Fundamental material property trends in the $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ series: crystal structure and thermal expansion

Christian Berger¹, Edith Bucher^{1,*} , Judith Lammer², Christina Nader¹, and Werner Sitte¹

¹ Chair of Physical Chemistry, Montanuniversitaet Leoben, Franz-Josef-Straße 18, A-8700 Leoben, Austria

² Graz University of Technology & Graz Centre for Electron Microscopy (ZFE), Institute of Electron Microscopy and Nanoanalysis (FELMI), Steyrergasse 17, A-8010 Graz, Austria

Received: 7 December 2020

Accepted: 27 January 2021

Published online:
25 February 2021

© The Author(s) 2021,
corrected publication 2021

ABSTRACT

Compounds from the series $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ ($0.1 \leq x \leq 0.7$) were synthesised by a sol–gel route. X-ray diffraction and Rietveld analysis showed that materials with $0 \leq x \leq 0.6$ crystallize as single-phase orthorhombic perovskites. The smaller ionic radius of Nd^{3+} compared to La^{3+} leads to a decrease in unit cell volume with increasing x . Elemental mapping by high-resolution scanning transmission electron microscopy with energy-dispersive X-ray spectroscopy confirms the homogeneous distribution of the A-site elements (La, Nd and Ca) in the perovskite (ABO_3) lattice. The thermal expansion behaviour of $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ ($0 \leq x \leq 0.6$) was characterized by dilatometry at $30 \leq T/^\circ\text{C} \leq 1000$ and $1 \times 10^{-3} \leq p\text{O}_2/\text{bar} \leq 1$. The thermal expansion coefficients of $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$, which were determined in regions I (40–530 °C) and II (530–990 °C), respectively, are almost independent of the Nd concentration in the range of ($0 \leq x \leq 0.6$) and increase slightly with decreasing $p\text{O}_2$. The transition from orthorhombic to trigonal modification, which is observed for $\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ at approx. 740 °C, is suppressed for all Nd-substituted compounds with $x \geq 0.1$.

Introduction

With a great versatility of elements which can occupy the A- and B-site positions, perovskite-type oxides ABO_3 offer the possibility of tailoring materials with a variety of properties for specific technological

applications (electronic-, ionic- or mixed-conductors, ferro- and piezoelectrics, thermistors, varistors, etc.) [1, 2]. In solid oxide cells (SOCs), which comprise solid oxide fuel cells (SOFCs) and solid oxide electrolysis cells (SOECs), perovskite-type oxides are applied as air electrode materials due to their high electronic and significant ionic conductivities and fast

Handling Editor: Till Froemling.

Address correspondence to E-mail: edith.bucher@unileoben.ac.at

<https://doi.org/10.1007/s10853-021-05851-z>

oxygen exchange kinetics [3–7]. SOC air electrode materials, which are optimized for operation temperatures of 650–850 °C, usually contain La^{3+} and Sr^{2+} on the A-site and mixed-valence transition metals on the B-site (Co, Fe) [4, 8]. However, the insufficient long-term stability of state-of-the-art SOC air electrodes under application-relevant conditions remains a critical factor and a challenge towards materials development. The degradation mechanism of materials from the $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ series frequently involves the surface segregation of Sr [9–11] driven (among other factors) by the size-mismatch between the host (La^{3+}) and substituent ion (Sr^{2+}) [12], and the reaction with acidic impurities such as volatile Cr- or Si-species and SO_2 [13–19]. A possible approach towards the improvement of long-term stability is, therefore, the replacement of Sr with different substituents (preferably with smaller ionic radius) and the decrease in the compound basicity [20, 21].

Recently, promising results with regard to fast oxygen exchange kinetics and high stability vs. SO_2 -poisoning were reported for Sr- and Co-free perovskites from the $\text{La}_{1-x}\text{Ca}_x\text{FeO}_{3-\delta}$ series [7, 22–24]. Price et al. reported that the solubility limit of Ca in $\text{La}_{1-x}\text{Ca}_x\text{FeO}_{3-\delta}$ is 38% [25]. In the series $\text{La}_{1-x}\text{Ca}_x\text{FeO}_{3-\delta}$ ($0.1 \leq x \leq 0.25$), $\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ showed the highest oxygen exchange activity [7, 23] and excellent long-term stability [26]. The results of long-term oxygen exchange measurements and post-test analyses indicated that the improved impurity tolerance of $\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ is due to lower compound basicity and the island-like formation pattern of secondary phases [20, 26].

In the present study, the solubility of 10–70% of Nd on the A-site of $\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ is investigated with the aims to further decrease compound basicity and to further improve long-term stability against impurity poisoning, while at the same time (to the greatest possible extent) maintaining the excellent properties of the original compound. With an ionic radius of 1.27 Å $\text{Nd}^{3+}(\text{XII})$ is smaller than (but still relatively close to) the ionic radius of $\text{La}^{3+}(\text{XII})$, which is 1.36 Å [12]. A-site substitution with Ce^{3+} or Pr^{3+} was avoided since both cations are capable of valence changes ($3+/4+$), which may introduce more complex changes in the material properties or lead to problems with phase stability. $\text{Sm}^{3+}(\text{XII})$ with an ionic radius of 1.24 Å and rare earth elements with even higher atomic numbers (i.e. even smaller ionic radii) were also considered unfavourable, since these

cations may lead to more significant changes in crystal structure and material properties compared to the original compound $\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$.

The present publication describes the synthesis of the compounds $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ ($0.1 \leq x \leq 0.7$) as well as characterization of the crystal structure and thermal expansion behaviour of the single-phase materials $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ ($0.1 \leq x \leq 0.6$) in comparison with $\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$. By analysis of XRD data with Rietveld refinement, information on phase purity and structural parameters (space group, bond length and angles, atom positions) was obtained. The thermal expansion behaviour was characterized by dilatometry in a wide range of temperatures (30–1000 °C) and oxygen partial pressures ($1 \times 10^{-3} \leq p\text{O}_2/\text{bar} \leq 1$).

Experimental

Sample preparation

A series of solid solutions $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ ($0.1 \leq x \leq 0.7$) was synthesised via a citric acid – ethylenediaminetetraacetate (EDTA) sol–gel process starting with stoichiometric amounts of the metal nitrates $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (all chemicals obtained from Sigma-Aldrich, analytical grade quality). These were mixed with distilled H_2O in a stainless steel vessel. Anhydrous citric acid and EDTA (one mole each per mole cations) were added after the metal nitrates were completely dissolved. Subsequently, 25% aqueous NH_3 solution was added

Table 1 Cation stoichiometry of compounds from the $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ series; data obtained from SEM–EDX analyses of sintered pellets are compared to theoretical values (in parentheses) calculated from the nominal composition. All values are given in atomic percent

Compound	La L	Nd L	Ca K	Fe K
$\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	40 (40)	–	9 (10)	51 (50)
$\text{La}_{0.7}\text{Nd}_{0.1}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	35 (35)	5 (5)	10 (10)	50 (50)
$\text{La}_{0.6}\text{Nd}_{0.2}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	30 (30)	10 (10)	10 (10)	50 (50)
$\text{La}_{0.5}\text{Nd}_{0.3}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	25 (25)	14 (15)	10 (10)	51 (50)
$\text{La}_{0.4}\text{Nd}_{0.4}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	20 (20)	20 (20)	9 (10)	51 (50)
$\text{La}_{0.3}\text{Nd}_{0.5}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	16 (15)	25 (25)	9 (10)	50 (50)
$\text{La}_{0.2}\text{Nd}_{0.6}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	10 (10)	30 (30)	9 (10)	51 (50)

Figure 1 (a) XRD patterns of calcined powders of $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ ($0 \leq x \leq 0.6$); plots (b) and (c) show details of (a) with reflections ascribed to the lattice planes (220), (022) in (b) and (321), (240), (123), (042) in (c) indicated with dashed lines.

until pH = 8 was reached and a clear dark red solution was obtained. The temperature was slowly raised to evaporate water and form a gel. Self-ignition and combustion of the dried gel occurred at approximately 500 °C.

The raw ash was crushed in an agate mortar and calcined at 1000 °C for 4 h (5 K min⁻¹ ramps for heating and cooling) in air. According to XRD, single-phase compounds were obtained for $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ with $x \leq 0.6$. Further increase in the Nd concentration to $x = 0.7$ led to the formation of the secondary phases CaO and $\text{Ca}_2\text{Fe}_2\text{O}_5$ (see Supplementary Material, Figure S-1 and Table S-1). The particle size distribution of the calcined powders was determined by use of a CILAS 1064L particle size analyser. After calcination, the d_{50} values of the powders were in the range of $18.6 \leq d_{50}/\mu\text{m} \leq 22.4$. A bench top roll-mill was used to grind the calcined powders until $0.5 \leq d_{50}/\mu\text{m} \leq 0.7$ was reached.

For thermal expansion measurements, cylindrical pellets were fabricated by uniaxial pressing. After sintering at 1150 °C for 10 h with heating and cooling rates of 1 K min⁻¹, the samples were approximately 5 mm in diameter and 8 mm long. The relative densities of the sintered samples of $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ with $x = 0$ [7] and $x = 0.3$ – 0.6 (this study) were in the range of 97–99% of the theoretical densities. (Relative densities of $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ with $x = 0.1$ – 0.2 were determined with 92% of the theoretical densities; however, since these two samples were not ideally cylindrical, the relative densities may be underestimated.)

X-ray diffraction and electron microscopy

XRD of the calcined powders was performed with a diffractometer (BRUKER-AXS D8 Advance ECO) using a Cu K α radiation source operated at 40 kV and 25 mA. The diffractograms were recorded at scanning rates of 0.01° s⁻¹. Rietveld refinement was performed by using the commercially available software TOPAS (Bruker) [27]. Lattice parameters were obtained from fits of the reflections' positions to an

Figure 2 (a) Lattice parameters of the orthorhombic unit cells (SG: $Pnma$) of $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ ($0 \leq x \leq 0.6$), (b) orthorhombicity (defined as $2(b-a)/(a+b)$ [30]) and (c) unit cell volume as a function of Nd concentration.

orthorhombic unit cell (space group $Pnma$). Reflection broadening was described by convolution of a Voigt function with a modified pseudo-Voigt function according to Thompson–Cox–Hastings [28].

Sample preparation for the TEM investigation was carried out on a focused ion beam (FIB) microscope FEI NOVA 200 Nanolab. TEM analyses were performed with a TITAN³ G2 60–300 from FEI at 300 kV accelerating voltage in scanning transmission electron microscopy mode (STEM). The microscope is equipped with a C_s -probe corrector and a Super-X detector system (FEI). STEM images were acquired with a high-angle annular dark-field (HAADF) and a bright-field (BF) detector. The software packages GMS 3 (Gatan) and Velox 2 (Thermo Fisher Scientific) were used to acquire HAADF images and EDX spectrum images.

The cation stoichiometry (Table 1) was obtained by energy-dispersive X-ray spectroscopy (EDXS) measurements in a scanning electron microscope (Cambridge, STEREOSCAN 250 MK3) equipped with an Oxford Instruments Mod. 6272 detector. To confirm the homogeneity of cation distribution, area scans on polished samples with 10 mm diameters were measured.

Dilatometry and differential scanning calorimetry

The thermal expansion behaviour of the materials was investigated between 30 and 1000 °C with heating rates of 1 K min^{−1} using a single-rod dilatometer DIL 402/PC4 (NETZSCH). Atmospheres with different oxygen partial pressures in range of $1 \times 10^{-3} \leq p\text{O}_2/\text{bar} \leq 1$ were obtained by O_2 -Ar gas mixtures using mass flow controllers (Teledyne HFC-302) at flow rates of 10 l h^{−1}.

Differential scanning calorimetry (DSC) was performed on selected sintered (1100 °C, 2 h, air) and finely ground powders using a High Temperature DSC 404 C Pegasus (NETZSCH). The sample (approximately 20–30 mg) was placed in an 85 μl Pt–Rh crucible. To minimize the influence of adsorbed humidity or CO_2 , the powders were heated in the calorimeter to 1000 °C, kept in 20% O_2 (rest Ar) and cooled to 20 °C before the actual experiments were started. The DSC measurements were performed between 20 and 1000 °C in 20% O_2 (rest Ar) with heating and cooling rates of 20 K min^{−1} and gas flow rates of 50 ml min^{−1}.

Table 2 Lattice parameters, unit cell volume and tolerance factor of compounds from the $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ series in comparison with similar perovskites

Compound	a/Å	b/Å	c/Å	V/Å ³	t	Ref
$\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	5.5105(3)	7.7985(4)	5.5341(3)	237.82	0.9530	[7]
$\text{La}_{0.7}\text{Nd}_{0.1}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	5.52401(14)	7.79782(13)	5.51433(12)	237.53	0.9498	This work
$\text{La}_{0.6}\text{Nd}_{0.2}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	5.52567(10)	7.78983(19)	5.50628(13)	237.01	0.9467	
$\text{La}_{0.5}\text{Nd}_{0.3}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	5.52654(9)	7.78229(17)	5.49680(12)	236.41	0.9436	
$\text{La}_{0.4}\text{Nd}_{0.4}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	5.53318(8)	7.78306(16)	5.49251(11)	236.54	0.9405	
$\text{La}_{0.3}\text{Nd}_{0.5}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	5.52776(9)	7.76461(17)	5.47637(11)	235.05	0.9374	
$\text{La}_{0.2}\text{Nd}_{0.6}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	5.53158(11)	7.75747(18)	5.46723(11)	234.61	0.9343	
NdFeO_3	5.4504(3)	5.5835(2)	7.7602(4)	236.16	0.9232	[33]
CaFeO_3	5.34967(9)	7.53558(14)	5.32356(10)	214.61	0.9474	[32]
LaFeO_3	5.5647(1)	7.8551(1)	5.5560(1)	242.86	0.9543	[31]

Figure 3 STEM-HAADF image of $\text{La}_{0.2}\text{Nd}_{0.6}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ in [010] zone axis (upper left); STEM-EDX elemental distribution maps of Fe, Fe and Nd, Nd, La and Ca based on net peak intensities after background subtraction.

Results and discussion

3.1 Crystal structure and cation distribution

XRD patterns of $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ ($0 \leq x \leq 0.6$) are shown in Fig. 1a. All reflections were assigned to the orthorhombic GdFeO_3 perovskite structure with the space group $Pnma$ (SG#62). With increasing Nd content, the reflections shift towards higher diffraction angles. This effect is shown in detail for the reflections ascribed to the lattice planes (220) and (022) in Fig. 1(b), and for the lattice planes (321), (240), (123) and (042) in Fig. 1(c). The separation of these reflections increases with increasing Nd concentration. Rietveld refinement was performed for all compounds $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ ($0 \leq x \leq 0.6$). The lattice parameters of the orthorhombic unit cells are plotted as a function of Nd concentration in Fig. 2a. Linear dependences of the unit cell parameters of the solid solutions on the Nd concentration are observed,

following Vegard's law [29]. No change in space group is observed within the investigated range of compositions (see also the plot of the orthorhombicity, defined as $2(b - a)/(a + b)$ [30], in Fig. 2b). The lattice parameters of the Nd-substituted compounds are given in Table 2, which also includes data of the unsubstituted materials LaFeO_3 [31], CaFeO_3 [32] and NdFeO_3 [33], and of $\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ [7]. Increasing substitution of La^{3+} with Nd^{3+} causes a linear decrease in the unit cell volume of $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ (Table 2 and Fig. 2(c)).

Goldschmidt's tolerance factor t (Table 2), which describes the deviation from the ideal cubic perovskite structure ($t = 1$) and may be used as an indicator of the relative stability of the structure, was calculated according Eq. 1 [34, 35].

$$t = \frac{x_A r_A + x_{A'} r_{A'} + x_{A''} r_{A''} + r_O}{\sqrt{2}(r_B + r_O)} \quad (1)$$

The variables x_A , $x_{A'}$ and $x_{A''}$ represent the occupancy of the A-sites of the perovskite lattice with $A = \text{La}$, $A' = \text{Ca}$ and $A'' = \text{Nd}$ (for example: $x_A = 0.2$, $x_{A'} = 0.2$ and $x_{A''} = 0.6$ in $\text{La}_{0.2}\text{Nd}_{0.6}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$). The symbols r_i denote the ionic radii of the species i (A- and B-site cations, oxygen). The following ionic radii from [12] were used: $r(\text{La}^{3+})(\text{XII}) = 1.36 \text{ \AA}$; $r(\text{Ca}^{2+})(\text{XII}) = 1.34 \text{ \AA}$, $r(\text{Nd}^{3+})(\text{XII}) = 1.27 \text{ \AA}$, $r(\text{Fe}^{3+}(\text{high spin}))(\text{VI}) = 0.645 \text{ \AA}$, $r(\text{O}^{2-})(\text{VI}) = 1.40 \text{ \AA}$. As indicated in Table 2, t decreases with increasing Nd concentration from LaFeO_3 ($t = 0.9543$) [31] over $\text{La}_{0.7}\text{Nd}_{0.1}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ ($t = 0.9498$) to CaFeO_3 ($t = 0.9474$), and subsequently to $\text{La}_{0.2}\text{Nd}_{0.6}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ ($t = 0.9343$) and NdFeO_3 ($t = 0.9232$).

As an example for the compounds from the LNCF series, $\text{La}_{0.2}\text{Nd}_{0.6}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ was analysed with atomically resolved STEM-EDX regarding the

Figure 4 (a) XRD pattern of $\text{La}_{0.2}\text{Nd}_{0.6}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ (circles) and fit obtained from Rietveld refinement (solid line); the grey line represents the difference plot between measured and calculated data. The high fit quality is indicated by the reliability parameters $R_{\text{exp}} = 5.39$, $R_{\text{wp}} = 7.96$ and $\chi^2 = 1.48$. (b) Crystal structure of $\text{La}_{0.2}\text{Nd}_{0.6}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ oriented along the crystallographic c -axis.

distribution of the cations La, Nd, Ca and Fe. The contrast in the STEM-HAADF image (Fig. 3, upper left image) results from the differences in the atomic numbers of the elements, with heavier elements appearing brighter than lighter ones. Due to the similar atomic numbers of La (57) and Nd (60), it is not possible to distinguish between those two elements solely based on the information from the HAADF image. However, the elemental distributions of La and Nd were determinable with STEM-EDX spectrum images. The elemental maps of La, Nd, Fe and Ca thus obtained are shown in Fig. 3. The Ca map is not as clear as those of La and Nd, due to the relatively low Ca signal intensities in the EDX spectra. However, the elemental distribution maps indicate that the cations are indeed homogeneously

Table 3 Atomic positions of compounds from the $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ series; all investigated materials crystallize in the orthorhombic space group ($Pnma$). Atomic positions of Ca and Nd were considered equivalent to those of La

	Site	x	y	z	Occ
$\text{La}_{0.7}\text{Nd}_{0.1}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	La	0.0263	$\frac{1}{4}$	0.9976	0.7
	Ca	0.0263	$\frac{1}{4}$	0.9976	0.2
	Nd	0.0263	$\frac{1}{4}$	0.9976	0.1
	Fe	0	0	$\frac{1}{2}$	1
	O1	0.4901	$\frac{1}{4}$	0.0619	1
	O2	0.2816	0.4590	0.7215	1
$\text{La}_{0.5}\text{Nd}_{0.3}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	La	0.0337	$\frac{1}{4}$	0.9938	0.5
	Ca	0.0337	$\frac{1}{4}$	0.9938	0.2
	Nd	0.0337	$\frac{1}{4}$	0.9938	0.3
	Fe	0	0	$\frac{1}{2}$	1
	O1	0.4836	$\frac{1}{4}$	0.0714	1
	O2	0.2835	0.4596	0.7197	1
$\text{La}_{0.3}\text{Nd}_{0.5}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	La	0.0387	$\frac{1}{4}$	0.9909	0.3
	Ca	0.0387	$\frac{1}{4}$	0.9909	0.2
	Nd	0.0387	$\frac{1}{4}$	0.9909	0.5
	Fe	0	0	$\frac{1}{2}$	1
	O1	0.4788	$\frac{1}{4}$	0.0772	1
	O2	0.2854	0.4575	0.7150	1
$\text{La}_{0.6}\text{Nd}_{0.2}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	La	0.0309	$\frac{1}{4}$	0.9945	0.6
	Ca	0.0309	$\frac{1}{4}$	0.9945	0.2
	Nd	0.0309	$\frac{1}{4}$	0.9945	0.2
	Fe	0	0	$\frac{1}{2}$	1
	O1	0.4836	$\frac{1}{4}$	0.0670	1
	O2	0.2816	0.4590	0.7177	1
$\text{La}_{0.4}\text{Nd}_{0.4}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	La	0.03603	$\frac{1}{4}$	0.9938	0.4
	Ca	0.03603	$\frac{1}{4}$	0.9938	0.2
	Nd	0.03603	$\frac{1}{4}$	0.9938	0.4
	Fe	0	0	$\frac{1}{2}$	1
	O1	0.4836	$\frac{1}{4}$	0.0744	1
	O2	0.2858	0.4589	0.7150	1
$\text{La}_{0.2}\text{Nd}_{0.6}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	La	0.0415	$\frac{1}{4}$	0.9953	0.2
	Ca	0.0415	$\frac{1}{4}$	0.9953	0.2
	Nd	0.0415	$\frac{1}{4}$	0.9953	0.6
	Fe	0	0	$\frac{1}{2}$	1
	O1	0.4761	$\frac{1}{4}$	0.0796	1
	O2	0.2892	0.4594	0.7133	1

distributed on the A- (La, Nd, Ca) and B-sites (Fe) of $\text{La}_{0.2}\text{Nd}_{0.6}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$. Similar behaviour is assumed for the elemental distribution in the other compounds from the LNCf series.

Under consideration of these results, the atomic positions of the La-, Nd- and Ca-sites in the Rietveld refinement of the XRD data were set equivalent for all investigated compounds of the LNCf series. As an

Table 4 Bond lengths and bond angles of compounds from the $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ series in comparison with similar perovskites. The numbers in parentheses denote standard deviations in units of the least significant digits

Compound	Fe-O1/Å	Fe-O2/Å	Fe-O2'/Å	Fe-O1-Fe/°	Fe-O2-Fe/°	Ref
$\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	1.98248(10)	1.99882(8)	1.98660(8)	159.11	156.92	[7]
$\text{La}_{0.7}\text{Nd}_{0.1}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	1.98248(8)	1.99882(5)	1.98660(5)	159.11	156.92	This work
$\text{La}_{0.6}\text{Nd}_{0.2}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	1.97986(5)	1.99517(4)	1.98550(3)	159.89	157.04	
$\text{La}_{0.5}\text{Nd}_{0.3}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	1.98421(5)	1.99352(3)	1.98996(3)	157.91	156.55	
$\text{La}_{0.4}\text{Nd}_{0.4}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	1.98681(4)	1.99092(3)	1.99601(3)	156.61	156.16	
$\text{La}_{0.3}\text{Nd}_{0.5}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	1.99027(5)	1.98836(3)	1.99928(3)	155.72	155.55	
$\text{La}_{0.2}\text{Nd}_{0.6}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	1.99014(5)	1.98801(3)	2.00313(3)	154.52	155.13	
NdFeO_3	1.55474(5)	2.56395(11)	2.27324(9)	157.13	127.75	[33]
CaFeO_3	1.92180(4)	1.91219(3)	1.92213(3)	159.5739	157.20	[32]
LaFeO_3	2.00(5)	2.002(3)	2.01(4)	157.60	157.60	[31]

example, the refined XRD pattern and the crystal structure of $\text{La}_{0.2}\text{Nd}_{0.6}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ are shown in Fig. 4a and Fig. 4b. The atomic positions of $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ ($0.1 \leq x \leq 0.6$) are given in Table 3. Table 4 shows bond lengths and bond angles of materials from the LNCF series in comparison with the unsubstituted compounds LaFeO_3 [31], CaFeO_3 [32], NdFeO_3 [33] and the Nd-free analogue $\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ [7]. Bond lengths and bond angles of $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ ($0 \leq x \leq 0.6$) are also shown as a function of Nd concentration in Fig. 5. Substitution of 10% La with Nd decreases the bond length between Fe and the apical oxygen (Fe1-O1, Fig. 5f), followed by an increase in the bond length from $x = 0.1$ to 0.3 in $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ (Fig. 5(a)). An increase with different slopes is observed at higher Nd concentrations ($x = 0.4$ to 0.6). While the bond lengths Fe1-O2 (Fig. 5(b)) decrease with increasing x , the bond lengths Fe1-O2' show similar trends to those of Fe1-O1 (Fig. 5c, decrease from $x = 0$ to $x = 0.1$ and increase with further increase in x). The presence of two different equatorial oxygen positions (O2 and O2') is due to a distortion of the FeO_6 octahedra [31, 33, 36]. Although Fe1-O2 and Fe1-O2' have different bond lengths, the bond angles of Fe1-O2-Fe1 and Fe1-O2'-Fe1 are equal. The bond angles Fe1-O2-Fe1 and Fe1-O2'-Fe1 (both shown in Fig. 5d), as well as Fe1-O1-Fe1 (Fig. 5e) increase from $x = 0$ to $x = 0.1$ and decrease from $x = 0.1$ to 0.6 .

The high-resolution HAADF image shown in Fig. 6b was used to perform a Fast Fourier Transformation (FFT) (Fig. 6d) to analyse the changes in the crystal structure when substituting Nd with La within the perovskite structure. For this purpose,

$\text{La}_{0.2}\text{Nd}_{0.6}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ was compared with the Nd-free compound $\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$. The reciprocal lattice spacings and angles measured from FFTs of $\text{La}_{0.2}\text{Nd}_{0.6}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ were compared with values obtained from simulations of electron diffraction patterns via JEMS [37]. Figure 6c depicts the simulated diffraction patterns of $\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ and $\text{La}_{0.2}\text{Nd}_{0.6}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ in [010] zone axis. A comparison of Fig. 6d with the simulations clearly reveals the changes in the crystal structure: spots from the (001), (00-1), (100) and (-100) lattice planes (marked in red squares) appear in the FFT as well as in the diffraction pattern simulation of $\text{La}_{0.2}\text{Nd}_{0.6}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$, but are not visible in the simulation of $\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$. The absence of further diffraction spots in $\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ (marked with dashed squares) is due to the fact that these reflections can be explained as orders of the inner missing spots.

3.2 Thermal expansion and phase stability

Thermal expansion coefficients α of $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ ($0 \leq x \leq 0.6$) were obtained from the slopes of $\Delta L/L_0$ vs. T curves (Figure S-2–S-5) in the temperature regions I ($40 \leq T/^\circ\text{C} \leq 530$) and II ($530 \leq T/^\circ\text{C} \leq 990$) and different oxygen partial pressures in the range of $1 \times 10^{-3} \leq p\text{O}_2/\text{bar} \leq 1$ (Table 5 and Fig. 7). A three-dimensional representation of the T - and $p\text{O}_2$ -dependence of the average α values ($50 \leq T/^\circ\text{C} \leq 1000$) is given in Figure S-6. At constant $p\text{O}_2$, the effect of Nd-substitution in the series $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ on the thermal expansion coefficient is relatively small, and the α values of $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ ($0.1 \leq x \leq 0.6$) are similar to those of $\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ [7]. At $p\text{O}_2 = 1$ bar, α

Figure 5 Bond lengths (a) Fe1-O1, (b) Fe1-O2, (c) Fe1-O2' and (d) bond angles Fe1-O2-Fe1 (equal to Fe1-O2'-Fe1) and (e) Fe1-O1-Fe1 of $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ ($0 \leq x \leq 0.6$) as a function of

Nd concentration; (f) labelling of the atomic sites using the example of $\text{La}_{0.2}\text{Nd}_{0.6}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ oriented along the crystallographic b -axis.

of $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ ($0 \leq x \leq 0.6$) is in the range of $(12.8 \pm 0.3) \times 10^{-6} \text{ K}^{-1}$ (region I) and $(15.3 \pm 0.5) \times 10^{-6} \text{ K}^{-1}$ (region II), and at 0.1 bar in the range of $(13.0 \pm 0.2) \times 10^{-6} \text{ K}^{-1}$ (region I) and $(15.7 \pm 0.2) \times 10^{-6} \text{ K}^{-1}$ (region II). At lower oxygen

partial pressure, i.e. $p\text{O}_2 = 0.01$ bar, α values are $(13.4 \pm 0.3) \times 10^{-6} \text{ K}^{-1}$ (region I) and $(17.4 \pm 0.9) \times 10^{-6} \text{ K}^{-1}$ (region II), and at 0.001 bar $(13.2 \pm 0.3) \times 10^{-6} \text{ K}^{-1}$ (region I) and $(18.4 \pm 0.4) \times 10^{-6} \text{ K}^{-1}$ (region II). The increase in α

Figure 6 (a) STEM bright-field image of $\text{La}_{0.2}\text{Nd}_{0.6}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$. The structure matches the superimposed projection of the unit cell along the $[010]$ zone axis; (b) STEM-HAADF image of $\text{La}_{0.2}\text{Nd}_{0.6}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ in $[010]$ orientation; (c) simulated diffraction patterns of $\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ (left) and $\text{La}_{0.2}\text{Nd}_{0.6}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ (right); (d) FFT of the HAADF image shown in (b).

with decreasing $p\text{O}_2$ (esp. at 1×10^{-2} and 1×10^{-3} bar) and increasing temperature (esp. in region II) is presumably due to the additional contribution of chemical

expansion caused by the formation of oxygen vacancies as observed with similar perovskites [7, 22, 23].

The α values of $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ ($0 \leq x \leq 0.6$), determined in temperature regions I and II at $p\text{O}_2 = 0.1$ bar, are similar to those of Nd-free lanthanum calcium ferrites like $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-\delta}$ ($13.1 \times 10^{-6} \text{ K}^{-1}$ [23]) and $\text{La}_{0.75}\text{Ca}_{0.25}\text{FeO}_{3-\delta}$ ($15.1 \times 10^{-6} \text{ K}^{-1}$ [22]), but significantly smaller than those of the state-of-the-art SOFC cathode material $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ ($18.9 \times 10^{-6} \text{ K}^{-1}$ [38]). Further, the thermal expansion coefficients of $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ ($0 \leq x \leq 0.6$) are relatively close (especially in temperature region I) to those of common solid electrolytes like 8YSZ ($10.8 \times 10^{-6} \text{ K}^{-1}$ [39]) or $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$ ($12.5 \times 10^{-6} \text{ K}^{-1}$ [40]).

As previously reported in the literature, the Nd-free compound $\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ shows a reversible transition from the orthorhombic (SG: $Pnma$) to the trigonal (SG: $R-3c$) structural modification at approximately 740°C [7, 25]. According to DSC measurements, substitution of La with Nd seems to suppress the structural transition in $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ ($0.1 \leq x \leq 0.6$) (Figures S-7 and S-8). While the DSC curve of $\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ shows an exothermal peak at approximately 740°C (previously attributed to the structural transition [7, 25]), no comparable

Table 5 Thermal expansion coefficients α of compounds from the $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ series in temperature regions I ($40 \leq T/^\circ\text{C} \leq 530$) and II ($530 \leq T/^\circ\text{C} \leq 990$) at different oxygen partial pressures

Compound	Thermal expansion coefficient $\alpha/10^{-6} \text{ K}^{-1}$			
	Region I (40–530 °C)			
$p\text{O}_2$ / bar	1	0.1	0.01	0.001
$\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}^*$	12.78 ± 0.07	12.79 ± 0.04	13.31 ± 0.13	13.53 ± 0.04
$\text{La}_{0.7}\text{Nd}_{0.1}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	12.78 ± 0.04	13.06 ± 0.04	13.54 ± 0.03	13.07 ± 0.02
$\text{La}_{0.6}\text{Nd}_{0.2}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	12.85 ± 0.04	13.16 ± 0.04	13.73 ± 0.04	13.48 ± 0.03
$\text{La}_{0.5}\text{Nd}_{0.3}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	13.24 ± 0.13	12.74 ± 0.07	12.90 ± 0.05	13.22 ± 0.03
$\text{La}_{0.4}\text{Nd}_{0.4}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	12.32 ± 0.08	12.68 ± 0.07	13.10 ± 0.05	12.58 ± 0.06
$\text{La}_{0.3}\text{Nd}_{0.5}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	12.79 ± 0.04	13.22 ± 0.03	13.73 ± 0.03	13.14 ± 0.03
$\text{La}_{0.2}\text{Nd}_{0.6}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	12.96 ± 0.03	13.22 ± 0.03	13.73 ± 0.03	13.14 ± 0.03
Compound	Region II (530–990 °C)			
$\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}^*$	15.81 ± 0.13	16.03 ± 0.12	19.38 ± 0.16	19.18 ± 0.12
$\text{La}_{0.7}\text{Nd}_{0.1}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	14.83 ± 0.09	15.83 ± 0.15	16.99 ± 0.25	18.28 ± 0.05
$\text{La}_{0.6}\text{Nd}_{0.2}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	15.88 ± 0.14	16.05 ± 0.19	17.24 ± 0.25	18.58 ± 0.34
$\text{La}_{0.5}\text{Nd}_{0.3}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	15.72 ± 0.04	15.58 ± 0.18	16.79 ± 0.27	18.08 ± 0.32
$\text{La}_{0.4}\text{Nd}_{0.4}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	15.40 ± 0.16	15.76 ± 0.17	17.03 ± 0.26	18.10 ± 0.35
$\text{La}_{0.3}\text{Nd}_{0.5}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	14.88 ± 0.09	15.47 ± 0.15	17.10 ± 0.26	18.12 ± 0.30
$\text{La}_{0.2}\text{Nd}_{0.6}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$	14.88 ± 0.09	15.47 ± 0.15	17.10 ± 0.26	18.12 ± 0.30

*Temperature regions for $\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ are I (30–750 °C) and II (750–1000 °C)

Figure 7 Thermal expansion coefficients of $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ ($0 \leq x \leq 0.6$) as a function of Nd concentration for different oxygen partial pressures in temperature regions I (40–530 °C) and

II (530–990 °C). Data for the Nd-free compound in temperature regions I (30–750 °C) and II (750–1000 °C) were taken from the literature [7].

peaks were observed in the DSC curves $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ ($0.1 \leq x \leq 0.6$).

Summary and conclusions

Single-phase perovskites from the series $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ with $0.1 \leq x \leq 0.6$ were synthesized and characterized with respect to crystal structure, chemical composition, thermal expansion behaviour and phase stability. All the investigated compounds of the $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ series crystallize in the orthorhombic space group $Pnma$. High-resolution transmission electron microscopy with energy-dispersive X-ray spectroscopy confirmed the homogeneous distribution of the A-site ions (La^{3+} , Nd^{3+} and Ca^{2+}) on the example of $\text{La}_{0.6}\text{Nd}_{0.2}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$. The thermal expansion coefficients of the materials from the LNCf series are in the

range of $(13\text{--}18) \times 10^{-6} \text{ K}^{-1}$ at 40–990 °C and $1 \times 10^{-3} \leq p\text{O}_2/\text{bar} \leq 1$. Differential scanning calorimetry indicated that substitution of La with Nd in $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ ($0.1 \leq x \leq 0.6$) suppresses the transition from the orthorhombic to the trigonal structural modification, which is observed in the Nd-free compound $\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$.

In future work, the materials from the series $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ will be characterized with regard to oxygen nonstoichiometry and electronic conductivity as a function of temperature and oxygen partial pressure. It would also be of interest to further investigate selected compositions of $\text{La}_{0.8-x}\text{Nd}_x\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ in terms of long-time stability, especially in comparison with the Nd-free perovskite $\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ and state-of-the-art SOC air electrode materials from the $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ series.

Acknowledgements

Financial support by the Austrian Ministry for Transport, Innovation and Technology (bmvit) and AVL List GmbH (Austria) within the programme 'Energieforschung (e!MISSION)' (Project No. 853626) is gratefully acknowledged. Furthermore, the authors would like to thank Valentin Dallago and Sebastian Rohner for laboratory work assistance, Karin Stanglauer for EDX analysis (all Montanuniversität Leoben) and Martina Dienstleder (Graz Centre for Electron Microscopy) for the FIB preparation.

Funding

Open access funding provided by Montanuniversität Leoben.

Compliance with ethical standards

Conflicts of interest There are no conflicts of interest.

Supplementary Information: The online version of this article (<https://doi.org/10.1007/s10853-021-05851-z>) contains supplementary material, which is available to authorized users.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- [1] Chiang Y-M, Birnie D, Kingery WD (1997) Physical Ceramics - Principles for Ceramic Science and Engineering. John Wiley & Sons Inc, New York
- [2] Tilley RJD (2008) Defects in solids. John Wiley & Sons Inc, Hoboken, New Jersey
- [3] Kendall K, Kendall M (2016) High-temperature Solid Oxide Fuel Cells for the 21st Century. Academic Press, Oxford, UK
- [4] Sun C, Hui R, Roller J (2010) Cathode materials for solid oxide fuel cells: a review. *J Solid State Electrochem* 14(7):1125–1144. <https://doi.org/10.1007/s10008-009-0932-0>
- [5] Hansen JB (2015) Solid oxide electrolysis—a key enabling technology for sustainable energy scenarios. *Faraday Discuss* 182:9–48. <https://doi.org/10.1039/C5FD90071A>
- [6] Dwivedi S (2020) Solid oxide fuel cell: Materials for anode, cathode and electrolyte. *Int J Hydrogen Energy* 45(44):23988–24013. <https://doi.org/10.1016/j.ijhydene.2019.11.234>
- [7] Berger C, Bucher E, Windischbacher A, Boese AD, Sitte W (2018) Strontium-free rare earth perovskite ferrites with fast oxygen exchange kinetics: experiment and theory. *J Solid State Chem* 259:57–66. <https://doi.org/10.1016/j.jssc.2017.12.019>
- [8] Marinha D, Dessemond L, Djurado E (2013) Comprehensive review of current developments in IT-SOFCs. *Current Inorg Chem* 3(1):2–22. <https://doi.org/10.2174/1877944111303010003>
- [9] Chen K, Jiang SP (2020) Surface segregation in solid oxide cell oxygen electrodes: Phenomena, mitigation strategies and electrochemical properties. *Electrochem Ener Rev*. <https://doi.org/10.1007/s41918-020-00078-z>
- [10] Develos-Bagarinao K, De Vero J, Kishimoto H, Ishiyama T, Yamaji K, Horita T, Yokokawa H (2019) Oxygen surface exchange properties and surface segregation behavior of nanostructured $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ thin film cathodes. *PCCP* 21(13):7183–7195. doi:<https://doi.org/10.1039/C9CP00606K>
- [11] Koo B, Kim K, Kim JK, Kwon H, Han JW, Jung W (2018) Sr segregation in perovskite oxides: Why it happens and how it exists. *Joule* 2(8):1476–1499. <https://doi.org/10.1016/j.joule.2018.07.016>
- [12] Shannon RD (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica A* 32:751–767. <https://doi.org/10.1107/S0567739476001551>
- [13] Harrison CM, Slater PR, Steinberger-Wilckens R (2020) A review of solid oxide fuel cell cathode materials with respect to their resistance to the effects of chromium poisoning. *Solid State Ionics* 354:115410. <https://doi.org/10.1016/j.ssi.2020.115410>
- [14] Ni N, Cooper SJ, Williams R, Kemen N, McComb DW, Skinner SJ (2016) Degradation of $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.95}(\text{Co}_{0.2}\text{Fe}_{0.8})\text{O}_{3-\delta}$ Solid Oxide Fuel Cell Cathodes at the

- Nanometer Scale and below. ACS Appl Mat Inter 8(27):17360–17370. doi:<https://doi.org/10.1021/acsami.6b05290>
- [15] Schrödl N, Bucher E, Gspan C, Egger A, Ganser C, Teichert C, Hofer F, Sitte W (2016) Phase decomposition in the chromium and silicon poisoned IT-SOFC cathode materials $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ and $\text{La}_2\text{NiO}_{4+\delta}$. Solid State Ionics 288:14–21. <https://doi.org/10.1016/j.ssi.2016.01.006>
- [16] Schrödl N, Egger A, Gspan C, Höschen T, Hofer F, Sitte W (2018) Phase decomposition of $\text{La}_2\text{NiO}_{4+\delta}$ under Cr- and Si-poisoning conditions. Solid State Ionics 322:44–53. <https://doi.org/10.1016/j.ssi.2018.05.002>
- [17] Egger A, Perz M, Bucher E, Gspan C, Sitte W (2019) Effect of microstructure on the degradation of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ electrodes in dry and humid atmospheres. Fuel Cells 19(4):458–471. doi:<https://doi.org/10.1002/fuce.201900006>
- [18] Bucher E, Gspan C, Hofer F, Sitte W (2013) Sulphur poisoning of the SOFC cathode material $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$. Solid State Ionics 238:15–23. <https://doi.org/10.1016/j.ssi.2013.03.007>
- [19] Budiman RA, Liu SS, Bagarinao KD, Ishiyama T, Kishimoto H, Yamaji K, Horita T, Yokokawa H (2019) Determination of factors governing surface composition and degradation of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ electrode under sulfur-contained air. J Electrochem Soc 166(6):F414–F422. doi:<https://doi.org/10.1149/2.0091906jes>
- [20] Bucher E, Berger C, Perz M, Egger A, Schrödl N, Gspan C, Sitte W (2018) Oxygen exchange kinetics of SOFC and SOEC air electrodes affected by long-term changes of surface composition. Paper presented at the 13th European SOFC & SOE Forum 2018, Lucerne, Switzerland,
- [21] Yokokawa H, Sakai N, Horita T, Yamaji K (2009) Impact of impurities on reliability of materials in solid oxide fuel cell (SOFC) stack/modules. In: Vielstich W, Yokokawa H, Gasteiger HA (eds) Handbook of fuel cells—fundamentals, technology and applications, vol 6. John Wiley & Sons, Ltd., pp 979–991
- [22] Berger C, Bucher E, Gspan C, Sitte W (2019) Crystal structure, oxygen nonstoichiometry, and mass and charge transport properties of the Sr-free SOFC/SOEC air electrode material $\text{La}_{0.75}\text{Ca}_{0.25}\text{FeO}_{3-\delta}$. J Solid State Chem 273:92–100. <https://doi.org/10.1016/j.jssc.2019.02.032>
- [23] Berger C, Bucher E, Sitte W (2017) Mass and charge transport properties of $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-\delta}$. Solid State Ionics 299:46–54. <https://doi.org/10.1016/j.ssi.2016.09.015>
- [24] Song J, Ning D, Bouwmeester HJM (2020) Influence of alkaline-earth metal substitution on structure, electrical conductivity and oxygen transport properties of perovskite-type oxides $\text{La}_{0.6}\text{A}_{0.4}\text{FeO}_{3-\delta}$ (A = Ca, Sr and Ba). PCCP. doi:<https://doi.org/10.1039/D0CP00247J>
- [25] Price PM, Rabenberg E, Thomsen D, Mixture ST, Butt DP (2014) Phase transformations in calcium-substituted lanthanum ferrite. J Am Ceram Soc 97(7):2241–2248. <https://doi.org/10.1111/jace.12891>
- [26] Berger C, Bucher E, Gspan C, Menzel A, Sitte W (2017) Impact of SO_2 on the oxygen exchange kinetics of the promising SOFC/SOEC air electrode material $\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$. J Electrochem Soc 164(10):F3008–F3018. doi:<https://doi.org/10.1149/2.0041710jes>
- [27] Bruker AXS Topas V5 (2014) General profile and structure analysis software for powder diffraction data, User's manual. Karlsruhe, Germany
- [28] Paufler P (1995) Young RA (ed.). The Rietveld Method. International Union of Crystallography. Oxford University Press 1993. 298 p. ISBN 0–19–855577–6. Cryst Res Technol 30(4):494–494. doi:<https://doi.org/10.1002/crat.2170300412>
- [29] Vegard L (1921) Die Konstitution der Mischkristalle und die Raumfüllung der Atome. Z Phys 5(1):17–26. <https://doi.org/10.1007/BF01349680>
- [30] Tamura H, Hayashi A, Ueda Y (1996) Phase diagram of $\text{La}_2\text{NiO}_{4+\delta}$ ($0 \leq \delta \leq 0.18$). II. Thermodynamics of excess oxygen, phase transitions ($0.06 \leq \delta \leq 0.11$) and phase segregation ($0.03 \leq \delta \leq 0.06$). Physica C 258(1–2):61–71
- [31] Falcón H, Goeta AE, Punte G, Carbonio RE (1997) Crystal structure refinement and Stability of $\text{LaFe}_x\text{Ni}_{1-x}\text{O}_3$ solid solutions. J Solid State Chem 133(2):379–385. <https://doi.org/10.1006/jssc.1997.7477>
- [32] Takeda T, Kanno R, Kawamoto Y, Takano M, Kawasaki S, Kamiyama T, Izumi F (2000) Metal–semiconductor transition, charge disproportionation, and low-temperature structure of $\text{Ca}_{1-x}\text{Sr}_x\text{FeO}_3$ synthesized under high-oxygen pressure. Solid State Sci 2(7):673–687. [https://doi.org/10.1016/S1293-2558\(00\)01088-8](https://doi.org/10.1016/S1293-2558(00)01088-8)
- [33] Blasco J, García J (1994) Structural, magnetic and electrical properties of $\text{NdNi}_{1-x}\text{Fe}_x\text{O}_3$ and $\text{NdNi}_{1-x}\text{Co}_x\text{O}_3$ systems. J Phys Chem Solids 55(9):843–852. [https://doi.org/10.1016/0022-3697\(94\)90009-4](https://doi.org/10.1016/0022-3697(94)90009-4)
- [34] Serra JM, Vert VB, Betz M, Haanappel VAC, Meulenberg WA, Tietz F (2008) Screening of a-substitution in the system $\text{A}_{0.68}\text{Sr}_{0.3}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ for SOFC Cathodes. J Electrochem Soc 155(2):B207–B214. doi:<https://doi.org/10.1149/1.2818766>
- [35] Sato T, Takagi S, Deledda S, Hauback BC, Orimo S (2016) Extending the applicability of the Goldschmidt tolerance factor to arbitrary ionic compounds. Scientific Reports 6:23592. <https://doi.org/10.1038/srep23592>
- [36] Hung M-H, Rao MVM, Tsai D-S (2007) Microstructures and electrical properties of calcium substituted LaFeO_3 as SOFC

- cathode. *Mater Chem Phys* 101(2–3):297–302. <https://doi.org/10.1016/j.matchemphys.2006.05.008>
- [37] Stadelmann P (2008) Electron Microscopy Software (Java Version) 3.2830U2008. 3.2830U2008 edn., CIME-EPFL Switzerland
- [38] Kharton VV, Yaremchenko AA, Naumovich EN (1999) Research on the electrochemistry of oxygen ion conductors in the former Soviet Union. II. Perovskite-related oxides. *J Solid State Electrochem* 3:303–326
- [39] Minh NQ, Takahashi T (1995) Chapter 4—Electrolyte. In: Takahashi NQM (ed) Science and technology of ceramic fuel cells. Elsevier Science Ltd, Oxford, pp 69–116. doi:<https://doi.org/10.1016/B978-044489568-4/50005-0>
- [40] Hong SJ, Virkar AV (1995) Lattice parameters and densities of rare-earth oxide doped ceria electrolytes. *J Am Ceram Soc* 78(2):433–439

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.