Solid State Ionics 305 (2017) 7–15

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Temperature induced transitions in $La_4(Co_{1-x}Ni_x)_3O_{10+\delta}$; oxygen stoichiometry and mobility

Marius Uv Nagell[a], Wojciech Andrzej Sławiński[a,b], Ponniah Vajeeston[a], Helmer Fjellvåg[a], Anja Olafsen Sjåstad[a,*]

[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

ARTICLE INFO

Keywords:
Crystal structure
Synchrotron XRD
Ruddlesden-Popper
SOFC

ABSTRACT

We report on the structural properties of the $La_4(Co_{1-x}Ni_x)_3O_{10}$ 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]. $La_4Co_3O_{10}$ 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_2CoO_4 and La_2NiO_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 $La_4M_3O_{10}$ (M = Co, Ni) Ruddlesden Popper (RP3) type phases. Of these, $La_4Ni_3O_{10}$ is attractive for intermediate temperature solid oxide fuel cells (IT-SOFCs) due to appropriate electronic and ionic conductivities [1–4]. Substitution of cobalt improves the catalytic performance for cathodic oxygen reduction and also the $La_4(Co_{1-x}Ni_x)_3O_{10}$ solid solution has received attention as IT-SOFCs [1–4].

Detailed insight into structural properties, thermal expansion, and phase transitions is a required basis for understanding electronic properties and ionic transport. We have reported that the $La_4(Co_{1-x}Ni_x)_3O_{10}$ solid solution takes a slightly deformed monoclinic unit cell at room temperature; space group $P2_1/a$ [5], however, ambiguities concerning the space group exist in the literature. Our studies combined powder neutron with X-ray diffraction to benefit from strong scattering contrast for the lighter O-atoms. The $P2_1/a$ description is in line with high resolution powder synchrotron diffraction data for $La_4Co_3O_{10}$, $Nd_4Co_3O_{10}$ and $Nd_4Ni_3O_{10}$ [5–7] based on peak splitting and peak shape. On the other hand, this contrast the findings of Amow et al. for $La_4(Co_{1-x}Ni_x)_3O_{10}$ [1], however, their work suffered from inferior diffraction tools. The structure of $La_4Ni_3O_{10}$ 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 *Imm2* 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 $La_4Co_3O_{10}$ and $La_4Ni_3O_{10}$ undergo structural phase transitions [11,16,17]. For $La_4Co_3O_{10}$, a tetragonal structure exists above 580 °C [16,17]. For $La_4Ni_3O_{10}$ the corresponding reported transition temperatures vary considerably between 490 °C [3] to 700 °C [11]. Noteworthy, the corresponding n = 1 (RP1) solid solution phase $La_2Co_{1-x}Ni_xO_4$ 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.

---

* Corresponding author
E-mail address: a.o.sjastad@kjemi.uio.no (A.O. Sjåstad).

http://dx.doi.org/10.1016/j.ssi.2017.04.006
Received 13 November 2016; Received in revised form 3 March 2017; Accepted 7 April 2017

The electronic properties depend on Co/Ni composition; $La_4Co_3O_{10}$ is semiconducting (antiferromagnetic below 12 K), $La_4Ni_3O_{10}$ 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 $La_4Co_3O_{10}$ 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 $La_4Co_3O_{10.30}$ [6,17]. This resembles the situation for the La_2NiO_4 mixed oxygen conducting RP1 phase [19]. A noticeable difference is, however, that the oxidation of $La_4Co_3O_{10.00}$ takes place without change in average symmetry [17] whereas structural deformations occur for La_2NiO_4, probably triggered by strain relief. The maximum amount of interstitial O-atoms (δ) decreases rapidly with increasing Ni-content and δ is zero for $La_4Ni_3O_{10+\delta}$ 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 interstitialcy 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 $LaCoO_3$ [23], undergo electronic spin transitions that add to the chemical expansion. This is the case also for $La_4Co_3O_{10}$ evidenced by an endothermal anomaly at around 250 °C accompanied by changes in unit cell dimensions and thermal expansion [17,49]. The anomaly in $LaCoO_3$ is ascribed to a lower to higher spin state transition of Co(III) [24]. For $La_4Co_3O_{10}$ the mechanism is not understood. The anomaly in $La_4Co_3O_{10+\delta}$ 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 $La_4(Co_{1-x}Ni_x)_3O_{10+\delta}$ 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 $La_4(Co_{1-x}Ni_x)_3O_{10+\delta}$ and describe activation barriers for oxygen ion mobility and transport pathways based on theoretical modeling.

2. Experimental

2.1. Synthesis

Powders of $La_4(Co_{1-x}Ni_x)_3O_{10}$ (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 La_2O_3 (99.99%, Molycorp), $Ni(CH_3COO)_2{\cdot}4H_2O$ (≥ 99.0%, Sigma Aldrich), $Co(CH_3COO)_2{\cdot}4H_2O$ (reagent grade, Sigma Aldrich), citric acid monohydrate, $C_3H_4(OH)(COOH)_3{\cdot}H_2O$ (98%, Sigma Aldrich) and HNO_3 (68% VWR Chemicals) as reactants. La_2O_3 was glowed at 800 °C to remove CO_2 and H_2O based species. Exact metal content of $Ni(CH_3COO)_2{\cdot}4H_2O$ and $Co(CH_3COO)_2{\cdot}4H_2O$ 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, $x \leq 0.33$) or in static air ($x \geq 0.33$). 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, $CuK\alpha_1$ radiation $\lambda = 1.540598$ Å. High resolution SRXRD 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; $\lambda = 0.5049$ 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 $2 \leq 2\theta \leq 40.5°$ were rebinned into step size $\Delta(2\theta) = 0.005°$. 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 Mo*Kα* 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 $x \leq 0.33$, 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 $2\theta = 14°$ and 15.5° in steps of $\Delta(2\theta) = 0.010°$; data collection time 16 min. Peak fitting was performed using the program Fityk [26].

High temperature high resolution SRXD (HT-SXRD) data was collected for finely crushed powders of $La_4Ni_3O_{10}$ and $La_4Co_3O_{10+\delta}$ in 0.5 mm diameter sealed quartz capillaries; wavelength $\lambda = 0.5051$ Å at BM01B, ESRF. Data for the tetragonal phase of $La_4Ni_3O_{10}$ at 782 °C were collected for $7 \leq 2\theta \leq 40.5°$, rebinned to step size $\Delta(2\theta) = 0.005°$. 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 restraints 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-SXRD data within the range of the electronic transition for $La_4Co_3O_{10+\delta}$ were similarly collected, rebinned and analyzed by the Rietveld method. In addition, variable temperature data were collected of $La_4Co_3O_{10+\delta}$ (Pilatus 2 M pixel detector, Dectris, $\lambda = 0.6969$ 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 $1.8° \leq 2\theta \leq 49°$; step size $\Delta(2\theta) = 0.015°$. LaB_6 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 STA 449 F1 Jupiter and with a TGA Netzsch 209 F1 Libra, operating in N_2, synthetic air or O_2 (5 N, Aga); heating and cooling rates 10 °C/min. Pt-Rh samples holders were used for STA 499 F1 Jupiter whereas Al_2O_3 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