribution of a decomposition product to the otherwise antiferromagnetic or paramagnetic phases formed upon the reduction of $\text{La}_2\text{NiO}_3\text{F}_2$ (see section 3.1.3.2). Due to a weak hysteresis in field-dependent measurements (Figure 11 b), the presence of a ferromagnetic component can be assumed. The analysis of the reaction mechanism (see section 3.1.1) suggests that the ferromagnetic contribution originates from metallic Ni which is formed due to the strong decomposition of $\text{La}_2\text{NiO}_3\text{F}_2$ during the defluorination process. In accordance with previous findings made on the reduction of LaNiO_3 to LaNiO_2 ²², the Ni seems to be amorphous or nanocrystalline and, hence, its presence cannot be confirmed by diffraction experiments only (see section 3.1.1). Overall, the magnetic measurements on their own cannot reveal changes of the magnetic properties of the parent $\text{La}_2\text{NiO}_3\text{F}_2$ phase on reduction.

Figure 11: a) Magnetization vs. temperature curves of $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{ NaH}$ measured at $\mu_0 H = 1 \text{ T}$ (filled symbols, FC and ZFC curves overlap) and inverse susceptibility vs. temperature curves of $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{ NaH}$ with $x = 0.25, 0.5, 1, 1.5$ (open symbols); b) Magnetization vs magnetic field curves of $\text{La}_2\text{NiO}_3\text{F}_2 + 1.5 \text{ NaH}$ measured at 10, 100 and 300 K. Measurements of $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{ NaH}$ with $x = 0.25, 0.5, 1$ can be found in Figure S 9.

3.1.3.2 Determination of magnetic structures

In order to develop a deeper understanding of the magnetic properties of the phases after reduction, neutron diffraction data were recorded at low temperatures. The comparison between data measured at room temperature and at 10 K (Figure 12) shows the appearance of additional reflections in all

reduction reaction products. Since Ni^+ and Ni^{2+} ions do not possess a large spin moment, the intensity of the magnetic reflections is low so that only two reflections can be clearly observed.

Figure 12: Comparison between GEM bank 3 NPD data measured at room temperature (RT) and 10 K of $\text{La}_2\text{NiO}_3\text{F}_2$ and $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{NaH}$ with $x = 0.25, 0.5, 1, 1.5$. Reflections attributed to magnetic scattering are highlighted. Reflections, which could not be identified, are marked with *.

For the parent orthorhombic sample $\text{La}_2\text{NiO}_3\text{F}_2$ and the reduced samples $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{NaH}$ with $x = 0.25$ and 0.5 , the additional reflections could be indexed with a k-vector of $[1\ 0\ 0]$ based on the nuclear structures determined in section 3.1.2. The magnetic reflections in $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{NaH}$ with $x = 0.25$ and 0.5 can be attributed to the reduced monoclinic phase $\text{La}_2\text{NiO}_3\text{F}_{2-a}$ with an approximate composition of $\text{La}_2\text{NiO}_3\text{F}_{1.93}$. Since the number of additional reflections is low, the amount of additional refinement parameters was limited by using a magnetic subgroup approach, i.e. refining the magnetic intensities within one of the maximal magnetic subgroups of the nuclear structures.⁶⁴ By this approach, it is possible to limit the additional refinement parameters to a single parameter. This is due to the fact that the magnetic space group implies certain relative orientations of the magnetic moments of the Ni atoms. Robust refinements could be achieved based on the subgroups of the space groups *Cccm* and *C12/c1* with a magnetic k-vector of $[1\ 0\ 0]$, good fits (Figure 13) could be obtained in the magnetic space groups *C_{PC}'cm* (66.9.572) and *P_C2₁/c* (14.84), respectively, with the magnetic vectors of the Ni ions aligning parallel to the c-axis with G-type antiferromagnetic (AFM) ordering of the magnetic moments within the perovskite building blocks. The corresponding magnetic structures are shown in Figure 14 a) and b). It is also worth emphasizing that this inter- and intra-layer ordering of magnetic moments was in

principle also found for La_2NiO_4 and the stronger reduced $n = 3$ $\text{La}_4\text{Ni}_3\text{O}_8$ (67 % Ni^{+}) by DFT based calculations.⁶⁵

Figure 13: Rietveld analysis of magnetic structure of $\text{La}_2\text{NiO}_3\text{F}_2$ and $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{NaH}$ with $x = 0.25, 0.5, 1, 1.5$ of GEM bank 3 NPD data measured at 10 K.

Figure 14: Magnetic structure of $\text{La}_2\text{NiO}_3\text{F}_2$ (a) and $\text{La}_2\text{NiO}_3\text{F}_{2-a}$ (b) at 10 K. Arrows indicate the length of the magnetic vectors as obtained from the refinement of neutron diffraction data.

Remarkably, at 10 K, a strong difference is observed for the magnitudes of the magnetic moments refined for $\text{La}_2\text{NiO}_3\text{F}_2$ and for $\text{La}_2\text{NiO}_3\text{F}_{1.93}$ of $0.7(1) \mu_B$ and $1.62(7) \mu_B$, respectively. This is surprising, since it would be assumed that a higher magnetic moment ($2.83 \mu_B$ for Ni^{2+} (d^8), $1.73 \mu_B$ for Ni^+ (d^9)) would be found the more Ni^{2+} is present in the compound. It is known that superexchange interactions between adjacent layers are weak, and especially for the layered perovskite-related compounds of the $n = 1$ RP structure family A_2BO_4 with quasi-two dimensional B-O-B networks, highly anisotropic magnetic interactions can be expected.³²⁻³⁴ Further, superexchange interactions via fluoride ions are weaker as compared to oxide ions.³⁵

In this respect, a comparison of the magnetic properties and structures to the system of the $\text{La}_2\text{NiO}_{4+d}$ is also interesting. In $\text{La}_2\text{NiO}_{4+d}$, only the stoichiometric samples with $d = 0$ are reported to possess 3D antiferromagnetic ordering up to temperatures of 300 K⁶², while slightly over-stoichiometric compounds ($d > 0$) show considerably lower transition temperatures.⁶⁶ For $\text{La}_2\text{NiO}_3\text{F}_2$, where the oxidation state is maintained with regard to La_2NiO_4 , no 3D AFM ordering is present at ambient temperature²⁹, and the moments found at 10 K are significantly lower than the moment of La_2NiO_4 of $1.68 \mu_B$ (measured at 4 K)⁶². This highlights that the introduction of additional anions into the interstitial site weakens magnetic interactions between adjacent layers. For $\text{La}_2\text{NiO}_3\text{F}_{1.93}$, ordering is found at least at up to 100 K without a significant decrease of the magnetic moment compared to lower temperature (Figure 15). Further, the moment is close to the moment found for La_2NiO_4 at 4 K. For monoclinically distorted $\text{La}_2\text{NiO}_3\text{F}_{1.93}$, it appears that the structural distortion in combination with the change of the electron configuration strengthens the exchange between adjacent perovskite building blocks. This might be explained by the fact that the Ni-F-F-Ni super-superexchange, found in $\text{La}_2\text{NiO}_3\text{F}_2$ only, is partly replaced by Ni-F-Ni superexchange interactions, resulting in a strengthening in the 3D AFM interactions (Figure 15).

Figure 15: Magnetic moments as a function of measurement temperature of $\text{La}_2\text{NiO}_3\text{F}_2$ and $\text{La}_2\text{NiO}_3\text{F}_{1.93}$ in $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{NaH}$ with $x = 0.25$. For $\text{La}_2\text{NiO}_3\text{F}_2$, FC and ZFC measurements showed a Néel temperature of 49 K²⁹, the neutron powder diffraction data suggests a higher transition temperature ($> 55 \text{ K}$); the exact Néel temperature could, however, not be determined.

We would like to emphasize that it was not possible to draw robust and reliable conclusions about the magnetic properties and /or ordering scenarios for the stronger reduced phases. Even though additional reflections (marked with *) are present in the samples $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{NaH}$ with $x = 0.5, 1$ and 1.5 (Figure 12 and Figure 13), they could not be indexed successfully by testing different $n \times m \times l$ superstructures with reasonably small $n, m, l \in \mathbb{N}$. Their analysis is impeded by the small number of identifiable reflections with low intensities, which show in one case overlapping with one neighboring nuclear reflection of another phase. The absence of these additional reflections in the ambient temperature measurements renders possible that they belong to a magnetic ordering process. However, a clear assignment would require that the higher reduced phases could be prepared in a phase purer state. With respect to the fact that no long-range magnetic ordering could be induced into the stronger reduced phases and $\text{La}_3\text{Ni}_2\text{O}_6$ ²⁵ and $\text{La}_4\text{Ni}_3\text{O}_8$ ²⁴, this opens up exploratory space for future studies.

4 Conclusions

In this article, we have shown that the selective extraction of fluoride ions from $\text{La}_2\text{NiO}_3\text{F}_2$ can result in the formation of the first single layer T'-type compound $\text{La}_2\text{NiO}_3\text{F}$ derived from $n = 1$ RP-type $\text{La}_2\text{NiO}_3\text{F}_2$ containing only Ni as the transition metal cation. In comparison to the reduction of the pure oxides, this is facilitated by the high anion content of the starting material $\text{La}_2\text{NiO}_3\text{F}_2$, which can be considered key for the formation of T'-type compounds, which do not tend to allow for overall anion contents y in A_2BX_y with $y < 4$.

On reductive defluorination of $\text{La}_2\text{NiO}_3\text{F}_2$, the structural changes are complex and can be understood with the aid of DFT-based calculations, showing the strong impact of the introduction of even small amounts of d^9 configured Ni^+ cations on structural distortions. These distortions were found to play a key role for inducing long range magnetic ordering in partly reduced monoclinic $\text{La}_2\text{NiO}_3\text{F}_{1.93}$ by increasing the strength of the Ni-X-X-Ni superexchange interactions between adjacent perovskite

building blocks. Further, also the higher reduced compounds show small indication for the presence of long-range magnetic ordering, although their magnetic structure could not be determined.

Clearly, this article has shown that the defluorination of $\text{La}_2\text{NiO}_3\text{F}_2$ can provide a synthetic pathway for new magnetic materials, which cannot be obtained from the pure oxides easily. In a follow-up article, we will show that recently developed fluoride-ion-batteries⁶⁷⁻⁷¹ can also serve as a means to obtain such compounds with low-valent Ni species.

5 Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org>.

- Quantitative analysis and refined lattice parameters and unit cell volumes of room temperature XRD data of $\text{La}_2\text{NiO}_3\text{F}_2$ and reduction reaction products $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{ NaH}$ ($0.25 \leq x \leq 2.5$); Rietveld refinements of XRD data measured at room temperature of $\text{La}_2\text{NiO}_3\text{F}_2$ and reduction reaction products $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{ NaH}$ ($0.25 \leq x \leq 2.5$); comparison of selected angular range of $\text{La}_2\text{NiO}_3\text{F}_2 + 2.5 \text{ NaH}$ indicating the presence of amorphous or nanocrystalline Ni; Rietveld refinements of XRD data of re-oxidized reduction reaction products $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{ NaH}$ with $x = 0.5, 1$ and 1.5 ; X-ray diffraction patterns of reduction reaction products $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{ NaH}$ with $x = 1$ and $x = 1.5$ after being exposed to F_2 gas for 15 min at various temperatures; coupled Rietveld refinements of $\text{La}_2\text{NiO}_3\text{F}_2 + 1 \text{ NaH}$ of GEM bank 1-6 NPD and XRD data measured at room temperature; coupled Rietveld refinements of $\text{La}_2\text{NiO}_3\text{F}_2 + 0.25 \text{ NaH}$ of GEM bank 1-6 NPD and XRD data measured at room temperature using with a model with space group C12/m1 for the monoclinic phase $\text{La}_2\text{NiO}_3\text{F}_{2-\text{a}}$; comparison between refined diffraction patterns of orthorhombic #2 $\text{La}_2\text{NiO}_3\text{F}_{2-\text{c}}$ (T-type structure) and tetragonal $\text{La}_2\text{NiO}_3\text{F}_{2-\text{d}}$ (T'-type structure) in $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{ NaH}$ with $x = 1.5$ of GEM bank 3 and 4 NPD data measured at room temperature; high-angle annular dark field (HAADF) images of measured crystals; unit-cell parameters of $\text{La}_2\text{NiO}_3\text{F}_2$ and phases within the reduction reaction products $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{ NaH}$ with $x = 0.25$ and $x = 1.5$ determined from Fast-ADT measurements; atomic positions of structural models refined from Fast-ADT measurements by the dynamical approach in the Jana2006 program; data acquisition, structure solution and dynamical refinement parameters of the crystals used for structure determination; magnetization vs. magnetic field curve of $\text{La}_2\text{NiO}_3\text{F}_2 + x \text{ NaH}$ with $x = 0.25, 0.5, 1$ and 1.5 measured at 10, 100 and 300 K.

6 Conflicts of interest

The authors declare no conflicts of interest.

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