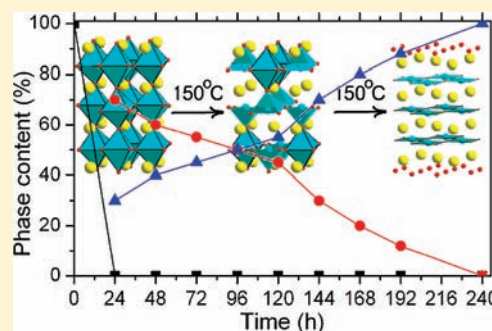


Low-Temperature Solvothermal Approach to the Synthesis of $\text{La}_4\text{Ni}_3\text{O}_8$ by Topotactic Oxygen Deintercalation

Colin K. Blakely, Shaun R. Bruno, and Viktor V. Poltavets*

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, United States

ABSTRACT: A chimie douce solvothermal reduction method is proposed for topotactic oxygen deintercalation of complex metal oxides. Four different reduction techniques were employed to qualitatively identify the relative reduction activity of each including reduction with H_2 and NaH , solution-based reduction using metal hydrides at ambient pressure, and reduction under solvothermal conditions. The reduction of the Ruddlesden–Popper nickelate $\text{La}_4\text{Ni}_3\text{O}_{10}$ was used as a test case to prove the validity of the method. The completely reduced phase $\text{La}_4\text{Ni}_3\text{O}_8$ was produced via the solvothermal technique at $150\text{ }^\circ\text{C}$ —a lower temperature than by other more conventional solid state oxygen deintercalation methods.



INTRODUCTION

Conventional high-temperature ($\geq 750\text{ }^\circ\text{C}$) solid state synthetic techniques result in the preparation of thermodynamically stable products, while the low-temperature chimie douce (soft chemistry) approach allows for the formation of new metastable phases with unique structural features. During soft chemistry transformations extensive parts of the original framework are retained, i.e., such reactions are often topotactic in nature. In spite of the low diffusion coefficients of ions in solids at lower temperatures, there are many examples of topotactic reactions performed at or even below room temperature. For example, alkali metal intercalation can be performed at $-78\text{ }^\circ\text{C}$ in $\text{NH}_3(\text{l})$, as in the case of $\text{Li}_x\text{Mo}_2\text{SbS}_2$ synthesis.¹

Due to a large ionic radius and double charge, the diffusion of O^{2-} can be expected to be prohibitively slow for any reactions to occur at room temperature. Strikingly, it has been shown that it takes only 12 h to transform $\text{SrCoO}_{2.5}$ into SrCoO_3 by oxidation in a sodium hypobromite solution at $0\text{ }^\circ\text{C}$.² These reaction conditions are in sharp contrast with the traditional high oxygen pressure method of SrCoO_3 preparation (2000 bar at $300\text{ }^\circ\text{C}$).³ This anomaly can be attributed to the strong oxidation power of sodium hypobromite as well as the higher stability of SrCoO_3 at lower temperatures. While oxygen intercalation reactions can be performed at $0\text{ }^\circ\text{C}$, the inverse process, topotactic oxygen deintercalation, always requires higher temperature. Oxygen deintercalation is conventionally performed by reaction in flowing H_2 or NH_3 at temperatures above $300\text{ }^\circ\text{C}$.^{4–6} Recently, metal hydrides were introduced as powerful low-temperature agents for topotactic oxygen deintercalation.^{7,8} These reagents gave access to new metastable compounds inaccessible by reduction with H_2 , such as $\text{La}_3\text{Ni}_2\text{O}_6$,⁹ SrFeO_2 ,¹⁰ and CaFeO_2 .¹¹ Solid state reductions have become possible at temperatures as low as $210\text{ }^\circ\text{C}$ due to the high chemical activity of NaH and CaH_2 .¹² Novel highly reduced phases with unusual coordination polyhedrons were

prepared by this topotactic method, for example, $\text{LaBaCoO}_{4.25}$ with Co(I) in square planar coordination¹² and $\text{Sr}_3\text{LaFe}_{1.5}\text{Co}_{1.5}\text{O}_{7.5}$ with three-coordinate Fe(II)/Co(II).¹³

A solid state reduction using metal hydrides generally requires intimately grinding the reagents as well as sealing the reaction mixture in glass ampules and often involves intermediate regrinding/rescaling steps. Unreacted metal hydrides and metal hydroxide byproducts must be removed by washing with methanol or NH_4Cl in methanol solution.

One can consider performing topotactic oxygen deintercalation in the presence of organic solvents in order to improve reaction kinetics and to eliminate the necessity of grinding/sealing operations. Reduction using metal hydrides in solvents is a classical method in organic chemistry; nevertheless, to the best of our knowledge, this technique has never been employed for the topotactic oxygen deintercalation of extended oxides. While NaBH_4 has been employed for metal oxides reduction in aqueous solution^{14–23} and in organic solvents,²³ it was used as a source of H_2 and reduction did not occur in a topotactic manner. Considering that topotactic oxygen deintercalation at temperatures below $200\text{ }^\circ\text{C}$ is an unexplored area, it is possible that many new metastable transitional metal oxides can be prepared in the $50\text{–}150\text{ }^\circ\text{C}$ temperature range. With this fact in mind, a new lower temperature method of oxygen deintercalation is needed. In this paper, we investigate the relative efficiency of a novel topotactic oxygen deintercalation method that exploits the reductive power of metal hydrides in common organic solvents. The results obtained for this method are compared with more conventional experimental techniques including reduction in the solid state using metal hydrides and H_2 gas as well as metal hydride reduction in organic solvents at ambient pressure.

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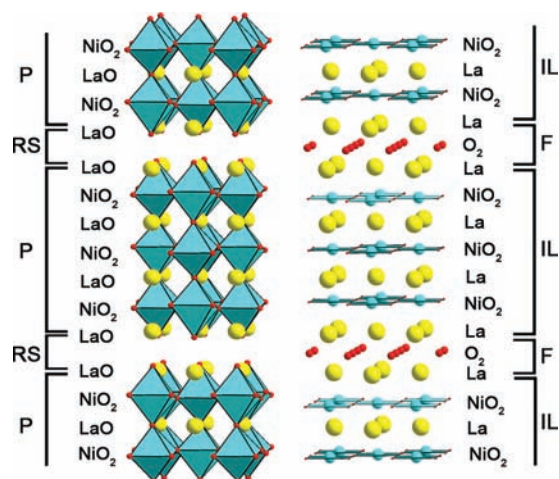


Figure 1. Structure models of $\text{La}_4\text{Ni}_3\text{O}_{10}$ (left) and $\text{La}_4\text{Ni}_3\text{O}_8$ (right) with denoted layers and structural blocks: P, perovskite; RS, rock salt; IL, infinite layer; F, fluorite. Yellow, cyan, and red balls represent La, Ni, and O atoms, respectively.

EXPERIMENTAL SECTION

$\text{La}_4\text{Ni}_3\text{O}_{10}$ was synthesized by the sol–gel Pechini technique as described previously.²⁴ The final sintering was performed under oxygen flow at 1150 °C for 200 h with 4 intermittent grindings.

Four different experimental reduction methods, solid state utilizing NaH or H_2 , solution, and solvothermal, were used. For solid state reactions where H_2 was used as the reducing agent, 400 mg (0.449 mmol) of $\text{La}_4\text{Ni}_3\text{O}_{10}$ was finely ground and then spread evenly on the bottom of an alumina boat. The materials were fired at 200, 250, or 300 °C for up to 15 days under a pure H_2 flow. In the solid state reaction employing NaH as a reducing agent, 400 mg (0.449 mmol) of $\text{La}_4\text{Ni}_3\text{O}_{10}$ was ground with NaH (13.47 mmol) under a nitrogen atmosphere in a glovebox and then loaded into a glass ampule and covered with a vacuum adapter. The ampule was removed from the glovebox, evacuated, and flame sealed. Samples were annealed at 100–200 °C for up to 10 days with intermediate regrinding/resealing every 24–48 h. Products were washed with anhydrous methanol under a nitrogen atmosphere to remove any remaining NaH or NaOH and then dried under vacuum for 1 h.

In the solution-based reactions, high-boiling solvents including triethylene glycol dimethyl ether (bp = 216 °C), diethylene glycol dimethyl ether (bp = 162 °C), and ethylene glycol (bp = 197 °C) were used. A 200 mg (0.22 mmol) amount of $\text{La}_4\text{Ni}_3\text{O}_{10}$ with an excess of NaH (0.66–13.2 mmol) was loaded into a 100 mL Schlenk flask in a nitrogen glovebox. The flask was then charged with 20 mL of a high-boiling solvent as well as a Teflon stir bar, fitted with a reflux condenser, and placed in a temperature-regulated (25–200 °C) oil bath. Aliquots were periodically removed, washed with anhydrous methanol, and analyzed to determine phase composition.

The solvothermal reactions proceeded as follows: 200 mg (0.22 mmol) of $\text{La}_4\text{Ni}_3\text{O}_{10}$ and NaH (2.22–6.6 mmol) were added to a 45 mL Teflon sleeve to avoid reaction with the steel vessel. The Teflon sleeve was then charged with 20 mL of anhydrous pentane, after which was inserted into a steel autoclave and treated solvothermally at either 150 or 200 °C for up to 10 days. The products were washed under nitrogen with multiple aliquots of anhydrous methanol to remove any unreacted NaH or NaOH and then dried for 1 h under vacuum to remove any solvent. All samples were stored in a glovebox under nitrogen atmosphere.

The samples were characterized by powder X-ray diffraction (PXRD) on a Bruker D8 Advanced with a DAVINCI design diffractometer using $\text{Cu K}\alpha$ radiation. The patterns were recorded at room temperature with a step size of 0.02° (2θ) on a zero background sample holder. Relative

Table 1. Products of $\text{La}_4\text{Ni}_3\text{O}_{10}$ Reduction by Different Techniques

reagent/solvent	reaction temperature (reaction time), autogenous pressure for solvothermal condition	relative content (%) of $\text{La}_4\text{Ni}_3\text{O}_{10}$ / $\text{La}_4\text{Ni}_3\text{O}_9$ / $\text{La}_4\text{Ni}_3\text{O}_8$ (normalized to 100% total)
H_2	300 °C (100 h)	0/0/100
	250 °C (120–360 h)	0/100/0
	200 °C (360 h)	no reaction
NaH	200 °C (240 h)	0/30/70
	150 °C (240 h)	no reaction
NaH /triglyme	200 °C (168 h)	0/100/0
	150 °C (120 h)	10/90/0
NaH /diglyme	200 °C (168 h), 2.9 atm	0/30/70
	150 °C (240 h)	0/90/10
NaH /pentane	200 °C (240 h), 59.7 atm	0/0/100
	150 °C (72 h), 15.7 atm	0/25/75

amounts of $\text{La}_4\text{Ni}_3\text{O}_{10}$, $\text{La}_4\text{Ni}_3\text{O}_9$, and $\text{La}_4\text{Ni}_3\text{O}_8$ have been estimated as a ratio of the main peak intensities.

RESULTS AND DISCUSSION

The crystal structure of the Ruddlesden–Popper (RP) nickelate $\text{La}_4\text{Ni}_3\text{O}_{10}$ can be described as an intergrowth of rock salt and perovskite blocks (Figure 1). As shown earlier, the low-temperature reduction of $\text{La}_4\text{Ni}_3\text{O}_{10}$ proceeds through oxygen deintercalation from the LaO layers in the perovskite blocks of the structure and results in two distinct line phases: $\text{La}_4\text{Ni}_3\text{O}_9$ and $\text{La}_4\text{Ni}_3\text{O}_8$.^{4,25} Besides the presence of oxygen vacancies, $\text{La}_4\text{Ni}_3\text{O}_9$ is structurally similar to $\text{La}_4\text{Ni}_3\text{O}_{10}$. On the contrary, formation of $\text{La}_4\text{Ni}_3\text{O}_8$ occurs through an oxygen deintercalation followed by a structural change in the $(\text{LaO})_2$ part of the structure, resulting in a transformation from rock salt to fluorite arrangement (Figure 1).^{4,25} As a result of this structural transformation, the so-called triple layer T' -type structure is formed with infinite NiO_2 planes and nickel is exclusively in square-planar coordination. While both reduced nickelates, $\text{La}_4\text{Ni}_3\text{O}_9$ and $\text{La}_4\text{Ni}_3\text{O}_8$, can be prepared by reduction of $\text{La}_4\text{Ni}_3\text{O}_{10}$ under H_2 flow at ~ 350 °C, different concentrations of H_2 have to be utilized. $\text{La}_4\text{Ni}_3\text{O}_9$ is produced when 5–10% H_2 is used, while synthesis of $\text{La}_4\text{Ni}_3\text{O}_8$ requires pure H_2 flow. Reaction at higher temperatures results in complete decomposition of both phases with La_2O_3 and Ni as the decomposition products.

In our experiments, we chose the topotactic reduction of $\text{La}_4\text{Ni}_3\text{O}_{10}$ as a model system. This selection was based on the existence of two possible reduction products ($\text{La}_4\text{Ni}_3\text{O}_9$ and $\text{La}_4\text{Ni}_3\text{O}_8$), which can qualitatively indicate the activity of the reducing agents. The progress of each reaction was monitored via PXD since the main peaks of all 3 three nickelates can be easily distinguished in powder diffraction patterns.⁴

Reduction of $\text{La}_4\text{Ni}_3\text{O}_{10}$ in flowing H_2 (100%) at different temperatures has been utilized as a benchmark for comparison with other techniques. The final composition of the reactions clearly demonstrates a rapid decrease in H_2 activity with decreasing temperatures (Table 1). While the most reduced $\text{La}_4\text{Ni}_3\text{O}_8$ nickelate can be prepared at 300 °C, only $\text{La}_4\text{Ni}_3\text{O}_9$ formed at 250 °C. No reaction was detected at 200 °C, confirmed by the sole presence of $\text{La}_4\text{Ni}_3\text{O}_{10}$.

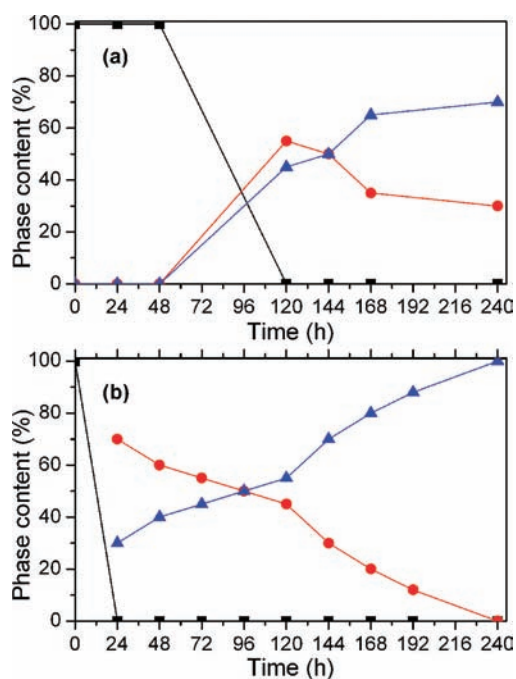


Figure 2. Phase composition versus reaction time during $\text{La}_4\text{Ni}_3\text{O}_{10}$ reduction with NaH at 200 °C: (a) solid state reaction, (b) solvothermal conditions. $\text{La}_4\text{Ni}_3\text{O}_{10}$, black squares; $\text{La}_4\text{Ni}_3\text{O}_9$, red circles; $\text{La}_4\text{Ni}_3\text{O}_8$, blue triangles. Relative phase content is normalized to 100% total.

NaH showed high reducing activity in the solid state reduction of $\text{La}_4\text{Ni}_3\text{O}_{10}$ at 200 °C, where $\text{La}_4\text{Ni}_3\text{O}_8$ was the major product (Table 1, Figure 2a). While we were unable to prepare a pure phase sample even after annealing for 10 days with 5 intermediate grindings, ΔT of -100 °C in comparison with H_2 reaction is rather impressive. The activity of NaH in solid state reduction declines sharply at lower temperatures, with no reaction observed at 150 °C.

Surprisingly, reduction of $\text{La}_4\text{Ni}_3\text{O}_{10}$ by NaH in triglyme at 200 °C resulted in the intermediate nickelate, $\text{La}_4\text{Ni}_3\text{O}_9$, as the most reduced reaction product (Table 1). While a pure phase sample can be prepared faster (in 4 days) and easier (no re-grinding/resealing) than in the case of the reported solid state reduction, the inability to form the most reduced product is essentially a failure of the method. At 150 °C, reduction with NaH in triglyme under ambient pressure produces almost pure $\text{La}_4\text{Ni}_3\text{O}_9$. By these results, one can see that oxygen diffusion in nickelates is sufficient at this temperature for oxygen deintercalation to occur. Since no reaction was observed in the solid state reduction at 150 °C, there must be a limiting process absent in the presence of solvent.

The reaction of $\text{La}_4\text{Ni}_3\text{O}_{10}$ with NaH is summarized below



Since the eutectic temperature in the NaH–NaOH system, 450 °C,²⁶ is much higher than the reaction temperature under consideration, reduction without the presence of a solvent is a purely solid state process and involves diffusion of NaH through NaOH(s) to the nickelate surface. Due to the relatively high solubility of NaOH in glyme ethers, the nickelate particle surface

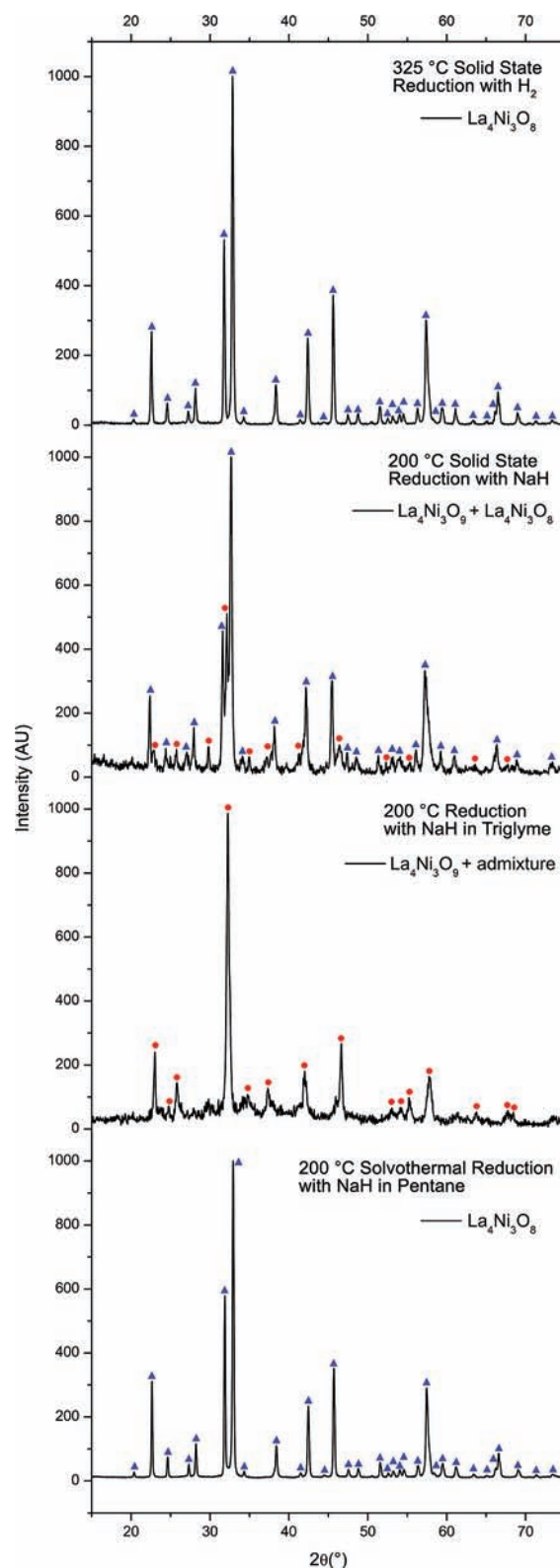


Figure 3. Representative PXD patterns for the reduction products prepared by different experimental methods. $\text{La}_4\text{Ni}_3\text{O}_9$, red circles; $\text{La}_4\text{Ni}_3\text{O}_8$, blue triangles.

opens up constantly for further reaction with NaH. Even at lower temperature, 100 °C, $\text{La}_4\text{Ni}_3\text{O}_9$ forms slowly in the reaction with NaH/diglyme.

Reduction in autoclaves was initially tried as a convenient alternative to reaction in the presence of solvents under reflux. Additionally, a large number of solvents can be used at temperatures above their boiling points, i.e., solvothermal conditions. Reduction of $\text{La}_4\text{Ni}_3\text{O}_{10}$ by NaH in diglyme (bp = 162 °C) at 200 °C led to the most reduced nickelate, $\text{La}_4\text{Ni}_3\text{O}_8$, as the major phase. Therefore, at 200 °C the reducing activity of NaH in diglyme under solvothermal conditions is comparable with that of solid NaH and higher than NaH in triglyme at ambient pressure.

The solvothermal reduction performed with NaH in pentane (bp = 36.1 °C) at 200 °C resulted in pure phase $\text{La}_4\text{Ni}_3\text{O}_8$. While the reaction is kinetically hindered and it takes 10 days to prepare the single phase, simplicity of procedure and the purity of the product are advantageous over solid state reduction with NaH in this case (Figure 2).

Representative PXD patterns for the reduction products prepared by four different experimental methods are shown in Figure 3. Pure $\text{La}_4\text{Ni}_3\text{O}_8$ without any peaks of admixture phases can be prepared by reduction with H_2 at 325 °C or by reduction with NaH at solvothermal condition at 200 °C. Highly crystalline products are formed in both cases. The full width at half maximum (FWHM) for the main $\text{La}_4\text{Ni}_3\text{O}_8$ reflections, (1 1 0) and (1 0 7), were 0.113(8)° and 0.131(5)° 2θ for the H_2 reduction product and 0.111(4)° and 0.146(3)° 2θ for $\text{La}_4\text{Ni}_3\text{O}_8$ prepared by the solvothermal reduction method. Cell parameters were refined as $a = 3.9708(1)$ Å and $c = 26.106(1)$ Å after reaction with H_2 at 325 °C and $a = 3.9705(2)$ Å and $c = 26.103(2)$ Å after solvothermal preparation at 200 °C.

$\text{La}_4\text{Ni}_3\text{O}_8$ was also obtained as a main phase by the solvothermal reduction with NaH in pentane at 150 °C. The solubility of both NaH and NaOH is expected to be much lower in nonpolar solvents like pentane than in the polar glyme ethers; therefore, the reducing power of NaH in pentane cannot be attributed to reagent/product solubility.

There is a clear correlation between formation of $\text{La}_4\text{Ni}_3\text{O}_8$ and autogenous pressure in autoclaves (Table 1). The pressure inside of the autoclaves was calculated by employing the Clausius–Clapeyron equations.²⁷ Above the critical temperature of pentane (196.7 °C), the van der Waals equation was used with $a = 18.99 \text{ L}^2 \text{ atm mol}^{-2}$ and $b = 0.146 \text{ L mol}^{-1}$.²⁷ The effect of pressure could be related to many factors: changes in relative surface energy of the nickelates, an increase in solubility of either the reagent or the byproduct, and/or changes in the oxygen diffusion coefficients. Since the autogenous pressure was important for both polar and nonpolar solvents, we do not believe that surface energies or NaOH and NaH solubilities played the determining role.

Nucleation of a new phase can be a limiting step for topotactic transformations at such low reaction temperatures. In a solid–solid nucleation, a change in specific volume that occurs must be accommodated elastically, leading to a strain energy effect. Oxygen diffusion coefficients in *ab* planes can be expected to be much higher than in the *c* direction in the nickelates under consideration; therefore, the seeds of reduced nickelates presumably form epitaxially on any crystal facets except (00*l*) ones. In previously reported oxygen deintercalation reactions of these nickelates, large changes in *c* cell parameters were observed. For example, the *c* parameter decreases by 1.9% during reduction of $\text{La}_4\text{Ni}_3\text{O}_{10}$ to $\text{La}_4\text{Ni}_3\text{O}_9$. Further oxygen deintercalation of $\text{La}_4\text{Ni}_3\text{O}_9$ to $\text{La}_4\text{Ni}_3\text{O}_8$ leads to a striking 4.9% decrease in the *c* parameter. Formation of strained coherent interfaces raises the

free energy of the system and can hinder the homogeneous nucleation. It is possible that the pressure during reduction at solvothermal condition decreases the nucleation energy of the reduced nickelates—an effect that should be particularly important at lower temperatures. While it is not possible to uniquely attribute the pressure effect to increased reduction activity, our results give direction for further development of this low-temperature topotactic oxygen deintercalation method. As we established, higher pressure is favorable for this reaction to occur. At the same time, the autogenous pressure becomes lower at lower temperatures; therefore, reduction under an externally generated pressure of inert gas might allow extending reaction to lower temperatures.

CONCLUSION

A novel solvothermal topotactic oxygen deintercalation method employing metal hydrides and organic solvents was described and validated via reduction of $\text{La}_4\text{Ni}_3\text{O}_{10}$ to $\text{La}_4\text{Ni}_3\text{O}_8$ at 150 °C. The relative reduction activities of different conventional solid state reduction techniques were compared to determine the reductive power of the proposed solvothermal method. Introduction of pressure is favorable and leads to formation of pure $\text{La}_4\text{Ni}_3\text{O}_8$ at lower temperatures than previously reported. Experiments are underway to investigate whether new metastable complex oxides can be synthesized by the proposed method.

AUTHOR INFORMATION

Corresponding Author

*Phone: 517-355-9715, ext. 388. Fax: 517-353-1793. E-mail: poltavets@chemistry.msu.edu.

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