



Low Temperature Formation of Ruddlesden-Popper-Type Layered $La_2CoO_{4\pm\delta}$ Perovskite Monitored via *in situ* X-ray Powder Diffraction

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Abstract: In this contribution low temperature formation of Ruddlesden-Popper (RP)-type layered La2CoO4±0 perovskite was optimized via in situ X-ray powder diffraction (XRPD). Starting from LaCoO₃ a stoichiometric transformation to $La_2CoO_{4\pm\delta}$ and CoO can be achieved by controlled reduction with H₂. The challenge of this reaction is the use of appropriate amounts of H₂ in a defined temperature region. If the amount of H₂ is too high, complete reduction of the perovskite occurs. If temperatures are not appropriate, intermediate phases seem to hinder the transformation to $La_2CoO_{4\pm\delta}$ or lead to a complete decomposition to simple oxides. Based on in situ XRPD experiments, temperature window and required amount of H₂ for the transformation of LaCoO₃ to La₂CoO_{4±0} were determined. Systematic experiments reveal that 650 °C is the optimal temperature for the complete transformation of LaCoO₃ into $La_2CoO_{4\pm\delta}$ and CoO/Co⁰. The information was then transferred to realize bulk synthesis of La_2CoO_{4\pm\delta} at 650 °C in a tube furnace without extended heat treatments at elevated temperatures.

Introduction

The interest in Ruddlesden-Popper (RP)-type layered perovskites began after the studies on the structure of potassium nickel fluoride (K₂NiF₄) single crystals by Balz and Plieth in 1955.^[1] Later on, Ruddlesden and Popper introduced Sr₂TiO₄, Ca₂MnO₄, and SrLaAlO₄ to be isostructural to K₂NiF₄.^[2] Today, materials possessing K₂NiF₄ structure are referred to as "RP-type". The general formula of an RP-type perovskite can be given as A_{n+1}BO_{3n+1} or AO(A_nBO_{3n}) perovskite layer sandwiched between the rock-salt type layers (Fig. 1).

RP-type layered perovskites attract great attention due to their mixed ionic-electronic conductivity (MIEC) and excellent oxygen-ion diffusion as well as proton conductivity.^[3-10] They are

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employed as electrode materials in solid oxide fuel cells (SOFCs),^[8,9,11-15] rechargeable metal-air batteries,^[16,17] as well as solar cell materials^[18] and oxygen separation membranes.^[19] The physicochemical properties of pure or cation-substituted $La_2MO_{4+\delta}$ (M = Ni, Cu) compounds have been comprehensively studied. Due to their high oxygen ion conductivity, they are interesting cathode materials particularly for intermediate temperature (IT: 600<T<800 °C) SOFC applications.[5,9,11,20-24] Cationic substitution as well as the oxygen content of RP-type perovskites change not only their structural but also their electronical properties significantly which is favorable for IT-SOFCs.^[10, 20, 25, 26] Beside energy-oriented applications, such as in SOFCs, RP-type perovskites are used as catalysts in numerous heterogeneously catalyzed reactions. Among others, they are used as catalysts for oxidation of CO,^[27] decomposition of NO,^[28] combustion of methane,^[29] decomposition of N₂O,^[30] or oxygen evolution reaction (OER).[31-34]



Figure 1. Crystal structure of an RP-type (A_2BO_4) tetragonal perovskite for n = 1. Color codes of the atoms: (gray) A, (blue) B, (red) O.

In general, conventional solid-state reactions performed above 1000 °C are used for the synthesis of RP-type perovskites.^[4,13,35-41] However, also other methods are used including sol-gel synthesis,^[42] co-precipitation,^[41,43] spray pyrolysis,^[15] hydrothermal flow synthesis,^[44] or combustion methods.^[24,45] These methods are usually implemented in combination with high temperature treatments (\geq 1000 °C). On the other hand, Du et al. reported the low temperature synthesis of several RP-type La_xCa_{3-x}Mn₂O₇ compounds, starting from mixing metal nitrate solutions with citric acid, subsequent calcination at 700 °C followed by hydrothermal treatment.^[29] Diffraction patterns

showed the presence of impurities such as La₂O₃. In addition, Weng et al. achieved the formation of La₂NiO₄ via a continuous hydrothermal flow synthesis (CHFS) after heat treatment at 700 °C for 3h which was claimed to be the lowest temperature used for the synthesis of La₂NiO₄.^[46] In fact, the synthesis of an RP-type perovskite can be rather challenging, depending on the desired chemical composition. In this regard, RP-type La₂CoO_{4+δ} perovskite has been less in the focus of scientific reports compared to its Ni or Cu analogues,^[38] although it can tolerate significant amounts of oxygen up to a δ of 0.16 upon spontaneous topotactic oxidation at room temperature in air.[35] This makes $La_2CoO_{4+\delta}$ a very good candidate as a cathode material for IT-SOFCs.^[9] The main drawback in the synthesis of $La_2CoO_{4t\delta}$ is mainly caused by the extremely easy oxidation of Co²⁺ to Co³⁺ resulting in the formation of undesired perovskite compounds containing Co3+ [38, 47] Therefore, relatively low oxygen partial pressures $(p(O_2))$ or reductive atmosphere is required for a successful synthesis.^[35] Moreover, the formation of La₂CoO₄₊₅ as well as of the A- or B-site substituted analogues require synthesis temperatures higher than 850 °C in order to acquire almost phase pure products.^[3, 35, 36, 38, 39, 42, 48-53] For instance, Guo et al. reported the sol-gel synthesis of RP-type La_2XO_4 (X = Ni, Co) perovskites.^[42] They show that the synthesis temperature of 850 °C did not lead to formation of pure La₂CoO₄, but to a mixture of La₂CoO₄ and LaCoO₃. The formation of La2CoO4 was completed only at higher temperature (1100 °C).^[42] Similarly, Le Dréau et al.,^[38] as well as Babkevich et al.^[39] performed solid-state reactions with extended heating at very high temperatures (>1000 °C) for 24 or 48 h to produce La₂CoO_{4+δ} single crystal or La₂CoO₄ polycrystalline material, respectively.

The most convenient strategy to investigate structural changes of a material or formation of new phases under nonambient conditions is the use of *in situ* structure characterization techniques. In this respect, *in situ* diffraction is an ideal tool. Several papers reported *in situ* diffraction studies on structural phase transitions of La₂CoO_{4+δ}.^[36] In addition, the structural phase transitions of La₂CoO_{4+δ}.^[50] or Ni-substituted La₂CoO_{4±δ} ^[54] upon calcination were also reported. However, the formation of non-substituted polycrystalline La₂CoO_{4±δ} at temperatures as low as 650 °C has not been reported so far.

The main goal of this work was to establish a strategy for a low temperature synthesis of an RP-type $La_2CoO_{4\pm\delta}$ by controlled reduction of $LaCoO_3$. In order to mimic the reaction conditions with respect to temperature and gas flow, we performed *in situ* X-ray powder diffraction (XRPD) experiments under controlled reductive atmosphere at different temperatures.

Results and Discussion

In Figure 2, the XRPD pattern of the phase-pure LaCoO₃ synthesized at 700 °C via hard templating method is shown. The crystal structure of LaCoO₃ exhibits a rhombohedral symmetry with the space group R $\overline{3}$ c and consists of eight corner-sharing CoO₆ octahedral units with one La ion positioned in the center

(Fig. 2, inset). Rietveld refinements performed prior to the *in situ* experiments are summarized in the Supporting Information (Fig. S1).

Figure 2. Qualitative phase analysis of the *in situ* XRPD data of the assynthesized LaCoO₃ collected in pure N₂ gas at room temperature (RT). Tick marks represent the reference reflection positions of LaCoO₃ as obtained from the Inorganic Crystal Structure Database (ICSD): ICSD-236314,^[55] (inset) crystal structure of LaCoO₃ (space group: $R\overline{3}c$). The symbol (*) represents the perovskite reflections coming from secondary W radiation. Color codes of the atoms: (gray) La, (blue) Co, and (red) O.

Figure 3 shows the bright field scanning transmission electron microscopy (BF-STEM) image and energy dispersive X-ray spectroscopy (EDX) analyses of the as-synthesized LaCoO₃. The average particle size is in the range of 30-35 nm (Fig. 3a). The nanoparticles are agglomerated due to sintering at elevated temperature (700 °C). EDX analyses in Fig. 3b and c indicate a homogeneous distribution of lanthanum and cobalt.

Figure 3. Investigation on the morphology and the elemental analysis of the as-synthesized $LaCoO_3$: (a) BF-STEM image, (b, c) EDX mapping analyses: (b) La (6.3 at%, green), and (c) Co (4.2 at%, red).

The N₂ gas adsorption-desorption isotherms of as-synthesized LaCoO₃ are shown in the Supplementary Information (Fig. S2). A specific surface area of 5 m²g⁻¹ was calculated with the BET method.^[56] Since the synthesis temperature was 700 °C, sintering followed by severe agglomeration of particles is the reason for the low specific surface area of LaCoO₃.

In order to mimic the reaction parameters for the formation of La₂CoO_{4±0}, the as-synthesized LaCoO₃ was heated under protective atmosphere to different temperatures (550, 650, and 750 °C) and then controlled reduction was performed. First of all, the sample was heated in pure N₂ gas from room temperature





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(r.t.) to the according temperatures with a heating rate of 20 °Cmin⁻¹. After reaching the desired temperatures, the gas atmosphere was changed to a continuous flow (10 mLn min⁻¹) of a 10% H₂/90% N₂ gas mixture. In the next step, diffraction patterns were collected under isothermal conditions. The reduction is a very fast process which is not easy to monitor with in-house diffractometers. Therefore, for monitoring the reduction, data were collected in a small 20 range between 28 and 40°. This reduced data collection time per dataset to 5 min. After finishing the reduction, diffraction data for Rietveld refinements were collected over a larger 20 range.



Figure 4. Temperature-dependent *in situ* XRPD patterns of the as-synthesized LaCoO₃ heated to 550 °C. After reaching the desired temperature, data were collected isothermally. Data collection time per patterns was 5 min. Each pattern is numbered for the sake of simplicity in the discussion. The reference reflection positions were obtained from ICSD as follows: LaCoO₃: ICSD-236314,^[55] HTT-La₂CoO_{4±6}: ICSD-245657,^[54] LTO-La₂CoO_{4±6}: ICSD-173514,^[64] La₂O₃: ICSD-56771,^[65]. Patterns 1 and 22 were recorded in pure N₂ at r.t., while patterns 2 to 15 were recorded under reductive atmosphere at 550 °C.

In Figure 4, temperature-dependent *in situ* XRPD patterns are shown which display significant structural changes of the assynthesized $LaCoO_3$ under reductive atmosphere at 550 °C.

After exposure to the H₂/N₂ gas stream for about 15 min at 550 °C, formation of some intermediate phase(s) was observed (pattern 4). These are most probably oxygen deficient, so-called brownmillerite-type, La₂Co₂O₅ or La₃Co₃O₈ and/or RP-type La₄Co₃O₁₀ or La₄Co₃O₉ perovskites. The phase diagrams for La-Co-O compounds propose the formation of La₄Co₃O₁₀ from LaCoO₃ under controlled $p(O_2)$ at temperatures ≥ 1100 °C.^[57-59] La₄Co₃O_{10±δ} belongs to the family of RP-type perovskites (with n = 3) and was investigated previously for its electronic and magnetic properties as well as its kinetic stability.^[57, 60-63] It is a triple layered (n = 3) perovskite that can form during a transformation from LaCoO₃ to La₂CoO_{4±δ} under reductive atmosphere,^[57] as proposed by reaction 1:

$4LaCoO_3 \rightarrow La_4Co_3O_{10\pm\delta} + CoO + (1-(\pm\delta)/2) O_2 \quad \ (reaction \ 1)$

According to *in situ* XRPD studies reported by Radovic et al., commercial LaCoO₃ was heated up to 900 °C in a gas mixture of 4% H₂/96% N₂.^[66] Their study showed the formation of some brownmillerite-type perovskites such as La₃Co₃O₈ and La₂Co₂O₅ in a temperature range between 375-425 °C. The formation of La₄Co₃O₁₀ was observed at 425 °C, while the sample was completely decomposed to La₂O₃ and reduced to metallic Co (Co⁰) at 600 °C. La₂O₃ and Co⁰ were stable upon heating to 900 °C.^[66] It is important to note that La₄Co₃O_{10±δ} compounds are known to be thermodynamically unstable below ca. 1400 °C in air.^[57] The oxygen stoichiometry of La₄Co₃O_{10±δ} is highly dependent on the temperature and $p(O_2)$.^[60] According to the phase diagram reported by Adachi et al., a precisely controlled $p(O_2)$ is required to stabilize La₄Co₃O₁₀.^[57]

Not only the structures of intermediate RP-phases, such as $La_4Co_3O_{10}$, but also the structure of La_2CoO_4 depend strongly on the $p(O_2)$,^[63] as oxygen stoichiometry changes with $p(O_2)$. The crystal structure of La_2CoO_4 changes as function of $p(O_2)$ and temperature.^[38,54] In this regard, mainly four different phases are known to exist for La2CoO4. These are high temperature tetragonal (HTT), low temperature orthorhombic (LTO), low temperature tetragonal (LTT) and high temperature orthorhombic (HTO) phases.^[36] In addition, Le Dréau et al. reported another phase transition from LTO to high temperature less orthorhombic (HTLO) phase in the temperature range between 140-160 °C.^[38] In Figure 5 the crystal structures of LaCoO₃ and the RP-type oxygen stoichiometric HTT- and LTO-La₂CoO₄ are shown. The crystal structure of LaCoO₃ is rhombohedral with space group $R\bar{3}c$ (Fig. 5a), whereas La₂CoO₄ can crystallize in various symmetries depending on temperature treatments. Therefore, determination of the space group is not straightforward. It is known that the HTT-phase of La₂CoO₄ crystallizes in tetragonal symmetry with space groups I4/mmm or P42/nmc (Fig. 5b), while the LTO-phase crystallizes in orthorhombic symmetry with the space groups Bmab or Pmcb (Fig. 5c).^[50]

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Figure 5. Crystal structures: (a) LaCoO₃, (b) HTT-La₂CoO₄ (space group: μ/mmn), and (c) LTO-La₂CoO₄ (space group: *Bmab*). Color codes of the atoms: (gray) La, (dark blue) Co, and (red) O.

The crystal structure of La₂CoO₄ consists of one LaCoO₃ perovskite layer positioned in the center of the unit cell along the crystallographic *c*-axis which is squeezed between intercalating LaO layers (Fig. 5b, c). In our study, the crystal structure of $La_2CoO_{4\pm\delta}$ formed at 650 °C is in accordance with the HTTphase (space group I4/mmm), while the structure obtained after cooling to r.t. is likely the LTO-phase (space group Bmab). Exact identification of the intermediate phase(s) is not straightforward in the current study due to the complicated crystal structures of the RP-phases caused by non-stoichiometric oxygen contents. Additionally, the positions of the reflections of the intermediate phases are located relatively close to each other and reflection broadening complicates the situation as well. Only neutron diffraction experiments (not subject of the present study) would allow assigning the intermediate phases more accurately with respect to oxygen content of $La_2CoO_{4\pm\delta}$.

Starting the reduction at 550 °C, transformation from unassigned intermediate phase(s) to high temperature tetragonal (HTT) La₂CoO_{4±δ} is observed after approximately 20 min of exposure to reductive atmosphere (Fig. 4, pattern 6). The formation of La₂CoO_{4±δ} is proposed to occur according to reaction 2:^[57]

 $La_4Co_3O_{10\pm\delta} \rightarrow 2La_2CoO_{4\pm\delta} + CoO + (1-(\pm\delta)/2) O_2$ (reaction 2)

The reflection intensities of HTT-La₂CoO_{4±δ} increased with time, while those of the intermediate phases decreased accordingly (patterns 6 to 15). On the other hand, La₂O₃ was detected starting from pattern 13. This corresponds to 60 min treatment under reductive atmosphere and is evidence for the decomposition of La₂CoO_{4±δ}. Although HTT-La₂CoO_{4±δ} was obtained already at 550 °C under controlled gas atmosphere, the presence of intermediate phases seem to hinder the complete formation of HTT-La₂CoO_{4±δ}. Instead, decomposition to La₂O₃ is observed. After 70 min (pattern 21), the atmosphere was changed back to pure N₂ but the decomposition could not be stopped and in the end, a mixture of La₂O₃, intermediate RP-phases and low temperature orthorhombic (LTO) La₂CoO_{4±δ} was obtained (pattern 22).

In the next experiment, LaCoO₃ was heated from r.t. to 650 °C under N₂ atmosphere (Fig. 6, patterns 1 and 2). The significant peak shift to lower 2 θ values in pattern 2 compared to pattern 1 is due to thermal expansion at elevated temperatures. After data collection at 650°C under pure N₂, the atmosphere was switched to H₂/N₂ (patterns 3 to 11). During exposure to reductive atmosphere for about 10 min, formation of some intermediate phase(s) was observed. However, those phases disappeared upon further reduction at 650 °C. Pattern 5 in Fig. 6 shows the rapid formation of a new phase, as two new reflections emerged at 30.9 and 32.2° (2 θ). The positions of these two new reflections indicated the formation of HTT-La₂CoO_{4±δ} which is proposed to occur according to reaction 2. The formation of HTT-La₂CoO_{4±δ} was completed at 650 °C after about 15-20 min of reduction.



Figure 6. Temperature dependent *in situ* XRPD patterns of the as-synthesized LaCoO₃ performed during heating to 650 °C. After reaching the temperature, data were collected isothermally. Data collection time per patterns was 5 min. Each pattern is numbered for the sake of simplicity in the discussion. Patterns 1 and 2 were recorded in pure N₂ at r.t. and at 650 °C, respectively. Patterns 3 to 11 were recorded under reductive atmosphere at 650 °C, while pattern 12 was recorded under pure N₂ at r.t.

Rietveld refinements of a dataset collected *in situ* at 650 °C provide information about the phase composition of the sample (Fig. 7). From the refinement a phase composition of 88 wt% La₂CoO_{4±0} and 12 wt% Co⁰ was obtained. Formation of metallic Co is an indication that CoO, which forms during the reduction, is further reduced (reactions 3). The values obtained correspond exactly to the theoretical composition expected for a

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stoichiometric reduction of LaCoO₃ to the RP phase and metallic Co (reaction 3b). The formation of either CoO or metallic cobalt is expected for the stoichiometric reduction reaction of LaCoO₃.^[67, 68] If the reduction stops at CoO (reaction 3a), 15.8 wt% of CoO and 84.2 wt% La₂CoO_{4±0} need to be formed. Even though the intensities of the CoO and/or Co⁰ are low and correspond only to max 16 wt% CoO and 13 wt% Co⁰, one should note that on a molar basis 1 mole of CoO is formed per mole of La₂CoO₄.

The data also show the presence of an additional reflection which cannot be assigned to any of the known brownmillerite or RP-phases. Since the reflection is not present after cooling anymore, the formation of an additional, so far unknown high temperature metastable phase can be assumed.



Figure 7. Rietveld refinement plot of data collected at 650 °C under reductive atmosphere. The star indicates the presence of an unidentified phase which is only present at 650 °C. Tick marks: upper HTT- $La_2CoO_{4\pm0}$, lower Co^{0} ^[69]

After finishing the reduction, the gas atmosphere was switched back to pure N₂, the sample was cooled to r.t., and data were collected accordingly (pattern 12, Fig. 6). Rietveld refinements of the data indicated the transformation from HTT to LTO-La₂CoO_{4±δ} after cooling in pure N₂ (Supporting Information Fig.S3). Some of the HTT RP-phase remained but disappeared after exposure of the sample to air (not shown here). In the absence of intermediate phase(s), the sample is stable as RP-type La₂CoO_{4±δ}. On the other hand, the presence of intermediate phase(s) destabilizes the structure of La₂CoO_{4±δ} so that the sample oxidizes back to LaCoO₃ under atmospheric conditions (Supplementary Information, Fig. S4) or completely decomposes.

The *in situ* studies evidence the important influence of reduction time on the formation of the desired RP-phase. As expected, reduction at higher temperature (750 °C) is faster but since low reaction temperatures are preferred, this experiment will not be discussed here. Nonetheless, *in situ* XRPD data collected at 750 °C under controlled atmosphere can be found in the Supplementary Information (Fig. S5).

Based on the results obtained from the *in situ* studies, information on H_2 dosing time as well as temperature was then

transferred to the *ex situ* synthesis of La₂CoO_{4±0} in a laboratory tube furnace. In order to probe the time required for H₂ dosing, 100 mg of pure LaCoO₃ (Fig. 8a, Fig. S6) were heated in a continuous N₂ flow to 650 °C. Then the gas changed to a mixture of 10% H₂/90% N₂ (with a flow rate of 10 mLn min⁻¹). Fig. 8 shows the *ex situ* XRPD patterns and the corresponding qualitative phase analyses. It is evident that the formation of La₂CoO_{4±0} is influenced significantly by H₂ dosing time. Already after 10 min, 68 wt% La₂CoO_{4±0} and 4 wt% CoO have formed. 28 wt% LaCoO₃ remained (Fig.8b, Fig. S7). Increasing dosing time to 15 min leads to about 78 wt% La₂CoO_{4±0}, CoO (5 wt%), and metallic Co (2 wt%), and 15 wt% remaining LaCoO₃ (Fig. 8c, Fig.S8). After 17 min dosing LaCoO₃ is completely reduced and the phase composition has changed to 88 wt% La₂CoO_{4±0}, 7 wt% CoO and 5 wt% metallic Co (Fig. 8d, Fig. S9).



Figure 8. *Ex situ* XRPD patterns collected after reduction of LaCoO₃ in a tube furnace showing the influence of H₂ dosing time on the formation of La₂CoO_{4±5}. From bottom to top: (a) before dosing at r.t., after dosing at constant temperature (650 °C): (b) 10 min, (c) 15 min, (d) 17 min, and (e) 20 min. Crystal structure data for CoO were taken from ref [70].

The results for the samples reduced in a tube furnace confirm the data obtained by *in situ* XRD experiments. The formation of La₂CoO_{4±0} was completed at 650 °C for a given flow of hydrogen after about 15-20 min. Dosing H₂ for 20 min caused partial decomposition of the sample that is visible by small La₂O₃ reflections (Fig. 8e). From these results it can be concluded that

dosing of 10% H₂/90% N₂ (with a flow rate of 10 mLn min⁻¹) for 17 min is an upper limit for the successful formation of La₂CoO_{4±0} under the experimental conditions used in this work. Further dosing may cause a full decomposition and reduction of the product.



Figure 9. (a) STEM image of the sample obtained after reduction for 17 min and (b) overlay of the elemental distribution of La and Co as obtained by EDX for the same agglomerate (green La-Co phase, red Co-containing phase).

In order to investigate the distribution of La and Co after the reduction experiment, high resolution scanning transmission electron microscopy (STEM) was performed. The images demonstrate the formation of particles consisting mainly of Co (CoO and/or Co) on the surface of La₂CoO_{4±δ} (Fig. 9). An overlay of the element distribution determined by EDX analysis shows areas with a more homogeneous La-Co distribution (green) belonging to La₂CoO₄ and Co-containing (red) particles. EDX analyses of the particles shown in red reveal that they consist mainly of Co and/ or CoO.

Conclusions

In this work, we present the design of a practical low temperature synthesis method for an RP-type layered La2CoO4±0 perovskite. Starting from LaCoO₃, a stoichiometric reduction reaction to La_2CoO_{4\pm\delta}, CoO and/or metallic Co takes place. In this respect, in situ XRPD played a key role for the identification of optimal synthesis parameters and provided a direct insight into the formation of $La_2CoO_{4\pm\delta}$. Starting from $LaCoO_3$, the formation of $La_2CoO_{4\pm\delta}$ was found to be completed at 650 °C in less than 30 min under in situ reactions conditions while at lower temperatures intermediates are formed as by-phases. The presence of intermediate phases caused by too low reaction temperatures was shown to destabilize $La_2CoO_{4\pm\delta}$. Additionally, for a successful reduction, an appropriate amount of hydrogen has to be calculated. Too high amounts of hydrogen cause excessive reduction of the RP phases and La_2O_3 and Co are formed. Using hydrogen already at the start of heating will also lead to a complete decomposition of the perovskites.

The *ex situ* synthesis experiments in a tube furnace showed that the formation of La₂CoO_{4±0} is a matter of hydrogen dosing time at constant temperature. The formation of La₂CoO_{4±0} was achieved at 650 °C with a defined hydrogen flow rate after relatively short time. We found that the formation of La₂CoO_{4±0} was completed in less than 20 min, while further dosing caused partial decomposition of the sample. If the presence of CoO

and/or Co does not negatively affect the properties of the material for a specific application, the low temperature synthesis reported in this paper is more convenient and practical compared to what has been reported elsewhere for the synthesis of polycrystalline La₂CoO_{4±0}.

Nonetheless, it is important to note that the crystal structure of $La_2CoO_{4\pm\delta}$ is governed by temperature treatment as well as oxygen stoichiometry, as discussed before. From XRPD data, it is very difficult to assign the oxygen stoichiometry for the *in situ* and the *ex situ* synthesized $La_2CoO_{4\pm\delta}$ in the present work. As a consequence, determination of the oxygen stoichiometry using neutron diffraction is mandatory, although the mobility of oxygen ions is pronounced at high temperatures which can make the analysis of *in situ* diffraction data of $La_2CoO_{4\pm\delta}$ rather difficult.

Experimental Section

Synthesis of LaCoO₃

Hard templating method was used as illustrated in Fig. 10. A commercial porous carbon (Carbotech, Rütgers 1407) with a specific surface area of 1200 m²g⁻¹ and a pore volume of 0.81 cm³g⁻¹ was used as the template. The metals were introduced into the pores of the carbon host via hard templating method, as described by Schwickardi and co-workers.^[71, 72] The details regarding the amounts and the concentrations of the metal nitrate precursors are provided in Table 1. In brief, 5 g of porous carbon was impregnated with solutions of the mixed precursors upon continuous stirring. The impregnated sample was first dried overnight at 50 °C and then calcined in air in a muffle furnace according to a fixed temperature program. First, the samples were heated to 350 °C (heating rate of 2 °C min⁻¹) and kept at this temperature for 2 h. Then, the temperature was increased to 700 °C (heating rate of 0.5 °C min⁻¹) and the sample was left in the furnace to cool to room temperature.



Figure 10. The synthesis scheme used for the production of LaCoO₃: hard-templating method using porous carbon (represented by the gray balls) as the template. Impregnated carbon was dried at 50 °C overnight in air and subsequently calcined at 700 °C for 20 min to obtain the product.

Table 1. Details about the metal nitrate precursors.						
Precursor	Supplier	Purity (%)	Molecular weight (gmol ⁻¹)	Molar concentration of the aqueous solution (mol L ⁻¹)		
La(NO ₃) ₃ .6H ₂ O [a]	Fluka Chemika	≥99.0	433.02	2.65		
Co(NO ₃) ₂ .6H ₂ O	Sigma- Aldrich	>98	291.03	3.75		

[a] 1. 898 mL, [b] 1.342 mL: Corresponding amounts of the aqueous solutions used for 5 g of porous carbon.

Bulk synthesis of La2CoO4±δ

100 mg of the as-synthesized LaCoO₃ was heated in a tube furnace from 25 to 650 °C in a continuous N₂ flow (heating rate of 20 °C min⁻¹). At 650 °C, 10 mLn min⁻¹ of a 10% H₂/90% N₂ gas mixture was flushed into the furnace at constant temperature. The H₂/N₂ gas mixture was dosed for various time periods, i.e., 10, 15, 17 and 20 min, in order to evaluate the influence of dosing time on the products. A fresh sample was used for each experiment. After dosing, the sample was cooled to room temperature under pure N₂ gas.

Characterization

An Anton Paar XRK900 reaction chamber mounted on a PANalytical X'Pert Pro diffractometer working with CuK $\alpha_{1,2}$ radiation ($\lambda = 1.5406$ Å) was used for the heating experiments. The powder sample was placed on a MACOR sample holder with 10 mm diameter. Data were collected in Bragg-Brentano geometry. A secondary monochromator was mounted on the diffractometer. Data of the starting compound were collected at 25 °C under pure N2 gas with 100 s per step with a step width of 0.0167° and a 20 range from 15 to 80°. Data were collected with an X'Celerator real-time multi-strip position sensitive detector (PSD). The assynthesized sample was heated under pure N2 atmosphere to 550 °C, 650 °C, and 750 °C with a heating rate of 20 °Cmin⁻¹. Once the desired temperatures were reached, 10 mLn min⁻¹ of 10% H₂/90% N₂ gas mixture was dosed to the sample for a defined time period at constant temperature. Data were collected continuously with 100 s per step in a 20 range from 28 to 40° with a step width of 0.0334°. Each pattern was recorded for 5 min. After that H_2 gas was switched off and pure N_2 was flushed through the reaction chamber during the rest of the experiment. In situ XRPD data were also collected after cooling to 25 °C with 100 s per step with a step width of 0.0167° and a 20 range from 15 to 80°.

Data of the *ex situ* synthesized La₂CoO_{4+δ} powder were collected on a STOE diffractometer in transmission geometry with monochromatic Mo radiation ($\lambda = 0.7093$ Å). The instrument was equipped with a primary Ge(111) monochromator. Data were collected using a Mythen 1K detector for 20 s per step in a 20 range from 5 to 50°. The sample was sealed in a 0.5 mm (Ø) borosilicate glass capillary.

Scanning Transmission Electron Microscopy (STEM) was performed with a Hitachi HD-2700 instrument (CS-corrected dedicated STEM, 200 kV, Cold FEG) to which an Energy Dispersive X-ray Spectrometer (EDX) is attached (EDAX Octane T Ultra W 200mm2 SDD, TEAM-Software). The as-made sample was analysed using a HITACHI S-5500 microscope operating at 30 kV. Elemental analysis was performed using a Thermo Fisher Scientific EDX system (NORAN[™] System 7) with an UltraDry EDS detector. The powder sample was embedded in Spurr-resin and sectioned in slices of 30-50 nm thick. The sample was measured on a Cu grid with a lacey carbon film.

 N_2 gas adsorption-desorption isotherms of the as-synthesized $LaCoO_3$ were measured using the automated gas sorption system (Quantachrome NOVA 3200e apparatus). The sample was outgassed at 90 °C for about 24 h before the measurement. The measurement was performed using N_2 gas at liquid N_2 temperature and the data were analyzed according to the Brunauer-Emmett-Teller (BET) method.

Data visualization and analysis

The simulation and visualization of crystal structures were performed using the Diamond software.^[73] The reference crystallographic data were obtained from the Inorganic Crystal Structure Database (ICSD). The references are provided in the figure captions. Rietveld refinements were performed with TOPAS5.^[74]

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FULL PAPER

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FULL PAPER

In this work, we present the low temperature formation of (RP)-type Ruddlesden-Popper $La_2CoO_{4\pm\delta}$ layered perovskite using in situ X-ray powder diffraction (XRPD) performed under controlled gas atmosphere. After determination of the hydrogen dosing time and required temperature for а successful synthesis of the RP-type perovskite, we could achieve the stoichiometric reduction to the RP phase and CoO and/or Co⁰ already at 650 °C.



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Low Temperature Formation of Ruddlesden-Popper-Type Layered $La_2CoO_{4\pm\delta}$ Perovskite Monitored via *in situ* X-ray Powder Diffraction