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Nickel incorporation in perovskite-type metal oxides – implications on reducibility

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Abstract

Nickel is often applied in heterogeneous catalysis for its high catalytic activity towards a large variety of reactions at affordable price. Nickel reduction from perovskite-type mixed oxides is increasingly exploited to generate active and stable Ni catalysts. To investigate implications of the host perovskite structure on Ni reducibility, Ni was incorporated on the B-site of three perovskite-type mixed metal oxides of different lattice symmetries (LaFeO_3 – orthorhombic, LaCoO_3 – rhombohedral and $\text{La}_{0.3}\text{Sr}_{0.55}\text{TiO}_3$ – cubic). Structural parameters of the phase pure undoped and Ni-doped perovskites were determined using synchrotron X-ray diffraction (XRD) and Ni K-edge X-ray absorption (XAS). Rietveld refinement and extended X-ray absorption fine structure (EXAFS) data fitting were used to verify that at this substitution level Ni enters the B-site and adopts its coordination environment. Expansion of the unit cell was found in LaCoO_3 and $\text{La}_{0.3}\text{Sr}_{0.55}\text{TiO}_3$, whereas contraction was observed in the case of LaFeO_3 . X-ray absorption spectra showed that Ni-containing unit cells exhibit the same symmetry as the host perovskite-type mixed oxides. The mean oxidation state of Ni was found to be equal in all three cases irrespective of the host lattice (+2.5). Lattice symmetry had significant effect on lowering the Ni reduction temperature determined by hydrogen temperature programmed reduction and a correlation between reduction temperature and crystal tolerance factor was found.

Keywords

Perovskites, Nickel, Segregation, Reduction, Incorporation

1. Introduction

The structure of perovskite-type mixed oxides (PMOs) of composition $ABO_{3\pm\delta}$, where A is a lanthanide, alkaline or earth alkaline element and B a transition metal, stabilizes a large number of compositions [1-3]. In the PMO unit cell the larger A-site cation is twelve-fold coordinated to oxygen, whereas the B-site cation is located at the corners of the unit cell in the center of oxygen octahedra. The only pre-requisite for successful incorporation of an element into the PMO lattice besides abundance of charge neutrality is the geometric constraint due to the different ionic radii [3]. The PMO lattice is formed for suitable ratios between A and B-site cation radii, this condition being described by the Goldschmidt tolerance factor (eq. 1)

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \quad (1)$$

where r_A , r_B , and r_O represent the ionic radii of the corresponding metal cations and of the oxygen anions, respectively [1]. The ideal, cubic crystal structure is observed for $t=1.0$. PMOs of rhombohedral and orthorhombic lattice symmetries are formed for $0.75 \leq t \leq 1.0$ [4]. The stability of the PMO lattice also allows for the partial substitution of either A- or B-site elements to form compositions of type $A_{1-x}A'_x B_{1-y}B'_y O_{3\pm\delta}$ and for the stabilization of metals in unusual oxidation states [3, 5]. For such mixed compositions crystal symmetry of the material is often dictated by the ionic radii of the most abundant A- and B-site metal cations [6-9]. Incorporation of chemical elements in the PMO lattice can therefore not only be used to stabilize higher metal oxidation states compared to their common oxides but also to tailor the local coordination environment of the metal cation [10]. Distortions caused by the introduction of dopants are known to have an effect on the electronic structure and as consequence on a manifold of material properties. A theoretical study on the stability of precious

metal cations at the B-site of $\text{LaFeO}_{3\pm\delta}$ and $\text{CaTiO}_{3\pm\delta}$ indicated that the stability of the precious metal cations in the solid solution strongly depends on the PMO lattice energy, hence on symmetry and the tolerance factor [11]. These calculations assumed the formation of a solid solution and the presence of one type of unit cell throughout the material. However, later the formation of separate PMO phases was predicted upon doping depending on the elements present in each unit cell [12].

In heterogeneous catalysis control of the metal oxidation state is a crucial aspect of catalyst development. Often only a specific oxidation state catalyzes the desired chemical reaction, whereas others exhibit no catalytic activity. Nickel is used in heterogeneous catalysis for its high activity at low price compared to noble metals. A high Ni oxidation state is desirable and should be therefore stabilized for some applications such as the catalysis of the oxygen evolution reaction [13]. For other reactions high Ni reducibility might be advantageous as is the case when Ni containing PMOs are used as catalyst precursors, which are reduced to form metallic Ni nanoparticles segregating to the PMO surface and serving as catalytically active Ni particles. Such Ni particles can be incorporated e.g. in solid oxide fuel cell anodes [14, 15] or exploited as supported catalysts for reforming and hydrogenation reactions [16, 17]. The reduction of the material at low temperatures may be advantageous as it allows formation of the active Ni particles to be conducted *in situ* in the reactant stream and at operation temperatures. Therefore, the question needs to be addressed whether Ni reduction temperature can be tailored by appropriate selection of a PMO host lattice.

In this work we demonstrate that Ni can be inserted at the B-site of cubic ($\text{La}_{0.3}\text{Sr}_{0.55}\text{TiO}_{3\pm\delta}$), orthorhombic ($\text{LaFeO}_{3\pm\delta}$) and rhombohedral ($\text{LaCoO}_{3\pm\delta}$) PMOs forming a solid solution. We also demonstrate that the different host lattices directly

affect its local coordination environment and that this has significant influence on the reduction temperature of the incorporated Ni.

2. Experimental

Perovskite-type mixed oxides (PMOs) of composition $\text{LaFeO}_{3\pm\delta}$ (LFO), $\text{LaFe}_{0.95}\text{Ni}_{0.05}\text{O}_{3\pm\delta}$ (LFNO), $\text{LaCoO}_{3\pm\delta}$ (LCO) and $\text{LaCo}_{0.95}\text{Ni}_{0.05}\text{O}_{3\pm\delta}$ (LCNO) were synthesized via the amorphous citrate process [18]. Suitable amounts of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, 99.999 % trace metals basis), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma-Aldrich, ≥ 99.95 % trace metals basis), $\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, ≥ 98 %) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, 99.999 % trace metals basis) were each dissolved in water and thoroughly mixed before being added to an aqueous solution of citric acid (Sigma-Aldrich, ACS reagent, ≥ 99.5 %). The overall molar ratio of metal nitrates to citric acid was 1:1.05. The precursor solution was stirred at 70°C for 60 min before the solvent was evaporated under reduced pressure at 70°C for 12 h. The resultant solid precursor foam was crushed to a fine powder and then subjected to calcination in air at 800°C for 5 h (5°C/min to 200°C; then, 10°C/min to 800°C) to obtain the calcined PMO samples. Mixed metal oxides with nominal composition $\text{La}_{0.3}\text{Sr}_{0.55}\text{TiO}_{3-\delta}$ (LST) and $\text{La}_{0.3}\text{Sr}_{0.55}\text{Ti}_{0.95}\text{Ni}_{0.05}\text{O}_{3-\delta}$ (LSTN) were synthesized using a citrate-gel method[15] involving a final calcination step at 960°C for 6 h. Nickel-free PMOs (LFO, LCO and LST) were also loaded with Ni by wet impregnation from an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ followed by drying at 70°C for 12 h and calcination at 500°C for 2 h (5°C/min to 200°C; then, 10°C/min to 500°C) to produce 1.5 wt% NiO/ $\text{LaFeO}_{3\pm\delta}$ (Ni/LFO), 1.5 wt% NiO/ $\text{LaCoO}_{3\pm\delta}$ (Ni/LCO) and 2.1 wt% NiO/ $\text{La}_{0.3}\text{Sr}_{0.55}\text{TiO}_{3-\delta}$ (Ni/LST). Nickel load on impregnated samples was adjusted to fit the Ni load on LFNO, LCNO and LSTN. For all compositions the calcination

conditions were selected to obtain highly phase pure and crystalline materials. Prior to analysis the samples were ground to a fine powder in an agate mortar.

Phase purity of the powder materials was verified by powder X-ray diffraction (XRD) on a Bruker D8 Advance instrument operated with Ni-filtered Cu K α -radiation, variable slits and an energy sensitive line detector (LynxEye). Diffractograms were collected using an acquisition time of 4 s and a step size of 0.03° between 15° and 150° (2 θ). *In situ* XRD patterns were collected on single perovskite phase powder samples (LFO, LFNO, LCO, LCNO, LST and LSTN) on the same Bruker D8 Advance instrument using a XRK 900 reactor chamber (Anton Paar, Austria). The diffraction patterns were scanned using a step size of 0.05° 2 θ in the range 20° $\leq$ 2 θ $\leq$ 65°. The sample was loaded in its calcined state before heating from 30°C to 800°C (12 °C/min) in 10 vol% H₂/N₂ while at every 100°C interval heating was paused to record the diffraction pattern.

Temperature programmed reduction (TPR) experiments were conducted on calcined samples using a bench top TPDRO-1100 (ThermoElectron) instrument equipped with mass flow controllers and a thermal conductivity detector to measure H₂-consumption. TPR were conducted in a flow of 20 mL/min 10 vol% H₂/Ar at STP (0°C and 10⁵ Pa) with a heating ramp of 5°C/min while sample temperature was monitored using a K-type thermocouple placed in the middle of the bed.

Ni K-edge (8.333 keV) X-ray absorption spectra were acquired *ex situ* on pelletised samples in fluorescence mode at the X10DA (SuperXAS) beamline of the Swiss Synchrotron Light Source (SLS, Villigen, Switzerland) using a five element SD detector. The required X-ray energies were scanned using a Si(111) monochromator. The Demeter software package (version 0.9.24) [19] was used to reduce and model all data. The radial distribution function (R) was obtained by Fourier transforming k³-

weighted EXAFS functions typically in the range of 3.0 - 12.0 Å⁻¹ after application of a Hanning window function. NiO (99.99 % trace metals basis, Sigma) and Ni foil references were measured in transmission mode using ionization chamber detectors. EXAFS spectra of the impregnated samples were fitted to the NiO structure, whereas crystallographic structure files of LaFeO₃, LaCoO₃ and SrTiO₃ were used to fit Ni on the perovskite B-site. A-site substitution and vacancies in SrTiO₃ were taken into account for the fit through adjustment of the theoretical coordination numbers. Displayed spectra are not phase shift corrected.

The tolerance factor (t) of LST was calculated using the expression derived by Ubic *et al.* using the pseudocubic lattice constant (a_{pc}) instead of the ionic radii of all lattice ions (equation 2) [20]

$$t = \frac{a_{pc} - 0.05444}{0.66046 \cdot (r_B + r_O)} - 1.981012 \quad (2)$$

where r_B and r_O represent the effective ionic size of the B-site cation and oxygen anion, respectively. The value of a_{pc} was obtained from the refined XRD data. This method was preferred over the traditional Goldschmidt tolerance factor [1], as it assumes complete ionic bonding and a zero size for cation vacancies, which was found to be an inaccurate description of the A-site in substoichiometric PMOs [20]. Equation 2 also takes into account the covalent bond character. Thus, t-values for LCO and LFO were calculated using the bond valence model proposed by Brown [21] and equation 3 derived by Sidey for the bond length (R) between metal cations and oxygen anions in metal oxides [22].

$$R = R_0 - b \cdot \ln(V/N) \quad (3)$$

where, R_0 denotes the tabulated bond valence parameters, b equals to 0.37 [23]. V represents the formal cation valence and N its coordination number. Values for R

were then used in the alternative expression of the Goldschmidt's tolerance factor (equation 4)

$$t = \frac{R_{AO}}{\sqrt{2} \cdot R_{BO}} \quad (4)$$

where R_{AO} and R_{BO} are the bond lengths between A- and B-site cations and oxygen anions, respectively as calculated from equation 3.

High resolution XRD data on powder samples were collected at the X04SA (MS-Powder) beamline of the Swiss Synchrotron Light Source. Samples were diluted with diamond powder (1:1 by mass) serving as internal standard and loaded into a quartz capillary (OD 0.3 mm, wall thickness 0.01 mm), which was rotated during measurement (1 Hz). A 1-D MYTHEN II strip detector covering an angular range of 120° was used for data acquisition at a total acquisition time of 8 min [24]. The measurements were conducted using X-ray radiation at 15.95 keV.

Rietveld refinements were performed with GSAS-II [25]. Data was fitted in the range of about $10\text{-}100^\circ$ 2θ with the background subtracted (10-20 cosine terms). Beam parameters were determined using a reference sample (Si, NIST640D). In a first step, only phase fractions and cell parameters were fitted, after which more parameters were added (site occupancy for oxygen anions and A-site cations, sample position, and Debye-Waller factors). Finally, also position parameters were fitted with the constraint that atoms remain on the same Wyckoff position, i.e. that the system maintains the same space group and symmetry is not reduced. The size of the single crystalline domains was determined during Rietveld refinement and using the Scherrer equation [26].

The specific surface area (SSA) of the calcined powders was calculated from N_2 -adsorption isotherms at -196°C according to the Brunauer-Emmet-Teller (BET)

model. Adsorption data was acquired using a Quantachrome Autosorb I instrument. Prior to SSA determination the samples were treated under vacuum at 300°C for 2 h.

3. Results

3.1 X-ray diffraction

The physico-chemical properties of the samples are summarized in Table S1. The phase purity and crystal symmetry of all powder samples were assessed using powder X-ray diffraction (XRD). Figure 1-a shows diffractograms collected for the series $\text{La}_{0.3}\text{Sr}_{0.55}\text{TiO}_{3-\delta}$ (LST), $\text{La}_{0.3}\text{Sr}_{0.55}\text{Ti}_{0.95}\text{Ni}_{0.05}\text{O}_{3-\delta}$ (LSTN) and impregnated $\text{NiO}/\text{La}_{0.3}\text{Sr}_{0.55}\text{TiO}_{3-\delta}$ (Ni/LST). The reflections of the cubic perovskite-type mixed oxide (PMO) structure are clearly visible and labeled according to their Miller indices. No indication of NiO was found in the case of Ni/LST, which indicates that NiO domains, if present at all, were extremely small or in low concentrations. The diffractograms of $\text{LaFeO}_{3\pm\delta}$ (LFO), $\text{LaFe}_{0.95}\text{Ni}_{0.05}\text{O}_{3\pm\delta}$ (LFNO) and $\text{NiO}/\text{LaFeO}_{3\pm\delta}$ (Ni/LFO) show the reflections indexed as an orthorhombic PMO (Figure 1-b), while the diffractograms of $\text{LaCoO}_{3\pm\delta}$ (LCO), $\text{LaCo}_{0.95}\text{Ni}_{0.05}\text{O}_{3\pm\delta}$ (LCNO) and $\text{NiO}/\text{LaCoO}_{3\pm\delta}$ (Ni/LCO) reported in Figure 1-c are indexed as a rhombohedral PMO. No reflections of secondary phases besides the main PMO phase could be identified on any of the samples.

All samples displayed comparable values of crystallite size and specific surface area (SSA) with the exception of LSTN, which showed an increased size of the single crystalline domains compared to all other samples. NiO could be detected on the impregnated samples (Ni/LFO, Ni/LCO and Ni/LST) only by high resolution XRD using synchrotron radiation. These diffractograms were used for structural refinement and are presented in Figure S1 in the supporting information. Table 1 summarizes

the results obtained by the Rietveld refinement of each sample. Good quality refinements were obtained for Ni-free materials LFO, LCO and LST with well-defined atom positions evidenced by their small Debye-Waller factors. The unit cell dimensions obtained from the fits closely match the published values [6, 27, 28]. A small oxygen deficit (δ) of 0.014 was found for LFO, whereas δ had a higher value of 0.048 in LST in agreement with published data [6, 29].

It is evident that Ni impregnation did not affect the structural parameters of the PMO lattice as the cell volume did not change between LFO and Ni/LFO, LCO and Ni/LCO as well as between LST and Ni/LST. This indicates that Ni incorporation is avoided during impregnation of the PMO support material and the subsequent calcination and that Ni is likely accommodated in a separate phase. Indeed a secondary NiO phase could be found, which consisted of small, strained particles and therefore exhibited broad reflections in the corresponding high resolution XRD patterns. Crystallite diameters obtained from the refinement were in the range of 5-10 nm (Table S1). Where refined, the NiO unit cell dimensions ($a = 4.130 \text{ \AA}$, $4.131 \text{ \AA}$ for Ni/LFO and Ni/LCO, respectively) was substantially smaller than the value reported for bulk NiO ($a = 4.178(1) \text{ \AA}$). The strained lattice is likely caused by the stress induced on the small NiO particles by the presence of the support oxide surfaces on which they were assembled [30].

Synchrotron XRD also did not indicate the presence of NiO on LSTN, LFNO and LCNO, which leads to the conclusion that Ni is able to adopt the coordination environment of the B-site element and that complete incorporation of Ni into the PMO lattice occurred during synthesis. Trace impurities not related to Ni could be detected in the case of LCNO, which did not influence the refinement results but affected the statistics for LCO based materials.

Incorporation of Ni into the PMO lattice stabilized higher Ni oxidation states (*vide infra*). It also resulted in an unit cell expansion of LSTN and LCNO in accordance with the larger ionic radius of the Ni^{3+} cation (0.56 Å) compared to either Ti^{4+} (0.42 Å) or Co^{3+} (0.545 Å) [31]. In the case of LFNO, the unit cell was found to contract upon Ni substitution despite the larger size of Ni^{3+} cations compared to Fe^{3+} cations (0.55 Å). In this case, symmetry allowed for structural distortion upon rotation of the oxygen octahedra surrounding the B-site element (Figure S2). When viewed along the b-axis (Figure S2-a), the BO_6 octahedra rotate around their 4-fold symmetry axis. The rotation of the octahedra results in a denser structural packing and thus in a smaller unit cell. Nickel doping of LFO also influenced the occupancy of the two different O^{2-} sites (Figure S2-b): O1 on the four-fold axis of the bipyramid (Wyckoff position 4c, roughly parallel to the b-axis) and O2 in the equatorial plane (Wyckoff position 8d). Doping with Ni was found to introduce oxygen vacancies, which were found preferentially on the O1 site.

3.2 X-ray absorption near edge structure

X-ray absorption spectroscopy (XAS) was used to analyze the local coordination of Ni in the PMO samples. The normalized X-ray absorption near edge structure (XANES) at the Ni K-edge (8.333 keV) for the impregnated samples Ni/LFO, Ni/LCO and Ni/LST, displayed an intense whiteline followed by a local absorption minimum at 8.362 keV (Figure S3). A small pre-edge feature was present at around 8.335 keV, which was attributed to the $1s \rightarrow 3d$ transition [32, 33]. Both the whiteline and the pre-edge features are also observed in the XANES spectrum of the NiO reference (Figure S4) and the overall similarities suggest the presence of Ni as NiO in the impregnated samples, thus complementing the finding from XRD. The first derivative of the XANES spectra (Figure S3) revealed that the absorption edge (E_0) was located

at ca. 8.3455 keV in all impregnated samples as well as in the NiO reference. The derivative of the spectrum of NiO revealed a well-defined triple feature between 8.335 keV and 8.350 keV. The feature in the same energy range on the impregnated samples was rather ill-defined, which is likely an effect of self-absorption. All samples were measured in fluorescence mode due to their complex matrices, whereas reference spectra were collected in transmission mode.

The normalized XANES spectra of LFNO, LCNO and LSTN are displayed in Figure 2. All spectra exhibited distinct features and could be clearly distinguished from each other as well as from that of NiO and of the impregnated samples, despite sharing a similar whiteline to the one observed for the latter. The spectrum of LSTN (Figure 2-a) featured a shoulder on the high energy flank of its whiteline (8.353 keV, A), whereas the spectrum of LFNO (Figure 2-b) displayed a plateau between 8.355 keV and 8.365 keV (B). The spectrum of LCNO (Figure 2-c) contained a local minimum (C) in the same energy region similar to the one observed on the impregnated samples (Figure S3), however not to the same extent. Similar features in the Ni K-edge XANES have been previously observed also by other groups for Ni incorporated in LaFeO_3 [34], LaCoO_3 [35] and SrTiO_3 [36]. It is apparent that despite the clear differences between samples all Ni K-edge XANES include similar features such as the pre-edge, an intense whiteline and a significant dip centered at ca. 8.38 keV, which is followed by a strong feature at ca. 8.40 keV. Large differences in the XANES region were not necessarily expected as this region of the absorption spectrum is mainly influenced by oxidation state and the first coordination shell, which is always composed of six oxygen neighbors in octahedral coordination even in the case of NiO. It has been demonstrated that all of the above mentioned similarities are also present in the XANES of aqueous $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ complexes [32]. Therefore,

the differences in the XANES between samples originated from electron scattering from higher coordination shells, the distances of which as well as the scattering power of their constituent elements are significantly different due to the different crystal symmetry and composition (Table 2). If Ni was occupying sites of similar coordination also over higher coordination shells in LFNO, LCNO and LSTN, it would be reflected in the XANES region of these samples. Therefore, the differences between the spectra can be considered as fingerprints for the incorporation of Ni into the different host lattice, where it likely adopts the coordination environment of the host PMO B-site element.

Analysis of E_0 (Figure 2-d, Figure 2-e, Figure 2-f) revealed a shift to 8.347 keV for all samples, which indicates a higher oxidation state of Ni compared to the reference Ni^{2+} NiO (8.3455 keV). Woolley *et al.* [37] demonstrated previously that the correlation between Ni oxidation state and E_0 is not linear when using the maximum of the first derivative of the XANES, the correlation displays rather a polynomial shape. The edge position (8.347 keV) obtained through the method used in this work translates to an average Ni oxidation state of +2.5 according to their calibration. The oxidation state of Ni of less than 3+ is potentially also partially compensated by an increased oxidation state of the B-site as shown in the case of Fe^{4+} concentrations in LFNO [38].

3.3 Extended X-ray absorption fine structure

Fourier transformed spectra of all samples are displayed in Figure 3 while k^3 -weighted extended X-ray absorption fine structure (EXAFS) spectra of all samples are presented in Figure S5 in their non-phase shift corrected form. The fitted data is shown by the dashed lines and all results are summarized in

Sample Composition		Perovskite space group	SSA [m ² /g] ^a	Single crystalline domain size [nm] ^b	
				Perovskite	NiO
LST	La _{0.3} Sr _{0.55} TiO ₃		11.6 ± 0.5	129.0 ± 0.6	-
LSTN	La _{0.3} Sr _{0.55} Ti _{0.95} Ni _{0.05} O ₃	Pm-3m	12.4 ± 0.5	223 ± 2	-
Ni/LST	2.1 wt% NiO/La _{0.3} Sr _{0.55} TiO ₃		14.3 ± 0.5	149.3 ± 0.5	7.5 ± 0.5
LFO	LaFeO ₃		6.4 ± 0.5	149.8 ± 0.2	-
LFNO	LaFe _{0.95} Ni _{0.05} O ₃	Pnma	7.1 ± 0.5	156.6 ± 0.5	-
Ni/LFO	1.5 wt% NiO/LaFeO ₃		7.3 ± 0.5	153.9 ± 0.4	9.1 ± 0.2
LCO	LaCoO ₃		5.8 ± 0.5	138.4 ± 0.3	-
LCNO	LaCo _{0.95} Ni _{0.05} O ₃	R-3c	6.7 ± 0.5	122.5 ± 0.7	-
Ni/LCO	1.5 wt% NiO/LaCoO ₃		6.0 ± 0.5	128.7 ± 0.7	6.8 ± 0.3

^a specific surface area obtained from N₂ physisorption.

^b obtained from Scherrer equation and Rietveld refinement.

Table S2. The spectra of samples, in which Ni is incorporated into the PMO lattice according to XRD and XANES exhibited a peak at ca. 1.6 Å besides a broad feature ranging from 2.6 Å to 4.0 Å (LSTN - Figure 3-a, LFNO - Figure 3-b and LCNO - Figure 3-c). Fitting of scattering paths associated these features with the first oxygen coordination shell (Ni-O) and the contributions of A- and B-site cations, respectively. Clear differences were observed for the Ni-impregnated samples Ni/LST (Figure 3-d), Ni/LFO (Figure 3-e) and Ni/LCO (Figure 3-f). Besides the first oxygen coordination shell, the impregnated samples exhibited an additional and distinct peak at ca. 2.6 Å. This peak is common to the NiO reference and is associated to the second coordination shell of Ni, which consists of neighboring Ni atoms (Figure S6-c). Fitting of the average Ni-O bond distance for the impregnated samples resulted in a value of 2.05 Å for Ni/LFO, 2.03 Å for Ni/LCO and 2.07 Å for Ni/LST. Ni-Ni bond lengths of around 2.95 Å were found for all samples. These values were in reasonable agreement with the Ni-O bond distance of 2.07 Å and the Ni-Ni distance of 2.95 Å in NiO. Ni-O bond distances determined for the incorporated samples were distinctively shorter, 1.95 Å in LSTN and 1.98 Å in LFNO, which were slightly longer than the 1.93 Å reported for the Ni³⁺-O bond length in LaNiO₃ [33], presumably due to the lower Ni oxidation state in the samples. The decreased bond length when compared to NiO is explained by a stronger Ni-O interaction caused by the higher Ni oxidation state inside the PMO lattice as is illustrated by the shift in edge energy (E_0). The result of the fits demonstrates unambiguously that Ni is incorporated inside the LaFeO₃, LaCoO₃ and La_{0.3}Sr_{0.55}TiO₃ host lattices, when it is added during the synthesis.

3.4 EXAFS vs. XRD

Bond lengths between B-site elements and the surrounding oxygen sites (B-O) as well as between B-sites and A-sites (B-A) were calculated and compared to values

obtained from the fits of the EXAFS data (Table 2) using the structures obtained from the Rietveld refinements of the synchrotron XRD data. Lattice contraction upon incorporation of Ni into LaFeO_3 and unit cell expansion caused by Ni incorporation into LaCoO_3 and LaSrTiO_3 were apparent from the B-O and B-A bond lengths. However, average Ni-O and Ni-A bond lengths obtained from EXAFS data were generally lower than the corresponding average bond length determined by XRD. Such differences were to be expected. EXAFS data represent the local, distorted coordination environment of the B-cation substituent (in this case Ni). XRD data, in contrast, represent the average structure of the entire material. As only 5% of the B-cations are substituted, the Ni containing unit cells were likely strained as the lattice retains the original PMO structure. However, since statistical quality of EXAFS fits is generally worse than for Rietveld refinements, it is difficult to assess which method delivers more reliable numerical results with respect to the B-O (or Ni-O) bond distances. Nevertheless, because clear differences were found in both XANES and EXAFS analysis of Ni in the various host lattices at this substitution level, Ni likely adopts similar coordination to the corresponding host B-site element. In the case of impregnated samples, both techniques probe a homogeneous NiO phase and deliver similar results in most samples (Table 2). Differences between the values obtained by EXAFS fitting and refinement of XRD data were observed for the Ni-Ni bond distance in Ni/LFO and the Ni-O bond distance in Ni/LCO. This may suggest that actual errors in the measurements may be underestimated by the fitting or data refinement statistics.

3.5 Nickel reducibility

Temperature programmed reduction (TPR) is often used to determine reduction temperatures of reducible species by measuring H_2 consumption during a controlled

heating ramp [38]. The obtained reduction profile includes the entirety of all reduction processes occurring during the ramp and features can be assigned to individual reduction events or combinations thereof. TPR was used to determine the reduction temperatures of Ni species in the PMO samples and to assess the effect of host PMO structure and composition on Ni reducibility. The reduction profiles are reported in Figure 4. LST (Figure 4-a) experienced only minor H₂ consumption at temperatures between 550-650°C, which could be assigned to the single electron reduction of Ti⁴⁺ to Ti³⁺ [39]. In contrast, both Ni-containing samples Ni/LST and LSTN exhibited more pronounced reduction peaks. Reduction of Ni/LST already started at 250°C and continued to 600°C with a maximum around 500°C. The similar temperatures for the reduction onset to NiO (Figure 4-a) suggest the presence of Ni species of similar nature in Ni/LST and this observation supports that Ni in this sample adopts a structure very similar to NiO. Small changes in NiO reduction temperature can be explained by strain in the NiO phase on the impregnated materials observed by XRD. The fact that reduction of the impregnated Ni/LST continued to higher temperatures can be also justified by the close contact of the NiO entities and the PMO, which may act as an efficient oxygen donor, thus stabilizing NiO by its reducibility and extending the reduction interval to higher temperatures [40]. This is supported by the observation that the reduction peak of the LST support (Ti⁴⁺→Ti³⁺) was no longer visible, and had likely shifted towards lower temperatures to compensate for the oxygen loss in the LST support.

Reduction of LSTN occurred over a narrower temperature range at higher temperatures (450-650°C) and the reduction profile exhibited a distinct double feature with a less intense peak starting at 450°C and a higher peak starting just below 600°C. These two reduction events likely include the reduction steps Ni³⁺ →

Ni^{2+} , $\text{Ni}^{2+} \rightarrow \text{Ni}^0$ and $\text{Ti}^{4+} \rightarrow \text{Ti}^{3+}$. The presence of metallic Ni particles found on reduced LSTN [15] and the high Ni oxidation state derived from the XAS data supports the reduction of Ni to its metallic state and the assignment of the two-step reduction from Ni^{3+} to Ni^0 . It can be assumed that reduction of Ti^{4+} also occurred in LSTN as it was observed in LST. However, because Ni also reduces at similar temperatures the extent of Ti reduction is likely less than in LST. The fact that the LST host PMO contributed only to a small extent to the overall reduction can also be derived from the stable XRD patterns of LST and LSTN during TPR up to 800°C, which did not exhibit secondary phases even after high temperature reduction (Figure 5-a and Figure 5-d). This behavior agreed well with the stability of LST-type materials up to much higher temperatures of 1400°C [41].

NiO reduction in Ni/LFO occurred at a temperature comparable to the reduction of the NiO reference and completed at lower temperatures than those required for Ni/LST. Reduction of LFNO started at 150°C occurred likely via the two-step reduction of Ni species inside the PMO lattice ($\text{Ni}^{3+} \rightarrow \text{Ni}^{2+}$, $\text{Ni}^{2+} \rightarrow \text{Ni}^0$) with limited contribution from Fe [16]. Alternatively, a three-step reduction pathway via the Ruddlesden-Popper-type phase [42] and La_2NiO_4 as well as NiO intermediates has also been proposed for Ni in LFNO [43, 44]. However, previous work and the observed reduction of $\text{LaFe}_{0.8}\text{Ni}_{0.2}\text{O}_3$ at 600°C indicate that the LFNO reduction follows the two-step pathway. LFO (Figure 4-b) exhibited only limited reduction up to temperatures of around 650°C. The high temperature TPR feature corresponds to the start of the collapse of the PMO structure to metallic Fe and La_2O_3 [43, 45, 46], which was revealed in the *in situ* XRD data by the appearance of the La_2O_3 phase at 800°C (Figure 5-b).

Two reduction peaks between 270°C and 410°C were identified on LCO (Figure 4-c). These were followed by a high temperature process starting at 480°C and completing seemingly at 610°C. The reduction events below 410°C correspond to the reduction of $\text{Co}^{3+} \rightarrow \text{Co}^{2+}$ but also to Co^0 via the intermediary products of $\text{La}_4\text{Co}_3\text{O}_{10}$ ($\text{Co}^{2.7+}$), $\text{La}_2\text{Co}_2\text{O}_5$ (Co^{2+}) and $\text{La}_3\text{Co}_3\text{O}_8$ ($\text{Co}^{2.3+}$) [47, 48]. The presence of the intermediate phases was confirmed by the XRD data collected at 400°C and 500°C during reduction of LCO (Figure 5-c). At 600°C the PMO structure had completely collapsed, which is indicated by the exclusive presence of reflections of La_2O_3 and Co^0 . Nickel impregnation lowered the onset of the $\text{Co}^{3+} \rightarrow \text{Co}^{2+}$ reduction from 270°C on LCO to 210°C on Ni/LCO, but the high temperature reduction of Co^{2+} to Co^0 was not influenced. In contrast, incorporation of Ni in LCNO caused the high temperature reduction to shift towards lower temperatures compared to LCO, whereas the low temperature $\text{Co}^{3+} \rightarrow \text{Co}^{2+}$ reduction event occurred at similar temperatures to LCO. This resulted in the appearance of the La_2O_3 phase already in the XRD patterns collected at lower temperatures compared to LCO (Figure 5-f). Due to the extensive contribution of Co of the PMO host lattice to the overall reduction, the differences in the peak areas between LCO and LCNO or Ni/LCO were negligible and did not allow the accurate determination of the Ni reduction temperatures in neither Ni/LCO nor LCNO. Nevertheless, the absence of additional reduction features in LCNO indicates that Ni reduction occurred in the same temperature range of the Co reduction.

In summary, the reduction temperature of Ni within the three PMOs studied appeared to increase in the series $\text{LFNO} < \text{LCNO} < \text{LSTN}$. This series cannot be explained by differences in the oxidation states because XANES spectra revealed that Ni displayed an oxidation state of ca. +2.5 in the three materials. Differences in the structural parameters such as Ni-O and Ni-A bond distances cannot justify this order

either. The tolerance factor is another structural parameter in PMOs, which describes the mismatch of A- and B-site cation size and can be used to predict the symmetry and stability of PMOs [1]. Tolerance factors for LFO, LCO and LST calculated from equations 2-4 are 0.942, 0.97 and 0.993, respectively and increase in the same order as the Ni reduction temperature series. It thus appears as if the symmetry induced stability of the host lattice influences the reducibility of Ni within these three PMO lattices. The close relation between the tolerance factor and the overall lattice stability, which counteracts reduction [3, 49] justifies our interpretation. This is further supported by a theoretical study of Yanagisawa *et al.* [11], demonstrating a similar relation for Pd inside PMOs.

4. Conclusion

Nickel can be incorporated at the B-site of three structurally different perovskite-type mixed oxides and forms single phase materials as demonstrated by X-ray diffraction (XRD). Incorporation of Ni caused a unit cell volume decrease in the case of $\text{LaFe}_{0.95}\text{Ni}_{0.05}\text{O}_3$ (LFNO) due to denser crystal packing as a result of rotation of the BO_6 octahedra, whereas unit cell dimensions were found to increase in the case of $\text{LaCo}_{0.95}\text{Ni}_{0.05}\text{O}_3$ (LCNO) and $\text{La}_{0.3}\text{Sr}_{0.55}\text{Ti}_{0.95}\text{Ni}_{0.05}\text{O}_3$ (LSTN). The clear differences in the X-ray absorption near edge structure of the Ni K-edge indicate that the coordination environment of Ni is significantly different in each structure, which contradicts the formation of similar ANiO_3 unit cells ($A = \text{La}$ or Sr) irrespective of the host lattice. This was further supported by the differences in coordination shell radii observed during analysis of the extended X-ray absorption fine structure (EXAFS). Reasonable EXAFS fits could be achieved for the coordination environment of Ni using structural files of the undoped host lattices, which confirms the evidence obtained by XRD that Ni adopts the local coordination of the B-site element. Nickel impregnation always resulted in a separate NiO phase and no evidence of Ni incorporation was found. Nickel deposition as NiO caused a broadening of Ni reduction temperatures but did not significantly influence its onset temperature. Incorporation of Ni in different perovskite-type mixed oxides affected its reducibility during temperature programmed reduction experiments. This behavior could be correlated to the trend of the tolerance factors of the three host structures.

Since Ni was found to segregate to the perovskite surface forming catalytically active Ni particles after reduction of LFNO and LSTN the influence of lattice stability on the reducibility of Ni may be taken advantage of. Appropriate selection of the host perovskite-type mixed oxide can therefore be used as a facile and applicable way to

tune Ni reduction and segregation to produce active Ni functional materials depending on their expected operation temperature.

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Figures

Figure 1. Normalized powder X-ray diffraction patterns of a) LST-, b) LFO- and c) LCO-type materials. Space group symbols of the perovskite-type mixed oxide phase as well as the Miller indices of the main reflections are given for each material.

Figure 2. Normalized Ni K-edge X-ray absorption near edge structure (XANES) spectra of a) LSTN, b) LFNO and c) LCNO. The corresponding first derivatives are shown in d), e) and f), respectively. Dashed marker lines indicate the absorption edge energy (E_0).

Figure 3. Fourier transformed k^3 -weighted Ni K-edge EXAFS spectra and fits obtained for a) LSTN, b) LFNO, c) LCNO and the impregnated samples d) Ni/LST, e) Ni/LFO and c) Ni/LCO. Magnitude and imaginary part of the Fourier transformed data are also shown. Dashed lines indicate the range used for fitting.

Figure 4. Temperature programmed reduction profiles of a) LST-, b) LFO- and c) LCO-type materials in the temperature range $100^{\circ}C \leq T \leq 800^{\circ}C$. The reduction profile of NiO powder is displayed in a) for reference purposes

Figure 5. *In situ* X-ray diffraction patterns at 100°C intervals during temperature programmed reduction (30°C < T < 800°C) in 10 vol% H₂/N₂.

Table 1. Summary of Rietveld refinements on corresponding powder materials.

Sample	Phase	Unit cell parameters	U_{iso}^a (σ)	δ^b [-]	Quality of fit [%]
LST		$a = 3.894811$ (0.000010)	Sr^{2+} : 0.0004 (0.0004) La^{3+} : 0.0108 (0.0007) Ti^{4+} : 0.0058 (0.0001) O^{2-} : 0.0109 (0.0002)	0.049	$wR^c = 3.0$ $RF^d = 2.4$ $RF^{2d} = 4.6$
LSTN		$a = 3.89885$ (0.00001)	Sr^{2+} : 0.002 (0.004) La^{3+} : 0.008 (0.003) Ti^{4+} : 0.0054 (0.0004) O^{2-} : 0.0136 (0.0003) Ni^{2+} : 0.01 (0.03) Ni^{3+} : 0.01 (0.03)	0.055	$wR^c = 3.6$ $RF^d = 2.4$ $RF^{2d} = 5.5$
Ni/LST	LST	$a = 3.89497$ (0.00001)	Sr^{2+} : 0.002 (0.002) La^{3+} : 0.009 (0.002) Ti^{4+} : 0.0059 (0.0001) O^{2-} : 0.0108 (0.0002)	0.117	$wR^c = 3.2$ $RF^d = 2.4$ $RF^{2d} = 4.9$
	NiO	$a = 4.175076$ (-)	Ni^{2+} : 0.016 (0.002) O^{2-} : 0.019 (0.003)	-	$RF = 3.3$ $RF^{2d} = 3.7$
LFO		$a = 5.56500$ (0.00002) $b = 7.85513$ (0.00003) $c = 5.55613$ (0.00002)	La^{3+} : 0.00449 (0.00003) Fe^{3+} : 0.00311 (0.00004) $O1^{2-}$: 0.0041 (0.0007) $O2^{2-}$: 0.0057 (0.0004)	0.014	$wR^c = 2.7$ $RF^d = 2.7$ $RF^{2d} = 7.0$
LFNO		$a = 5.55742$ (0.00002) $b = 7.84813$ (0.00004) $c = 5.55248$ (0.00003)	La^{3+} : 0.00400 (0.00004) Fe^{3+} : 0.0026 (0.0003) $O1^{2-}$: 0.0024 (0.0008) $O2^{2-}$: 0.0067 (0.0006) Ni^{2+} : 0.0003 (0.0012)	0.058	$wR^c = 3.3$ $RF^d = 1.5$ $RF^{2d} = 4.7$
Ni/LFO	LFO	$a = 5.56501$ (0.00002) $b = 7.85532$ (0.00003) $c = 5.55600$ (0.00002)	La^{3+} : 0.00428 (0.00002) Fe^{3+} : 0.00304 (0.00004) $O1^{2-}$: 0.0059 (0.0006) $O2^{2-}$: 0.0055 (0.0003)	0.013	$wR^c = 2.7$ $RF^d = 1.3$ $RF^{2d} = 3.5$
	NiO	$a = 4.1304$ (0.0007)	Ni^{2+} : 0.244 (0.008) O^{2-} : 0.017 (0.004)	-	$RF^d = 1.4$ $RF^{2d} = 3.2$
LCO		$a = 5.44204$ (0.00006) $c = 13.09851$ (0.00009)	La^{3+} : 0.00546 (0.00003) Co^{3+} : 0.0006 (0.0010) O^{2-} : 0.0051 (0.0005)	-	$wR^c = 7.1$ $RF^d = 3.2$ $RF^{2d} = 9.5$
LCNO		$a = 5.44644$ (0.00006) $c = 13.1051$ (0.0001)	La^{3+} : 0.00403 (0.00005) Co^{3+} : 0.0016 (0.0001) O^{2-} : 0.0047 (0.0005) Ni^{2+} : 0.02 (0.02)	-	$wR^c = 7.3$ $RF^d = 3.4$ $RF^{2d} = 9.3$
Ni/LCO	LCO	$a = 5.44191$ (0.00003) $c = 13.09903$ (0.00006)	La^{3+} : 0.00483 (0.00003) Co^{3+} : 0.00216 (0.00008) O^{2-} : 0.00583 (-)	-	$wR^c = 7.1$ $RF^d = 1.6$ $RF^{2d} = 3.0$
	NiO	$a = 4.131$ (0.003)	Ni^{2+} : 0.005 (0.003) O^{2-} : 0.018 (0.007)	-	$RF^d = 2.0$ $RF^{2d} = 8.3$

^a isotropic Debye Waller factor
^b oxygen deficit
^c statistical quality of refinement
^d fit to respective phases

Table 2 Bond length of B-site element and its nearest neighbors in the perovskite-type lattice obtained from refined unit cell parameters as well as EXAFS fitting. Values are also given for Ni-O and Ni-Ni bonds in NiO on impregnated materials.

	Distance from XRD				Distance from EXAFS			
	Perovskite-type oxide		NiO		Perovskite-type oxide		NiO	
	B-O [Å]	B-A [Å]	Ni-O [Å]	Ni-Ni [Å]	Ni-O [Å]	Ni-A [Å]	Ni-O [Å]	Ni-Ni [Å]
LST	1.9474 (0.0005)	3.373 (0.001)	-	-	-	-	-	-
LSTN	1.94942 (0.00008)	3.3765 (0.0001)	-	-	1.95 (0.01)	3.27 (0.04)	-	-
Ni/LST	1.9475 (0.0005)	3.3731 (0.0004)	2.09 (0.02)	2.95 (0.02)	-	-	2.066 (0.009)	2.956 (0.009)
LFO	2.010 (0.002)	3.434 (0.001)	-	-	-	-	-	-
LFNO	2.00 (0.06)	3.4 (0.1)	-	-	1.95 (0.01)	n.a.	-	-
Ni/LFO	1.99 (0.002)	3.434 (0.001)	2.065 (0.004)	2.921 (0.004)	-	-	2.05 (0.01)	2.96 (0.01)
LCO	1.939 (0.002)	3.275 (0.001)	-	-	-	-	-	-
LCNO	1.9 (0.1)	3.3 (0.2)	-	-	1.98 (0.01)	3.29 (0.01)	-	-
Ni/LCO	1.94 (0.01)	3.275 (0.002)	2.07 (0.02)	2.92 (0.02)	-	-	2.03 (0.01)	2.95 (0.01)

Ni incorporation in perovskite-type metal oxides – implications on reducibility

Supporting information

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Figure S1. Normalized powder X-ray diffraction patterns and Rietveld refinement results of all samples obtained using synchrotron radiation at 15.95 keV and the GSAS II software package.

Figure S2. BO_6 octahedra viewed (a) along the crystallographic b -axis and (b) along the c -axis. Arrows represent differences in oxygen (green) and iron (red) positions between structure of $\text{LaFe}_{0.95}\text{Ni}_{0.05}\text{O}_3$ and LaFeO_3 magnified by a factor of 100. O1 and O2 denote different oxygen positions.

Figure S3. Normalized Ni K-edge X-ray absorption near edge structure (XANES) spectra of a) Ni/LST, b) Ni/LFO and c) Ni/LCO. The corresponding first derivative functions are shown in d), e) and f), respectively. Dashed marker lines indicate absorption edge energies (E_0) and positions of interest discussed in the text.

Figure S4. Normalized Ni K-edge X-ray absorption near edge structure (XANES) spectra of a) NiO and b) Ni^0 (Ni-foil). The corresponding first derivatives are shown in c) and d), respectively. Dashed marker lines indicate edge energies (E_0) and positions of interest discussed in the text.

Figure S5. k^3 -weighted Ni K-edge EXAFS obtained for a) LSTN, b) LFNO, c) LCNO and the impregnated samples d) Ni/LST, e) Ni/LFO and c) Ni/LCO. Data window used for Fourier transformation is also shown (data displayed in Figure 4 in the main text).

Figure S6. k^3 -weighted Ni K-edge EXAFS obtained for the reference materials a) NiO and b) Ni⁰ (Ni-foil). Data window used for Fourier transformation is indicated with dotted lines. Fourier transformed k^3 -weighted Ni K-edge EXAFS and obtained fits are displayed in c) for NiO and d) for Ni⁰. Data window used for fitting is also shown.

Table S1. Textural sample properties.

Sample Composition		Perovskite space group	SSA [m ² /g] ^a	Single crystalline domain size [nm] ^b	
				Perovskite	NiO
LST	La _{0.3} Sr _{0.55} TiO ₃		11.6 ± 0.5	129.0 ± 0.6	-
LSTN	La _{0.3} Sr _{0.55} Ti _{0.95} Ni _{0.05} O ₃	Pm-3m	12.4 ± 0.5	223 ± 2	-
Ni/LST	2.1 wt% NiO/La _{0.3} Sr _{0.55} TiO ₃		14.3 ± 0.5	149.3 ± 0.5	7.5 ± 0.5
LFO	LaFeO ₃		6.4 ± 0.5	149.8 ± 0.2	-
LFNO	LaFe _{0.95} Ni _{0.05} O ₃	Pnma	7.1 ± 0.5	156.6 ± 0.5	-
Ni/LFO	1.5 wt% NiO/LaFeO ₃		7.3 ± 0.5	153.9 ± 0.4	9.1 ± 0.2
LCO	LaCoO ₃		5.8 ± 0.5	138.4 ± 0.3	-
LCNO	LaCo _{0.95} Ni _{0.05} O ₃	R-3c	6.7 ± 0.5	122.5 ± 0.7	-
Ni/LCO	1.5 wt% NiO/LaCoO ₃		6.0 ± 0.5	128.7 ± 0.7	6.8 ± 0.3

^a specific surface area obtained from N₂ physisorption.^b obtained from Scherrer equation and Rietveld refinement.

Table S2. EXAFS fitting results.

Sample	scattering atom	N ^a	fitted parameters				R _{eff} [Å] ^f	
			S ₀ ^{2b}	σ ^{2c}	E ⁰ [eV] ^d	ΔR [Å] ^e		
Ni/LFO	O	6	0.9 (0.1)	0.007 (0.002)	-3 (1)	-0.03 (0.01)	2.05 (0.01)	Ref: NiO X _{red} ^{2g} = 59 R ^h = 0.014
	Ni	12		0.010 (0.002)		0.006 (0.009)	2.960 (0.009)	
LFNO	O	6	0.8 (0.1)	0.006 (0.002)	-7 (2)	-0.05 (0.01)	1.95 (0.01)	Ref: LaFeO ₃ X _{red} ^{2g} = 144 R ^h = 0.005
Ni/LCO	O	6	1.0 (0.1)	0.008 (0.002)	-4 (1)	-0.06 (0.01)	2.03 (0.01)	Ref: NiO X _{red} ^{2g} = 76 R ^h = 0.01
	Ni	12		0.010 (0.001)		-0.01 (0.01)	2.95 (0.01)	
LCNO	O	6	0.9 (0.1)	0.003 (0.002)	-4 (1)	0.05 (0.01)	1.98 (0.01)	Ref: LaCoO ₃ X _{red} ^{2g} = 31 R ^h = 0.015
	La	6		0.004 (0.001)		-0.04 (0.01)	3.29 (0.01)	
	O,Co	12		0.004 (0.003)		0.03 (0.05)	3.87 (0.05)	
	O,Co,O	6		0.003 (0.005)		0.003 (0.005)	3.972 (0.005)	
Ni/LST	O	6	1.04 (0.08)	0.007 (0.001)	-2.5 (0.7)	-0.023 (0.009)	2.066 (0.009)	Ref: NiO X _{red} ^{2g} = 115 R ^h = 0.009
	Ni	12		0.0085 (0.0007)		0.002 (0.006)	2.956 (0.006)	
LSTN	O	6	0.9 (0.2)	0.006 (0.002)	-5.8 (0.5)	0.09 (0.01)	1.95 (0.01)	Ref: SrTiO ₃ X _{red} ^{2g} = 690 R ^h = 0.03
	La	2.4		0.008 (0.004)		-0.10 (0.04)	3.27 (0.04)	
	Sr	4.4		0.008 (0.004)				
NiO	O	6	0.9 (0.1)	0.0040 (0.0009)	1.9 (0.8)	-0.018 (0.009)	2.071 (0.009)	Ref: NiO X _{red} ^{2g} = 115 R ^h = 0.009
	Ni	12		0.0050 (0.0003)		-0.007 (0.005)	2.948 (0.005)	
	O	8		0.007 (0.004)		-0.12 (0.03)	3.50 (0.03)	
Ni foil	Ni	12	0.82 (0.05)	0.0058 (0.0004)	6.4 (0.6)	-0.052 (0.004)	2.479 (0.004)	Ref: Ni ⁰ X _{red} ^{2g} = 1090 R ^h = 0.007
	Ni	6		0.009 (0.001)		-0.10 (0.01)	3.48 (0.01)	
	Ni	24		0.0081 (0.0009)		-0.063 (0.009)	4.322 (0.009)	
	Ni,Ni	96		0.004 (0.004)		0.21 (0.05)	4.94 (0.05)	

^a coordination number
^b amplitude reduction factor
^c Debye Waller factor
^d phase shift
^e radial distance relative to reference
^f effective distance
^g goodness of fit
^h misfit between the data and model