Direct Syntheses of Mixed Ion and Electronic Conductors La$_4$Ni$_3$O$_{10}$ and La$_3$Ni$_2$O$_7$ from Nanosized Coprecipitates

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The (La−Ni−O) binary oxide system forms a series of compounds with the general formula La$_{n+1}$Ni$_n$O$_{3n+1}$ whose structures are described by stacking along the *c*-axis of *n* finite LaNiO$_3$ perovskite layers separated by LaO rocksalt-like layers[1] and are similar to the Ruddlesden−Popper (RP) series.[2] As a consequence of their layered framework, the RP phases can accommodate a range of non-stoichiometries. Changes in the La:Ni ratio for the series can lead to different ionic and electronic behaviors. For example, the hyper-stoichiometric compound La$_2$NiO$_{4+\delta}$ (*n* = 1) possesses relatively large oxide-ion conductivity coupled with reasonable electronic conductivity at 700 °C (ca. 70 S cm^{-1} for the latter property).[3−5] In contrast, the slightly oxygen deficient *n* = 2 and *n* = 3 compounds (La$_3$Ni$_2$O$_{7-\delta}$ and La$_4$Ni$_3$O$_{10-\delta}$, respectively) are expected to possess a good balance of both ionic and electronic conductivity because of the increasing number of perovskite layers[3] (the latter property has been measured at 700 °C to be ca. 60 and 95 S cm^{-1}, respectively).[3] As the higher-order RP phases (*n* > 1) also exhibit good long-term stability,[3] they are potentially more suitable than the *n* = 1 compound as porous oxide-ion and electronic conducting cathode materials in solid oxide fuel cell (SOFC) devices.[6]

Multilayered RP nickelate phases were first reported by Wold and Arnott in 1959.[7] However, it was only as recently as 1994 that totally phase pure La$_4$Ni$_3$O$_{10}$ (*n* = 3) was successfully prepared by Sreedhar et al.[8] The same year, single phase La$_3$Ni$_2$O$_7$ (*n* = 2) was first reported by Zhang and Greenblatt.[9] The reason for the delay between these papers may be because the higher-order (La−Ni−O) RP phases (*n* > 1) are difficult to synthesize directly, as they proceed via the initial formation of intermediate phases such as La$_2$NiO$_4$ (*n* = 1), which then undergo further reactions.

To date, several different synthetic methods have been used to make (La−Ni−O) RP phases, including solid-state routes,[10,11] nitrate and citrate routes,[9,11,12] and Pechini routes.[3] However, these methods usually require multiple steps and lengthy processing times and are energy intensive. For example, Zhang and Greenblatt synthesized La$_4$Ni$_3$O$_{10}$ by heating the corresponding metal oxide powders at 1100 °C over 4−5 days with intermittent regrinding (homogenization) steps.[12] The large effort and time required to make such complex binary or higher phases can effectively be considered as a bottleneck to their purification, identification, and ultimately, their fundamental property measurement. Thus, if we are to discover new complex phases considerably faster in the future, we will ideally need to make them in high purity via more efficient/rapid synthetic routes and in fewer steps.

Continuous hydrothermal flow synthesis (CHFS) methods are increasingly being applied in the direct or more efficient manufacture of important technological nanoceramics or coprecipitates (the process is briefly described herein and in cited papers).[13] By varying the CHFS process conditions, we can achieve some control over particle properties and manufacture complex nanomaterials under relatively mild temperatures in a crystalline form. Examples include lithium-battery materials,[14] photocatalysts,[15] bioceramics,[13] ferroelectric materials,[16] superconductors,[17] etc. In the present work, several coprecipitates of lanthanum and nickel hydroxides were prepared with different La:Ni ratios in a CHFS system. These coprecipitates were subsequently heat-treated in air (in the corresponding La:Ni ratios) for the direct syntheses of phase-pure La$_4$Ni$_3$O$_{10}$ and La$_3$Ni$_2$O$_7$, respectively.

Metal hydroxide coprecipitate precursor slurries (see Figure 1) with La:Ni molar ratios of 4:3 and 3:2, respectively, were manufactured using a three-pump CHFS system with a flow rate of 20 mL/min for the superheated water feed

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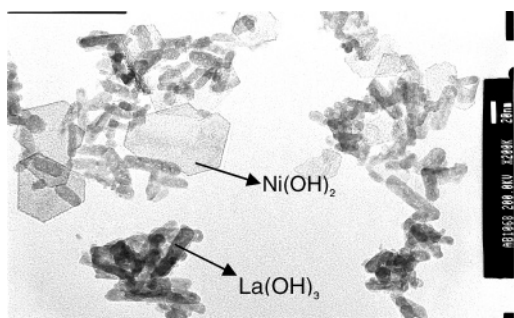
Figure 1. Transmission electron micrograph of the "as-prepared" metal hydroxide coprecipitate nanopowder with a 4:3 La:Ni ratio, made in the continuous hydrothermal flow synthesis system (bar = 20 nm).
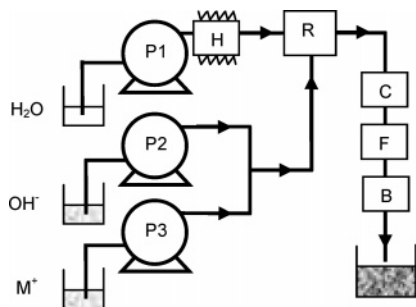

Figure 2. Scheme of the continuous hydrothermal flow system. Key: P = pump, C = cooling, F = filter, B = back-pressure regulator, R = reactor, and H = heater.

Figure 3. (a) XRD patterns of powder made by heat treatment of the La and Ni hydroxide coprecipitate with a 4:3 La:Ni ratio at 1075 °C in air for 1 h. Phase-pure (b) $La_4Ni_3O_{10}$ and (c) $La_3Ni_2O_7$ made from 12 h heat treatment in air of the 4:3 and 3:2 La:Ni ratio coprecipitates at 1075 and 1150 °C, respectively.

and 10 mL/min for the other solutions (Figure 2). Concentrations used herein were 0.1 and 1 M for the metal ion and KOH solutions, respectively. This gave a pH of 14 at the mixing Tee for metal salt/KOH (before it meets superheated water) and at the oulet of the backpressure regulator. The design and operation of the hydrothermal system, is described elsewhere[13] (see the Supporting Information for brief details). Samples CP4:3 and CP3:2 correspond to the coprecipitates made in the CHFS system with 4:3 and 3:2 La:Ni molar ratios, respectively.

Samples CP4:3 and CP3:2 were characterized by X-ray powder diffraction (XRD), which suggested a mixture of lanthanum and nickel hydroxide had formed in both cases (see the Supporting Information, Figure S1). Particle morphology for CP4:3 was evaluated using transmission electron microscopy (TEM), revealing hexagonal nickel hydroxide plates of ca. 80 nm in diameter that were intimately mixed with ca. 40×10 nm lanthanum hydroxide rods (Figure 1). Sample CP3:2 appeared very similar to CP4:3 under TEM investigation. The BET surface areas of samples CP4:3 and CP3:2 were found to be 82 and 74 m^2 g^{-1}, respectively.

Taking into account previous literature[8] detailing the temperatures at which the target phases ($La_4Ni_3O_{10}$ and $La_3Ni_2O_7$) are known to form, the coprecipitates CP4:3 and CP3:2 were heated at 1075 and 1150 °C, respectively, for a relatively short period of only 1 h each. The treatments yielded a mixture of $La_4Ni_3O_{10}$ and La_2NiO_4 for the former sample (Figure 3a) and a mixture of $La_3Ni_2O_7$ and La_2NiO_4 for the latter (see the Supporting Information, Figure S2).

Although unreacted NiO was not observed in the XRD patterns for the 1 h heat-treated samples, it can be assumed that on balance of mass, NiO is present but shielded by the mixed phases. This was further implied when the same "as-
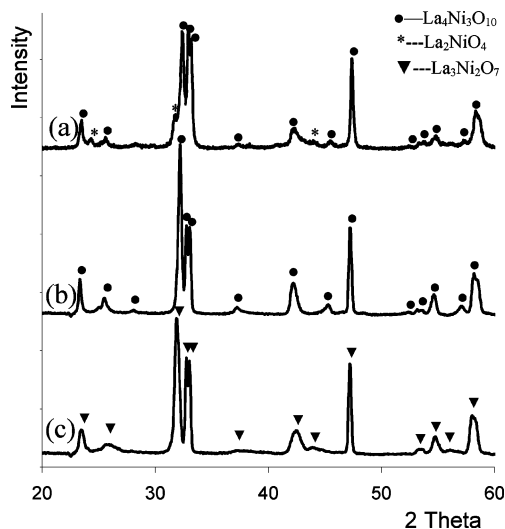
prepared" powders were heat treated for 12 h to give phase-pure $La_4Ni_3O_{10}$ (Figure 3b) and $La_3Ni_2O_7$ (Figure 3c), respectively (hereafter, these products are referred to HT4:3 and HT3:2, respectively). This result is highly significant, as to the best of our knowledge, this is the fastest and first reported direct synthesis of such materials from any precursor.

We speculated that the successful direct syntheses of HT4:3 and HT3:2, respectively, (not requiring any regrinding steps during syntheses) was due to the high intimacy of mixing achieved between the respective metal hydroxides for the initial coprecipitates (made in the CHFS system), which facilitated good mass transfer during the subsequent heat treatments to give phase pure products after 12 h. To validate our hypothesis, we separately prepared slurries of lanthanum hydroxide nanoparticles and nickel hydroxide nanoparticles in the CHFS system and then mixed them in a beaker at the appropriate 4:3 and 3:2 metal ratios, respectively, with ultrasonication and freeze drying (see the Supporting Information for details of the nanoparticle slurry mixing method). The dried mixtures were then subjected to a heat treatment for 12 h that was identical to those previously used for the syntheses of the corresponding samples HT4:3 and HT3:2. XRD patterns of the heat-treated products suggested that only a mixture of La_2NiO_4 and La_2O_3 were formed in both cases (see the Supporting Information, Figure S3), rather than the respective target phases. This reaffirmed our hypothesis that the high intimacy of mixing between the component hydroxides (and possibly small particle size) in the coprecipitates made in the CHFS system facilitated direct and phase pure syntheses of $La_4Ni_3O_{10}$ and $La_3Ni_2O_7$, respectively. Compared to more conventional room-temperature batch coprecipitation syntheses, where several phases can be formed at different times during the reaction, the CHFS method ensures both phases are simultaneously formed and intimately mixed. This allows us to overcome limitations of insufficient mass transfer that would normally exist for less homogeneous nanoparticle mixtures.

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Table 1. Refined Unit-Cell Parameters (nm, by XRD) and Oxygen Hyperstoichiometry/Deficiency Parameters, δ, for $La_{n+1}Ni_nO_{3n+1}$ (estimated standard deviations are given in parentheses)

n	a (nm)	b (nm)	c (nm)	space group	δ
2	0.54204(9)	0.54620(9)	2.0455(4)	*Fmmm*	−0.46(6)
3	0.54126(6)	0.54595(6)	2.8021(4)	*Fmmm*	+0.08(5)

X-ray powder diffraction studies were conducted on samples HT4:3 and HT3:2 using a Siemens D5000 X-ray diffractometer with Cu−Kα radiation (λ = 0.15418 nm). Data were collected over the 2θ range 5−110° with a step size of 0.02° and a count time of 10 s per step. The diffraction patterns were analyzed by Rietveld refinement using GSAS.[18] The previously reported face-centered structures[9,12] were used as starting models for refinement and gave satisfactory fits to $La_4Ni_3O_{10}$ (R_{wp} = 0.1234, R_p = 0.0868) and $La_3Ni_2O_7$ (R_{wp} = 0.1277, R_p = 0.0944) in space group *Fmmm*. It is noted here that neutron diffraction patterns of these two phases are more accurately described in space groups *Bmab* and *Amam*, respectively.[10] However, refinement in these lower-symmetry space groups failed to converge. The refined unit-cell parameters are summarized in Table 1. The constitution atomic ratios of the products were characterized using X-ray fluorescence (XRF), yielding La:Ni ratios of 1.46 (expected value 1.50) and 1.30 (expected value 1.33) for HT3:2 and HT4:3, respectively. These measured values were used along with thermogravimetric analytical data (see below) to calculate the oxygen hyperstoichiometry/deficiency parameters, δ, for each of the compounds.

To calculate the oxygen hyperstoichiometry/deficiency parameter, δ, for HT4:3 and HT3:2, respectively, we performed simultaneous thermogravimetric analyses (Polymer Labs STA 1500) under a flowing 5 mol % H_2−argon mixture by heating samples from room temperature to 700 °C at 2 K/min. The δ values were calculated by assuming the respective La−Ni−O compounds were reduced in the TGA apparatus to a mixture of lanthanum oxide and metallic nickel by 700 °C (details in the Supporting Information, Figure S4). Taking into account the very slight La deficiencies measured for the compounds by XRF, the TGA data suggested that δ = −0.46 ± 0.06 (oxygen deficient) and δ = +0.08 ± 0.05 (oxygen hyperstoichiometric) for HT4:3 and HT3:2, respectively (see the Supporting Information).

These compounds have previously been reported to be both oxygen hyperstoichiometric[10,11] and oxygen deficient.[3,9,12] Hence, it seems evident that synthesis routes and conditions play a major role on oxygen content. The δ values observed herein for HT4:3 and HT3:2 were relatively larger than those previously reported (δ range of −0.25 to +0.03).[3,9−11] As it is known that HT4:3 and HT3:2 are slightly lacking in lanthanum, it can be assumed that the relatively large deviation in the oxygen stoichiometry is due to the slight deviation in the relative metal stoichiometries.

Scanning electron microscope (SEM) analysis of the phase-pure heat-treated material HT4:3 revealed agglomerated round particles with a diameter of ca. 249 ± 41 nm
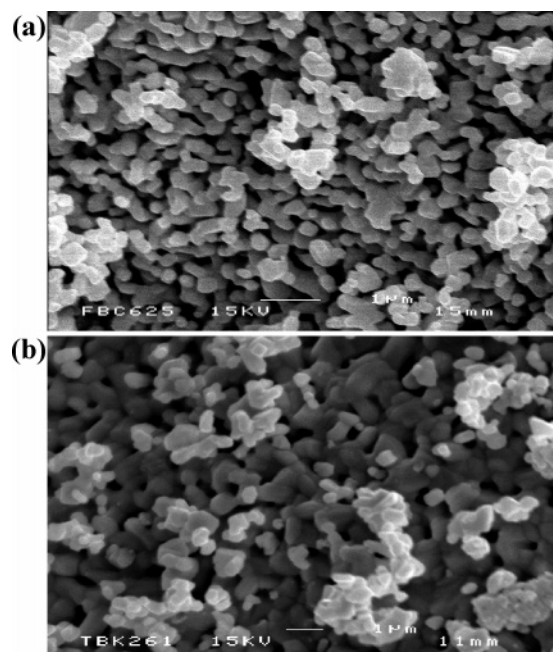
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Figure 4. Scanning electron micrograph of (a) $La_4Ni_3O_{10}$ (bar = 1 μm) and (b) $La_3Ni_2O_7$ (bar = 1 μm) made by a single heat treatment of the corresponding nanoparticle coprecipitates (4:3 and 3:2 La:Ni ratio, respectively) at 1075 and 1150 °C, respectively, in air for 12 h.

(Figure 4a) (range 153−336 nm on the basis of 50 particles measured). For sample HT3:2, agglomerated particles were observed with a particle diameter of ca. 424 ± 80 nm (Figure 4b) (range 335−625 nm on the basis of 50 particles). The specific surface areas suggested from the BET measurement were ca. 2.1 m² g⁻¹ for HT4:3 and <1 m²g⁻¹ for HT3:2.

The work reported herein has significant implications for the syntheses and isolation of complex or "difficult to make" materials that cannot currently be made directly or efficiently via conventional processing methods. Key to the discovery of new heterometallic phases is the speed at which we are able to isolate and characterize such materials. Hence, we foresee that the promising route developed herein could be coupled with a design of experiments (DOE) methodology to more systematically seek and generate new heterometallic phases that may currently lie undiscovered (elemental ratios, heating times, and heating temperatures being the variables in the DOE perhaps). This is an approach that we are currently pursuing, the results of which will be reported in due course.

Supporting Information Available: Comprehensive experimental details of syntheses and of the characterization equipment and drying methods (PDF). This information is available free of charge via the Internet at http://pubs.ac.org.

CM070134C