Temperature induced transitions in La$_4$(Co$_{1-x}$Ni$_x$)$_3$O$_{10+\delta}$; oxygen stoichiometry and mobility

Marius Uv Nagell$^a$, Wojciech Andrzej Sławiński$^{a,b}$, Ponniah Vajeeston$^a$, Helmer Fjellvåg$^a$, Anja Olafsen Sjåstad$^{a,b}$

$^a$ Department of Chemistry, Centre for Materials Science and Nanotechnology, University of Oslo, Norway
$^b$ ISIS Facility, Rutherford Appleton Laboratory, Harwell Oxford, Didcot, Oxfordshire OX11 0QX, United Kingdom

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ABSTRACT

We report on the structural properties of the La$_4$(Co$_{1-x}$Ni$_x$)$_3$O$_{10}$ solid solution at and above room temperature based on synchrotron powder diffraction data. The monoclinic $P2_1/a$ structure at ambient conditions transforms via an orthorhombic intermediate to a high temperature $I4/mmm$ tetragonal phase. Significant anisotropic strain causes peak broadening for some Bragg reflections of the monoclinic and orthorhombic phases. Smaller intensity deviations for the tetragonal structure are possibly caused by minor amounts (< 1%) of stacking faults along [001]. La$_2$CoO$_4$ shows oxygen hyperstoichiometry in air, however, in N$_2$ the oxygen stoichiometry is close to 10.00 for all x. Atomistic simulations were performed to evaluate total energies for potential polymorphs; and to calculate energies of formation of oxygen defects in terms of vacancies at apical O-sites towards the rock salt (RS) like layer, and within the perovskite blocks, in addition to interstitial oxygen atoms in the rock salt layers. cNEB simulations were performed for predicting energy barriers for mobility along various diffusion pathways. The barrier is lowest for tetragonal phase. Consistent with reports on La$_2$CoO$_4$ and La$_2$NiO$_4$ also the RP3 phase appears to have interstitial oxygen transport as the governing migration mechanism with a barrier height of around 0.40 eV.

1. Introduction

Unresolved mysteries still remain with respect to fully understand the complex structural and physical properties of La$_4$M$_3$O$_{10}$ (M = Co, Ni) Ruddlesden Popper (RP3) type phases. Of these, La$_4$Ni$_3$O$_{10}$ is attractive for intermediate temperature solid oxide fuel cells (IT-SOFCs) due to appropriate electronic and ionic conductivities [1]. La$_4$Co$_3$O$_{10}$ and La$_4$Ni$_3$O$_{10}$ with transition temperatures between 490 °C [3] and 580 °C [16,17] have received attention as IT-SOFCs [1]. Noteworthy, the corresponding n = 1 (RP1) solid solution La$_2$CoO$_4$ undergoes an orthorhombic-to-tetragonal transition at 490 °C [3]. In contrast, La$_2$NiO$_4$ shows oxygen hyperstoichiometry in air, however, in N$_2$ the oxygen stoichiometry is close to 10.00 for all x. Atomistic simulations were performed to evaluate total energies for potential polymorphs; and to calculate energies of formation of oxygen defects in terms of vacancies at apical O-sites towards the rock salt (RS) like layer, and within the perovskite blocks, in addition to interstitial oxygen atoms in the rock salt layers. cNEB simulations were performed for predicting energy barriers for mobility along various diffusion pathways. The barrier is lowest for tetragonal phase. Consistent with reports on La$_2$CoO$_4$ and La$_2$NiO$_4$ also the RP3 phase appears to have interstitial oxygen transport as the governing migration mechanism with a barrier height of around 0.40 eV.

Based on peak splitting and peak shape. On the other hand, this contrast the findings of Amow et al. for La$_4$(Co$_{1-x}$Ni$_x$)$_3$O$_{10}$ [1], however, their work suffered from inferior diffraction tools. The structure of La$_4$Ni$_3$O$_{10}$ was first reported by Seppänen in space group $Fmmm$ [8]. Additional complexity was reported by Mohan Ram et al. who discovered occasional intergrowth by high resolution electron microscopy [9]. Tkalich et al. concluded from powder neutron diffraction data best fit according to space group $Cmca$ [10], whereas an electron diffraction study by Zhang and Greenblatt gave $Immm$ as the highest symmetric space group compatible with observations [11]. Various other studies are at hand; see [12–15].

The high temperature structural properties, of relevance for several applications, are less explored. Both La$_4$Co$_3$O$_{10}$ and La$_4$Ni$_3$O$_{10}$ undergo structural phase transitions [11,16,17]. For La$_4$Co$_3$O$_{10}$, a tetragonal structure exists above 580 °C [16,17]. For La$_4$Ni$_3$O$_{10}$ the corresponding reported transition temperatures vary considerably between 490 °C [3] to 700 °C [11]. Noteworthy, the corresponding n = 1 (RP1) solid solution phase La$_2$Co$_{1-x}$Ni$_x$O$_4$ undergoes an orthorhombic-to-tetragonal transition between 150 and 350 °C for x = 1.0 and 0.8, and between 350 and 500 °C for x = 0.5 [18]. Both cases relate to octahedral tilts.
The electronic properties depend on Co/Ni composition; La₄Co₃O₁₀ is semiconducting (antiferromagnetic below 12 K), La₄Ni₃O₁₀ is metallic and Pauli paramagnetic. The Co- and Ni-atoms may adjust oxidation states on heterovalent substitutions or by O-defects. This will affect electronic and/or ionic conductivity. Stoichiometric La₄Co₃O₁₀ can be oxidized at ambient conditions by interstitial oxygen atoms (amount δ) entering the tetrahedral voids of the rock salt layer of the RP3 phase. The maximum O-content is La₄Co₃O₁₀.₃₀ [6,17]. This resembles the situation for the La₂NiO₄ mixed oxygen conducting RP1 phase [19]. A noticeable difference is, however, that the oxidation of La₄Co₃O₁₀.ₐₒ₀ takes place without change in average symmetry [17] whereas structural deformations occur for La₄Ni₃O₄, probably triggered by strain relief. The maximum amount of interstitial O-atoms (δ) decreases rapidly with increasing Ni-content and δ is zero for La₄Ni₃O₁₀₊δ which is reasonable since Ni already takes a very high average oxidation number of 2.67. In reducing atmospheres, these RP3 phases may possibly become oxygen deficient with vacancies in the perovskite blocks; however, the published experimental data are sparse and inconsistent. The conductivity mechanism and activation energies for defect formation and oxygen mobility are highly different for vacancy and interstitially mediated migration [20–22]. Extended knowledge on oxygen non-stoichiometry and ion transport is desirable for this solid solution of relevance as IT-SOFC material.

Unlike the situation for vacancy dominated defects in perovskite type oxides, the chemical expansion of RP3 phases with interstitial O-atoms is very moderate, which is important for manufacturing and use of high temperature components without crack formation. A few compounds, like LaCoO₃ [23], undergo electronic spin transitions that add to the chemical expansion. This is the case also for La₄Co₃O₁₀ evidenced by an endothermal anomaly at around 250 °C accompanied by changes in unit cell dimensions and thermal expansion [17,49]. The anomaly in LaCoO₃ is ascribed to a lower to higher spin state transition of Co(III) [24]. For La₄Co₃O₁₀, the mechanism is not understood. The anomaly in La₄Co₃O₁₀₊δ weakens rapidly on increasing δ and vanishes as well at a small 3% substitution of Co by Ni [5].

We focus currently on open issues for La₄(Co₀.₃₃Ni₀.₆₇)O₁₀₊δ at and above room temperature. In particular, we (i) revisit the monoclinic distortion with basis in Rietveld refinements of high-resolution powder synchrotron diffraction data with anisotropic strain broadening as a key parameter; (ii) describe a sequence of temperature induced phase transitions, from monoclinic, via orthorhombic to tetragonal symmetry, refine the tetragonal structure and discuss stacking faults as origin for systematic peak intensity/shape deviations; and (iii) provide oxygen non-stoichiometry data for La₄(Co₀.₃₃Ni₀.₆₇)O₁₀₊δ and describe activation barriers for oxygen ion mobility and transport pathways based on theoretical modeling.

2. Experimental

2.1. Synthesis

Powders of La₄(CoₓNi₁₋ₓ)O₁₀ (x = 0.00, 0.20, 0.33, 0.47, 0.67, 0.80, 0.93, and 1.00) were synthesized using the citric acid method as reported [5–7,17], with La₂O₃ (99.99%, Molycorp), Ni(CH₃COO)₂·4H₂O (≥99.0%, Sigma Aldrich), Co(CH₃COO)₂·4H₂O (reagent grade, Sigma Aldrich), citric acid monohydrate, C₆H₇(OH)(COOH)₂·H₂O (98%, Sigma Aldrich) and HNO₃ (68% WVR Chemicals) as reactants. La₂O₃ was glazed at 800 °C to remove CO and H₂O based species. Exact metal content of Ni(CH₃COO)₂·4H₂O and Co(CH₃COO)₂·4H₂O were determined gravimetrically. After drying overnight at 180 °C and calcination in static air at 450 °C for 24 h, powders were cold pressed and annealed for 24–48 h at 1000–1100 °C in flowing nitrogen (5 N, AGA, x ≤ 0.33) or in static air (x ≥ 0.33). Two or more annealings were done after intermediate grinding and re-pelletizing.

2.2. Powder X-ray (PXRD) and synchrotron X-ray (SRXRD) diffraction

PXRD data for phase analysis were collected on a Bruker D8 Discover with a Lynxeye detector, CuKa₁ radiation, λ = 1.540598 Å. High resolution SRXD data for structure refinements were obtained at the Swiss-Norwegian Beam Lines (SNBL, BM01B), ESRF, Grenoble, using a detector system with six Si(111) analyzer crystals. Monochromatic X-rays were obtained from a channel-cut Si(111) crystal; λ = 0.5049 and 0.5057 Å (two measurement campaigns). Finely crushed powders were filled in 0.5 mm diameter borosilicate capillaries and sealed. Data for the range 2 ≤ 20 ≤ 40.5° were rebinned into step size Δ(2θ) = 0.005°. Rietveld refinements were carried out using the Jana2006 program [25]; 7700 data points, 2657 Bragg reflections, and a maximum of 79 variables were used in the least square refinement.

2.3. High temperature (HT) PXRD studies

HT-PXRD data were collected in the RECX laboratory at the University of Oslo, with a Bruker D8 A25 instrument in reflection mode equipped with a Lynxeye XE detector for high energies, using MoKα radiation and focusing mirror optics. Heating was performed in an Anton Paar HTK1200 furnace with an alumina flat plate sample holder. The selected gas atmospheres corresponded to those during the final synthesis heat treatments (Argon, Aga, 4.6, was used for x ≤ 0.33, flowing and static overpressure; static air for all other samples) to avoid oxidation as a factor of structure change. Data were collected in steps of 100 °C up to 1150 °C between 2θ = 14° and 15.5° in steps of Δ(2θ) = 0.010°; data collection time 16 min. Peak fitting was performed using the program Fityk [26].

High temperature high resolution SRXD (HT-SXRDT) data was collected for finely crushed powders of La₄Ni₁₀O₁₀ and La₄Co₃O₁₀₊δ in 0.5 mm diameter sealed quartz capillaries; wavelength λ = 0.5051 Å at BM01B, ESRF. Data for the tetragonal phase of La₄Ni₁₀O₁₀ at 782 °C were collected for 7 ≤ 20 ≤ 40.5°, rebinned to step size Δ(2θ) = 0.005°, Rietveld refinements were performed with TOPAS [27]; using 6701 data points, 221 Bragg reflections, and a maximum of 21 variables. The background was modelled with a Chebyshev polynomial and peaks shapes by the modified Thompson-Cox-Hastings pseudo-Voigt function. Subsequent to no distance constraints initially, soft restraints were introduced with 1.95 Å as Ni–O bond lengths, and 2.65 Å as La–O bond lengths. The isotropic displacement factors were constrained for the La and Ni atoms. HT-SXRDT data within the range of the electronic transition for La₄Co₃O₁₀₊δ were similarly collected, rebinned and analyzed by the Rietveld method. In addition, variable temperature data were collected of La₄Co₃O₁₀₊δ (Pilatus 2 M pixel detector, Dectris, λ = 0.6969 Å, BM01A, ESRF) for the same temperature region. Data were collected for 10 s (+10 s read out/waiting) during heating at a rate of 10 °C/min up to 600 °C. The 2D images were integrated using Fit2D and rebinned into 1D datasets for 1.8° ≤ 2θ ≤ 49°; step size Δ(2θ) = 0.015°. LaB₆ was used as calibrant.

2.4. Thermal analysis (TGA) and oxygen content

Cerimetric titrations were used to determine average oxidation states and indirectly oxygen contents (δ) at room temperature [5]. The variation in oxygen stoichiometry δ was studied with a combined TGA-DSC Netzsch ST449 F1 Jupiter and with a TGA Netzsch 209 F1 Libra, operating in N₂, synthetic air or O₂ (5 N, Aga); heating and cooling rates 10 °C/min. Pt-Rh samples holders were used for STA 499 F1 Libra whereas Al₂O₃ for 209 F1 Libra. In all cases the same gas was sent at fixed rates over the balance and over the sample, 25 mL/min. In separate experiments, the oxygen stoichiometry (δ) was measured as the weight change relative to reference conditions of 400 and 1000 °C. Equilibrium was considered achieved after 60 min. Background and buoyancy effect corrections were performed using empty sample
Fig. 1. Peak profiles for (117)/(117), (020) and (200) of some selected La$_4$(Co$_{1-x}$Ni$_x$)$_3$O$_{10+\delta}$ samples represented with d-spacing to remove the effect of slightly different wavelengths during the measurement campaigns. The trend shows that the cell height (c) is increasing with increasing Ni content, whereas the in-plane dimensions (a, b) have an interesting jump for the $x = 0.20$ composition. Most interestingly is the clearly split peak of $x = 0.20$ and very flat peak of $x = 0.00$.

holders and identical measurement programs. Importantly, the TGA was used as means to produce samples with specific oxygen compositions, $\delta$. The samples were held at selected $T$, pO$_2$ conditions while carefully monitoring weight differences relative to a reference state.

2.5. Computational details

Total energies were calculated by the projected augmented plane-wave (PAW) implementation of the Vienna ab initio package (VASP) [29,30]. All calculations were made with the PBE [31] exchange correlation functional with Hubbard parameter correction (GGA + $U$), following the rotationally invariant form [32,33]. Effective $U$ values of 5 eV and 5.1 eV (with $J = 1$ eV) were used for Co-$d$ and Ni-$d$ states, respectively. We have systematically studied different $U$-parameters for several Ni and Co based compounds in our DFTBD data base and we found that 5.0 for Co and 5.1 for Ni gives better structural parameters and electronic structure of the most of the experimentally known systems. Hence, we fixed these parameters for all Ni and Co based systems. Moreover, the calculated lattice parameters are good agreement with the experimental findings. Ground-state geometries were determined by minimizing stresses and Hellman-Feynman forces using the conjugate-gradient algorithm with force convergence $< 10^{-6}$ eV Å$^{-1}$. Brillouin zone integration was performed with a Gaussian broadening of 0.1 eV during all relaxations. 512 k points in the whole Brillouin zone for the structure with a 600 eV plane-wave cutoff were found sufficient to ensure required accuracy. The k-points were generated using the Monkhorst-Pack method with a grid size of $8 \times 8 \times 8$ for structural optimization. A similar density of k-points and energy cutoffs were used to estimate total energy as a function of volume. Iterative relaxation of atomic positions was stopped when the change in total energy between successive steps was $< 1$ meV/cell. The oxygen diffusion barrier for the La$_4$Co$_{10}$O$_{12}$ phase was investigated with the cNEB method in a supercell approach [34,35]. A supercell with $2 \times 2 \times 1$ dimensions was used to ensure that the atoms are separated from their periodic image, providing a more accurate answer for the activation barrier in the dilute limit. The formation energy is calculated by using periodically repeated finite-sized supercells, artificial long-range elastic and electrostatic interactions between the periodic defect images can be introduced. However, when supercells of sufficiently large sizes are used, the interaction of the defect with the spurious periodic images and with the jellium background will become negligible. The formation energy of O defect is calculated in the following manner.

$$\Delta H_{\text{tot}}^{\text{def}}(O) = \left(E_{\text{tot}}^{\text{def}} - E_{\text{tot}}^{\text{bulk}}\right) + \sum_i n_i \mu_i$$

where $E_{\text{tot}}^{\text{def}}$ is the total energy of the supercell containing O defect and $E_{\text{tot}}^{\text{bulk}}$ is the total energy of the ideal supercell. $\mu_i$ indicates the number of atoms of type $i$ that have been added to ($n_i > 0$) or removed from ($n_i < 0$) the supercell when the defect is created. The $\mu_i$ is the corresponding chemical potentials of the defect species (O atom) that determine the flow of atoms between the atomic reservoirs and the host crystal. To determine the minimum energy path (MEP) through the climbing Nudged Elastic Band (cNEB) method, six replicas of the system were created, in each of which the diffusing O atom was moved by equidistant steps to positions between the initial and final states for the path obtained by linear interpolation.

3. Results and discussion

3.1. Space group ambiguity for La$_4$(Co$_{1-x}$Ni$_x$)$_3$O$_{10+\delta}$ at room temperature

The assignment of La$_4$(Co$_{1-x}$Ni$_x$)$_3$O$_{10+\delta}$, Nd$_4$Co$_{10}$O$_{12+\delta}$ and Nd$_4$Ni$_{10}$O$_{12+\delta}$ to space group P2$_1$/a (14) [5–7] is based on broadening of a subset of (hkl) diffraction peaks with high l-indices in high-resolution powder X-ray diffraction patterns and a few additional peaks in powder neutron diffraction patterns. Detailed insight in oxygen defects and structure in relation to temperature induced phase transitions, electronic transitions, as well as oxygen transport mechanism is based on the crystal symmetry. Note that low resolution diffraction data cannot give any conclusive answer. Our high resolution SRXRD data show for a large number of samples with different O- and Ni-content and at different temperatures, that (117) is broad and flat for Co-rich samples, see Fig. 1. A few samples show a clearly split (117), Fig. 1, which is token of evidence for at least two Bragg peak components consistent with a monoclinic distortion ($\beta \neq 90^\circ$) and importantly, for a peak shape that cannot be modelled by just strain or particle size broadening alone.

Based on systematic refinements, exploring orthorhombic, monoclinic and triclinic cells, with and without anisotropic strain broadening [36], the present statistical analysis supports the P2$_1$/a (14) description for La$_4$Co$_{10}$O$_{12+\delta}$. A summary of considered crystal structure models and refined parameters is presented in supplementary material (Tables S1 and S2). The (117) pairs of peaks become less broad, with less distinct flat structures, for higher Ni-contents. In all cases a significant anisotropic peak broadening is present. We conclude that P2$_1$/a (14) is appropriate also for Ni-rich samples, La$_4$Ni$_{10}$O$_{12+\delta}$ inclusion. Comparison of fitted patterns using anisotropic strain broadening in monoclinic (P2$_1$/a; 14) and orthorhombic (Bmeb; 64) descriptions are given in Fig. 2. Examples of Rietveld refinements of full patterns are given in supplementary material (Fig. S1).

3.2. Temperature induced structural transitions and phase diagram

The monoclinic La$_4$(Co$_{1-x}$Ni$_x$)$_3$O$_{10+\delta}$ samples turn tetragonal on heating. The temperature induced changes in the diffraction patterns are visualized in Fig. 3 in terms of 2D-plots showing the (117)/(117), (020), and (200) Bragg peaks. The transition may take place via an intermediate orthorhombic phase. The orthorhombic to tetragonal transition can be evaluated in terms of the orthorhombic splitting, $\Delta d = d_{(020)} - d_{(200)}$, however, it is difficult to trace the monoclinic to orthorhombic transition. These transitions appear as continuous second order phase transitions with no thermal anomalies visible in DSC data. The variations in $\Delta d$ are evident from Figs. 3 and 4 (lower part). Peak profiles from home laboratory data are given in Fig. S2.

The full width at half maximum (FWHM) of the composite (117)/(117) peak is controlled by the departure of $\beta$ from 90° in addition to anisotropic strain broadening that is possibly ($\gamma, \delta$) dependent. Fig. 4 shows the FWHM$_{(117)}$/FWHM$_{(020)}$ ratio which in the strain free case
should equal one for the orthorhombic and tetragonal structures. Owing to strain this ratio departs from one even at the highest temperatures where the structure is clearly tetragonal, Fig. 4. We therefore conclude that the monoclinic to orthorhombic transition is completed when the FWHM-ratio levels out. Such a constant level is achieved between 400 and 700 °C, however, exact transition temperatures cannot be given, Fig. 4 upper graph. In conclusion the data supports a temperature induced monoclinic to orthorhombic to tetragonal phase transitions for the entire RP3 solid solution.

The temperature for the orthorhombic to tetragonal phase transition decreases from around 1000 °C for La$_4$Co$_3$O$_{10.01}$ to 700 °C for La$_4$Ni$_3$O$_{9.97}$, Fig. 4, higher than earlier reported, 567 °C [17] and 485 °C [3], respectively. The discrepancies are probably rooted in the resolution of the diffraction data [17] and in the methods to determine transition temperatures. A complete phase diagram is proposed in Fig. 4. We have no evidence for major changes in transition temperature with oxygen stoichiometry, δ. In conclusion, the crystal structure of La$_4$(Co$_{1-x}$Ni$_x$)$_3$O$_{10+δ}$ is just moderately influenced by the substitution level (x).
The tetragonal structure of La$_4$Ni$_3$O$_{9.97}$ at 782 °C, space group I4/mmm (139), was refined by Rietveld analysis of high temperature SRXRD data, see fitted patterns in Fig. 5. The structure, Fig. S3, is identical to that of Sr$_4$Ti$_3$O$_{10}$ [37]. Refined crystallographic parameters are given in Table 1, along with interatomic Ni–O and La–O distances. Careful inspection of the Rietveld fit shows a few deviations between observed and calculated intensities; some Bragg peaks are asymmetric on the high angle side [(1 0 7); (1 1 14); (2 0 14)], some have broad additional intensity contributions [e.g. (1 0 9)], some are very sharp [e.g. (2 0 0)]. Considerations of lower symmetry structures, tetragonal and orthorhombic ones with or without expanded ab-plane, were unsuccessful. Furthermore, evaluations according to 38 different possible irreducible representations generated by ISODISTORT [38] did not provide significant improvements. One possible explanation for the intensity differences, which appear for (all) studied tetragonal phases independent of composition x, is stacking faults. Earlier HRTEM studies have revealed minor amounts of stacking faults in RP3 phases [9]. Test calculations where 1/2–1/2 stacking faults are randomly distributed along [001] did effect the relevant reflections and support the hypothesis. A (½, ½) shift would correspond to a segment of Dion-Jacobsen type structure, most likely being non-stoichiometric in nature owing to removal of 50% of the La-atoms at the 2D-defect interface. Also (0, ½) shift was considered, providing a positive effect on deviating intensity profiles. A more detailed analysis is required before this issue can be settled.

The interatomic distances in Table 1 show that the La–O separations are similar for the monoclinic from [5,6] and tetragonal structures. In both cases we observe a shortening of the La–O distances in the La–O rock salt layer compared to those for the perovskite block. The Ni–O distances for the octahedra in the triple perovskite block are quite close to the Ni–O distances in the Ni(III) based LaNiO$_3$ perovskite. Note that the heavy La and Co/Ni elements imply that O-coordinates are burdened with uncertainty. Soft distance restraints were used (see experimental) to assure realistic coordination within counting statistics.

The relative stability of possible symmetry modifications was obtained by simulations for Ba$_2$Zr$_3$S$_{10}$ (Pnmm; 69), Sr$_4$Ti$_3$O$_{10}$ (I4/mmm; 139), La$_4$Co$_3$O$_{10}$ (C2/m; 12), La$_4$Ni$_3$O$_{10}$ (Cmce; 64), and Nd$_4$Co$_3$O$_{10}$ (P2$_1$/a; 14) type arrangements. The total energy versus unit cell volume for potential polymorphs of La$_4$Co$_3$O$_{10}$ and La$_4$Ni$_3$O$_{10}$ are shown in Fig. 6 and Fig. S4, respectively. In both cases the orthorhombic structure is lowest in energy. The next energetically favorable phases are monoclinic (C2/m; 12 and P2$_1$/a; 14) and tetragonal (I4/mmm; 139). For all phases the calculated structural parameters and atomic positions are in good accordance with the experimental findings. At the equilibrium volume the energy difference between these four phases is indeed very small. This closeness in energy suggests that the relative appearance of these modifications will be sensitive to, and easily affected by external factors such as temperature, pressure and remnant lattice strain. The total energy calculations are done for an anticipated ferromagnetic ground state. According to variable temperature magnetization data and reported powder neutron diffraction data antiferromagnetism prevails at low temperature for La$_4$Co$_3$O$_{10}$. This oversimplification in the DFT modeling may give rise to differences in energies of some hundreds meV/f.u. With this in mind, the experimental and theoretical data are well in line for La$_4$Co$_3$O$_{10}$.
important to evaluate whether the dominant conduction pathway with the situation for the perovskite analogues LaCoO₃ and LaNiO₃ actually involves interstitial sites in the RS-layers. Recent MD and DFT studies of La₂CoO₄ and La₂NiO₄ concluded that an oxygen interstitiality mechanism is dominant [22,44,45]. To our knowledge no similar simulation studies are at hand for the RP₃ phases.

For oxygen-deficient materials ionic transport is often mediated via a vacancy hopping mechanism [46]. However, since the RS layer of the RP₃-structure allows interstitial O-atoms and thereby interstitial 2D-diffusion, this may dominate the currently studied materials. For La₂CoO₄ an interstitiality migration path is reported where an apical oxygen atom in moved out of the La–O plane and into the nearest available interstitial site, whilst an interstitial O-atom replaces the displaced apical oxygen [22]. According to Kushima et al. [22] this ion migration is enabled by cooperative tilting–untilting of CoO₆ octahedra. An accurate determination of the location and the mobility of different oxygen defects were currently done by means of cNEB computations. Owing to extensive computing requirements for supercell simulations, these studies were limited to a few polymorphs of La₄Co₃O₁₀. To reduce computational costs, we calculated the formation energy of O-defects in the different sites and the defect formation energy as described in [47,48]. The O-defects are of two categories; vacancies (see Fig. 9, labelled 1 to 7) and interstitial oxygen atoms (8 and 9) in tetrahedral voids in the rock-salt layer. The simulated configurations are shown in Fig. 10 and calculated formation energies are listed in Table 2. Compared to RP₁, there are more sites for O-vacancies in the RP₃ structure; i.e. apical O-atoms in the octahedra neighboring the RS-layers; and various O-atoms at vertices of octahedra connected by corner sharing. The calculated defect formation energy suggests that O-vacancies within the perovskite layer are much more favorable than in connection with the rock-salt layers (see Table S3). This finding is consistent with the recent in situ neutron diffraction study by Tomkiewicz et al., where the oxygen vacancies of RP₁, RP₂, and RP₃ phases were almost exclusively located within perovskite layers with only minimal vacancy concentration in the rock-salt layer [43]. It should be noted that insertion of O-ions in the interstitial region of the rock-salt layer is much more energetically favorable than the creation of O-vacancies.

Barrier heights were obtained from the cNEB simulations for different polymorphs and oxygen diffusion pathways, see Table 2. The magnitude of the barrier (see Fig. 10) indicates that any excess O in the rock-salt layers will be transported much more easily than by any O-vacancy mediated route. The second best situation is oxygen transport between sites 1 and 2. It is important to note that (in Fmmm) even though both 1–4 and 2–3 has similar barrier heights the jumping distance for 2 to 3 is 0.7 Å less than the 1 to 4 distance. As a result, the O transport is much easier for 2–3 (along the perovskite layer) than 1–4.
as shown by Table 2, the calculated O diffusion barrier heights indicate that the O transport will be faster in the high temperature polymorph than in any lower symmetry polymorph. It should be noted that earlier MD calculations for Pr2NiO4+δ predicted that oxygen hyperstoichiometry can lead to a “stiffening” of the structure and increased migration barrier for oxygen interstitials [20].

4. Conclusion

This comprehensive study of the La₄(Co₁₋ₓNix)₃O₁₀₊δ has provided new pieces of essential information. The room temperature crystal structure is slightly monoclinically distorted throughout the entire solid solution, however, an additional anisotropic strain broadening makes the analyses complicated. Based on the temperature dependence of the (117) peak broadening and the (200)–(020) peak splitting, transitions temperatures to an intermediate orthorhombic and to a high temperature tetragonal modification are determined. A striking aspect with the powder diffraction patterns of the tetragonal phases (I4/mmm) is a slight intensity mismatch for certain Bragg reflections. A number of possible explanations have been scrutinized. In conclusion it appears that minor amounts (< 1%) of stacking faults indeed would explain the observed intensity discrepancies. From an application point of view, the current study provides important variable temperature crystal structure data for materials of relevance for use in IT-SOFC. In this respect, a more detailed insight into the oxygen defect situation of the ruling high temperature structures is provided. Based on nudged elastic band calculations, we compare defect formation energies as well as activation barriers for oxygen mobility. Formation of interstitial O-defects in the rock salt layer is clearly favored relative to oxygen vacancies.

![Fig. 7. a) TGA/DSC curves for La₄(Co₁₋ₓNix)₃O₁₀₊δ during continuous heating at synthesis conditions and b) TG curves of La₄Co₃O₁₀₊δ (x = 0.00) and La₄Ni₃O₁₀₊δ (x = 1.00) from continuous heating experiments supplemented with data points from 20 h equilibrium experiments in air. TG data are given in terms of oxygen content (δ). The point with a ring (left figure) indicates that La₄Co₃O₁₀ had started to oxidize into LaCoO₃ and La₂O₃.](image)

![Fig. 8. Results from 20 h equilibrium experiments in two different atmospheres; left N₂ and right air. For the points with rings (left) La₄Ni₃O₁₀ had started to slowly decompose to La₂NiO₄ and NiO, whereas (right) of La₄Co₃O₁₀ had started oxidizing into LaCoO₃ and La₂O₃.](image)

![Fig. 9. Crystal structure of La₄Co₃O₁₀ in monoclinic (C2/m; 12) with perovskite (PS) and rock-salt (RS) layers. Computed O vacancy (marked as 1 to 7) and O interstitial (marked as 8 and 9) formation energies are highlighted with arrows and number. Legend for type of atom is given on the illustration.](image)
Among the various possible sites for O-vacancies, those inside the perovskite slabs of the RP3 structure are most favorable. The activation barriers for migration are lowest for the high symmetry modifications that actually are the ones being stable at the relevant high temperature conditions.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.ssi.2017.04.006.

Table 2
Calculated oxygen defect/interstitial formation energies, \( E_{\text{form}} \), in eV, and oxygen diffusion barrier heights (in eV) for different possible O sites in the La_{4}Co_{3}O_{10} polymorphs.

<table>
<thead>
<tr>
<th>O site</th>
<th>( E_{\text{form}} ) (in eV)</th>
<th>O-sites. Transport between</th>
<th>Barrier height (in eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C2/m</td>
<td>Cmce</td>
<td>Fmmm</td>
</tr>
<tr>
<td>1</td>
<td>5.4</td>
<td>5.5</td>
<td>5.1</td>
</tr>
<tr>
<td>2</td>
<td>4.0</td>
<td>4.2</td>
<td>3.9</td>
</tr>
<tr>
<td>3</td>
<td>4.0</td>
<td>4.2</td>
<td>3.9</td>
</tr>
<tr>
<td>4</td>
<td>5.2</td>
<td>5.3</td>
<td>5.1</td>
</tr>
<tr>
<td>5</td>
<td>4.0</td>
<td>4.2</td>
<td>3.9</td>
</tr>
<tr>
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<td>3.9</td>
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<tr>
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<td>3.9</td>
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<tr>
<td>8</td>
<td>2.5</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>9</td>
<td>2.6</td>
<td>2.4</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Among the various possible sites for O-vacancies, those inside the perovskite slabs of the RP3 structure are most favorable. The activation barriers for migration are lowest for the high symmetry modifications that actually are the ones being stable at the relevant high temperature conditions.

Acknowledgements

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References

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