Research Article

Preparation of Nanosized LaCoO$_3$ through Calcination of a Hydrothermally Synthesized Precursor

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A method for obtaining nanosized LaCoO$_3$ crystals from calcination of a precursor powder synthesized by a hydrothermal route is reported. Details concerning the evolution of the microstructure and formation mechanism of the perovskite phase were studied by powder X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy, Raman spectroscopy, and thermal analysis. It was found that the morphology of the sample progressively turns from a mix of fibers and rods to interconnected nanocrystals. It is determined that LaCoO$_3$ phase is produced by a reaction of cobalt and lanthanum oxides, the latter produced by a two-step dehydration process of La(OH)$_3$. Finally, it was found that nearly stoichiometric LaCoO$_3$ nanocrystals can be obtained at temperatures as low as 850°C. Nevertheless, whether higher calcination temperatures are used, appropriate reaction times and a controlled atmosphere are required in order to avoid formation of lanthanum carbonates and high density of lattice defects.

1. Introduction

Perovskite-type oxides (ABO$_3$; A: rare earth; B: transition metal) constitute an important class of strategic materials because of their electrical, mechanical, optical, magnetic, and catalytic properties [1–5]. This class of oxides has been used to fabricate efficient electrodes for solid oxide fuel cells [6–10], chemical sensors [11–14], oxygen-permeating membranes [15], and thermoelectric devices [16] as well as catalysts for combustion of CO, hydrocarbons, and NO$_x$ decomposition [17–21]. However, in order to incorporate these compounds in such technologies, it is required to obtain high-quality materials with controlled stoichiometry and microstructure, since the presence of large amounts of secondary phases frequently hinders its functional properties; therefore, single-phase samples are preferred.

Among perovskite-type oxides, rhombohedral LaCoO$_3$ exhibits interesting electrical and electrocatalytic properties. Nevertheless, it has been demonstrated that its microstructure, catalytic performance, and electronic and ionic conductivity depend strongly on the preparation method, which ultimately determines its potential applications [22]. For example, developing of reliable methods for obtaining nanosized LaCoO$_3$ powders with large specific surface area to be used as electrocatalysts is an active research field nowadays [23].

Often LaCoO$_3$ compound is produced by conventional solid state reaction of pure lanthanum and cobalt oxides, carbonates, and/or oxalates at calcination temperatures higher than 1200°C [24–26]. Although nearly single-phase LaCoO$_3$ samples have been obtained through this method, they are constituted by micrometric grains with composition gradients. Therefore, sintering at higher temperatures is required to promote homogeneous composition; nevertheless, the structural stability and the single-phase nature of the sample could be compromised. In order to overcome these difficulties,
extensive investigations have been performed for preparing finer and more homogeneous LaCoO₃ samples using alternative approaches. In this regard, low-temperature chemical routes such as coprecipitation [27], decomposition of heteronuclear complex [28–31], mechanochemical synthesis [32], combustion method [33], sol-gel [34], and pechini-type polymerizable complex [35] have been reported for obtaining pure LaCoO₃ nanopowders with well-defined chemical composition. However, often the properties of the obtained materials are tremendously sensitive to the experimental variables, and most of these processes are either complex or expensive, limiting their large-scale production. Thus, development of an inexpensive and reliable method for preparing pure phase and nanosized LaCoO₃ is still a challenge [36]. The recent approaches, especially wet-techniques, seek for a low-temperature route for synthesizing fine precursor powders, which allow obtaining pure phase samples after calcination [4]. Among them, the hydrothermal method seems to be a promising technique, since particles with controlled size and shape can be produced on tuning the synthesis parameters, such as pH, temperature, reaction time, chemical reagents concentration, and type of solvent [37]. Nevertheless, in order to gain control on the resulting physical properties, detailed understanding of the formation of LaCoO₃ phase from the obtained precursors is highly desirable.

The aim of this research is to explore an alternative preparation method for obtaining LaCoO₃ nanocrystals, which may contribute on the developing of a large-scale production route of nanosized LaCoO₃ with controlled properties. For this purpose, hydrothermal method was used to synthesize a precursor nanopowder that is calcined under air atmosphere. This route allows obtaining a homogeneous mix of precursor phases with large contact area. Therefore, lower calcination temperature is used to obtain the desired compound and composition gradients in the resulting material might be reduced.

2. Experimental Procedure

Lanthanum (III) nitrate hexahydrate (La(NO₃)₃·6H₂O; Aldrich, 99.99%), cobalt (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O; Aldrich, ≥98%), sodium hydroxide (NaOH; Baker, 98.1%), and ammonium hydroxide (NH₄OH; Baker, 28.0–30.0%) were purchased commercially and used as received without further purification. Briefly, an alkaline aqueous solution was prepared by mixing 80 mL of pure deionized water (Meyer, >18 MΩ cm) and 3.2 mL of NH₄OH as complexing agent [38, 39]. To the previous solution, 2.24 g of La(NO₃)₃·6H₂O and 1.50 g of Co(NO₃)₂·6H₂O were added in a stoichiometric molar ratio (1:1). Then, NaOH was dissolved in the mixture to raise pH to ~12.5 in order to promote deprotonation of ammonium and as precipitating agent. Then, the reaction solution was sealed in a stainless steel reactor with Teflon liner and heated up to 218°C in a muffle furnace for 48 h. Once the solution was cooled down to room temperature, the solid product was extracted by decantation, washed with deionized water several times, and vacuum filtered. The obtained precursor powder was analyzed by thermogravimetry and differential scanning calorimetry (TGA-DSC; NETZSCH STA 449F3).

Finally, the hydrothermally synthesized precursor powder was placed in an alumina crucible, introduced in a muffle furnace and heated for 3 h at the desired temperature under a nonprotective atmosphere (air). In order to study the formation process of LaCoO₃ phase several calcination temperatures were used, namely, 380, 490, 740, 850, 950, and 1050°C. These temperatures were chosen on the basis of the main thermal events revealed by the TGA-DSC analysis of the precursor powder.

The obtained samples were characterized by powder X-ray diffraction (XRD; Bruker D8 Discover Diffractometer using Cu-Kα radiation), scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS; Tescan Mira 3 electron microscope equipped with a Bruker Spirit X-ray detector), and micro-Raman spectroscopy using He-Ne laser as excitation source (λexc = 633 nm) in backscattering configuration (µ-BS; LabRAM HR-Olympus Micro Raman system).

3. Results and Discussion

3.1. The Precursor Powder. The X-ray pattern of the precursor powder obtained after the hydrothermal reaction reveals that it is composed of cubic Co₂O₄ (JCPDS 42-1467) and hexagonal La(OH)₃ (JCPDS 36-1481) phases (see Figure 1). No trace of LaCoO₃ was detected. Although La and Co ions could form metal-ammonia complexes, the difference of their oxidation-reduction potentials does not allow obtaining LaCoO₃ directly by coprecipitation. It is worth noting that Co(OH)₂ is not present in the precursor powder. This is because at room temperature Co³⁺ and OH⁻ species which react to produce a blue-green α-Co(OH)₂ precipitate, which spontaneously transforms to light pink β-Co(OH)₂ phase with higher thermodynamic stability. Then, at 153°C through a self-supported topotactic transformation, Co(OH)₂ produces Co₂O₃ [40–43]. On this basis, it is proposed that Co₂O₃ and La(OH)₃ precipitate from the aqueous solution following the chemical reactions:

\[
\text{La}^{3+} (aq) + 3\text{OH}^- (aq) \rightarrow \text{La(OH)}₃ (s) \quad (1)
\]

\[
\text{Co}^{2+} (aq) + 2\text{OH}^- (aq) \rightarrow \text{Co(OH)}₂ (s) \quad (2)
\]

\[
6\text{Co(OH)}₂ (s) + \text{O}_2 (g) \xrightarrow{\Delta} 2\text{Co₃O₄} (s) + 6\text{H}_2\text{O} (l) \quad (3)
\]

The SEM micrograph of the precursor powder is characterized by two clearly different morphologies (see Figure 2): fibers of around 100 nm in diameter and thicker hexagonal rods. These morphologies are associated with the cubic Co₂O₃ and hexagonal La(OH)₃ phases, respectively, as their habits suggest. In order to support the latter assumption, a selected area elemental analysis was performed. High content of Co was detected at regions corresponding to agglomerates of fibers (at.% La : Co : O 8.73 : 11.09 : 80.18); conversely, La-rich regions were found to be associated with the rod-like structures (at.% La : Co : O 14.44 : 4.71 : 80.85).
3.2. LaCoO₃ Nanocrystals: Microstructure and Formation Mechanism. The formation of the LaCoO₃ phase from calcination of the precursor powder was investigated using XRD technique. The X-ray patterns of the precursor calcined at different temperature are shown in Figure 1. On comparing the diffractograms of the precursor and that of the sample calcined at 380°C, it can be noted that the relative intensity of the reflections associated with hexagonal La(OH)₃ phase decreases notoriously, suggesting its thermal decomposition. Oppositely, the X-ray peaks of cubic Co₃O₄ remain sharp, indicating its thermal stability at this calcination temperature. As the calcination temperature increases up to 490°C, the peaks associated with La(OH)₃ are absent and some peaks located at 21.66, 26.89, and 29.17° are observed instead. These
peaks were identified as X-ray reflections coming from (T01), (100), and (011) planes of monoclinic LaO(OH) (JCPDS 19-0656), respectively. The decrease of the intensity of the X-ray peaks corresponding to La(OH)_3 indicates that LaO(OH) is generated due to its thermal decomposition.

When the precursor powder is calcined at 740°C, two new phases appear, hexagonal La_2O_3 (JCPDS 5-0602) and rhombohedral LaCoO_3 (JCPDS 48-0123). At this stage, LaO(OH) phase is not detected and the amount of Co_3O_4 has diminished. These results suggest that as the temperature rises LaO(OH) is progressively transformed to La_2O_3, which along with Co_3O_4 produces LaCoO_3 through a solid state reaction.

Finally, when the calcination temperature is further increased (850–1050°C), the X-ray peaks of Co_3O_4 and La_2O_3 monotonously quench, whereas those of LaCoO_3 get stronger. No minority phase could be detected while 1050°C was set as the calcination temperature.

The evolution of the morphology of the precursor powder as the calcination temperature is increased was studied by electron microscopy. The SEM micrographs of the calcined samples are shown in Figure 2. Similar morphologies like that of the precursor powder were observed in the sample calcined at 380°C: fibers and rods, but the surface of the latter’s seems rough. As the calcination temperature increases up to 490°C, the morphology is quite different, the fibers have been shortened, the rods are almost absent, and very small grains of tens of nanometers are observed. In the micrograph corresponding to the sample calcined at 740°C no rod-like structure was observed and the fibers seem to be merged, generating a granular structure with mean particle size of about 100 nm. Then, as the calcination temperature increases, the size of the grains does as well. It is proposed that the former grains merge to generate larger crystals under an annealing process.

In order to study the structural and vibrational properties further, the obtained samples were analyzed by micro-Raman spectroscopy. Figure 3 shows the Raman spectra of the precursor and the calcined samples. In the spectrum corresponding to the precursor powder, five peaks centered at 197, 485, 525, 623, and 694 cm\(^{-1}\) are observed. These frequencies match with the vibrational modes of cubic Co_2O_3 structure. The irreducible representation of the phonon modes of cubic Co_2O_3 at the center of the Brillouin zone is expressed by the equation:

\[
\Gamma = A_\text{lg} + F_\text{g} + F_\text{lg} + 3F_\text{g} + 5F_\text{1u} + 2A_\text{2u} + 2E_\text{u} + 2F_\text{2g}
\]

where \(A_\text{lg} \), \(F_\text{g} \), \(F_\text{lg} \), and \(F_\text{2g} \) modes are Raman active, four \(F_\text{1u} \) modes are infrared active, and the other is an acoustic mode \([44]\); the remaining vibrations are silent modes. While the peak at 694 cm\(^{-1}\) (\(A_\text{lg} \)) is attributed likely to vibrations of octahedral oxygen ions, \(E_\text{g} \) (485 cm\(^{-1}\)) and \(F_\text{2g} \) modes (197, 525, and 623 cm\(^{-1}\)) are related to combined vibrations of tetrahedral and octahedral oxygen \([45]\). Interestingly, regardless of the fact that the strongest X-ray reflection detected for the precursor powder corresponds to hexagonal La(OH)_3 (see Figure 1), no Raman active mode reported for this phase was observed (281, 336, and 451 cm\(^{-1}\)) \([46]\), indicating weak photon-phonon coupling.

The Raman spectrum of the sample calcined at 380°C is similar to that of the precursor powder. However, as the calcination temperature is increased (490°C), some weak peaks located at 122, 134, 310, 344, 382, and 425 cm\(^{-1}\) can be resolved. All these peaks were identified as Raman active modes of the monoclinic LaCoO_3 phase generated from thermal decomposition of La(OH)_3 \([47]\). Then, when the calcination temperature is set at 740°C, the peaks assigned to LaCoO_3 disappear, those related with Co_3O_4 and get broader, and a peak at 157 cm\(^{-1}\) along with a broadband centered at 640 cm\(^{-1}\) emerges. The broadband suggests the presence of a new phase with high content of structural defects. According to the X-ray measurements, both Raman signals might be associated with the formation of LaCoO_3. The irreducible representation of the phonon modes of the rhombohedral distorted perovskite structure of LaCoO_3 at \(\Gamma \) point is given by \([48]\):

\[
\Gamma = 2A_\text{1u} + 3A_\text{2g} + A_\text{1g} + 3A_\text{2u} + 4E_\text{u} + 5E_\text{g}.
\]

(5)

Among these vibrational modes, \(A_\text{1g} \) and \(E_\text{g} \) are Raman active, and \(A_\text{2u} \) and \(E_\text{u} \) are infrared active; the other modes are silent. Notoriously, neither \(A_\text{1g} \) nor \(E_\text{u} \) modes could be assigned to the observed signals. Kozlenko et al. \([49]\) acquired similar Raman spectra from their LaCoO_3 samples, attributing some peaks to silent modes activated due to lattice disorder. According to Ishikawa et al. \([50]\), while the Raman signal at 157 cm\(^{-1}\) is assigned to \(A_\text{2g} \) stretching mode of La atoms, the broadband at 640 cm\(^{-1}\) corresponds to \(A_\text{2g} \) breathing mode.

The Raman spectrum of the sample calcined at 850°C has only two peaks at 158 and 647 cm\(^{-1}\), corresponding to \(A_\text{2g} \) modes mentioned above. None of the Raman peaks associated with cubic Co_2O_3 phase are now observed, indicating
that Co has been incorporated completely in the perovskite structure. When the calcination temperature is increased (950°C), the low-frequency peak quenches, and the broadband shifts to higher frequencies (652 cm\(^{-1}\)), suggesting some kind of change in LaCoO\(_3\) lattice. When the calcination temperature is increased further (1050°C), the Raman spectrum is quite similar.

In order to elucidate the evolution of the chemical composition of samples obtained at different calcination temperature, an elemental analysis was performed. Table 1 summarizes the obtained results. It can be observed that in the range of 380–850°C the amount of oxygen decreases monotonously, indicating the thermal decomposition of the metal hydroxide. When the precursor powder was calcined at 850°C, the resulting elemental composition (La : Co : O at.% 20.95 : 22.02 : 57.02) corresponds nearly to that of stoichiometric LaCoO\(_3\). The slight deviation may be related to the remaining metal oxides traces. According to the X-ray measurements, the samples calcined at 950 and 1050°C are practically monophasic; however, the content of oxygen decreases dramatically in comparison with the sample obtained at 850°C. It is attributed to the reduction of LaCoO\(_3\) by atmospheric nitrogen producing NO\(_x\) gas [51]. The reduction of the surface of LaCoO\(_3\) grains might generate oxygen vacancies, which in turns migrate into the grain at such high temperatures, resulting in LaCoO\(_3\) lattice with high content of point defects.

The thermal transformations of the obtained precursor powder were studied by DTA-TGA (Figure 4). Initially, a gradual weight loss around 2.3% is observed up to ~250°C; it is associated with the release of adsorbed and structural water from the precursor powder. As the temperature increases two successive endothermic reactions develop: the first starts at 300°C, whereas the second initiates at 390°C, leading a weight loss of ~6.1 and ~2.0%, respectively. These thermal events are associated with two-step dehydration decomposition of lanthanum hydroxide to generate lanthanum oxide, having lanthanum oxide hydroxide as an intermediate product, according to the chemical reactions [52, 53]:

\[
\text{La(OH)}_3 (s) \xrightarrow{\Delta} \text{LaO(OH)} (s) + \text{H}_2\text{O} (g) \quad (6)
\]

\[
2\text{LaO(OH)} (s) \xrightarrow{\Delta} \text{La}_2\text{O}_3 (s) + \text{H}_2\text{O} (g) \quad (7)
\]

Table 1: Phase and elemental composition of the precursor powder and the samples obtained at different calcination temperature.

| Temperature (°C) | Phase composition (XRD) | La:Co:O at.% (EDS average) |
|------------------|-------------------------|----------------------------|
| Precursor        | *La(OH)_3 + Co_3O_4     | 12.16 : 13.73 : 73.01      |
| 380              | La(OH) + LaO(OH) + *Co_3O_4 | 11.48 : 14.19 : 74.33      |
| 490              | *LaO(OH) + Co_3O_4       | 20.08 : 22.38 : 57.54      |
| 740              | La_2O_3 + Co_3O_4 + *LaCoO_3 | 20.69 : 23.50 : 55.81      |
| 850              | La_2O_3 + Co_3O_4 + *LaCoO_3 | 20.95 : 22.02 : 57.02      |
| 950              | La_2O_3 + *LaCoO_3       | 29.47 : 26.32 : 44.21      |
| 1050             | *LaCoO_3                | 30.37 : 27.85 : 41.78      |

* Majority phase.

Figure 4: TGA-DSC thermograms of the precursor powder. The calcination temperature used for obtaining each sample is shown for reference: (a) 380, (b) 490, (c) 740, (d) 850, (e) 950°C, and (f) 1050°C.

Neumann and Walter [54] have found similar results; however, they determined by means of high-temperature X-ray diffraction that La(OH) phase persists even at temperatures as high as 550°C, when La(OH) is completely transformed to La_2O_3.

Then as the temperature reaches 470°C, TGA curve becomes less pronounced, and a weight loss of ~1.5% throughout the interval of 470–700°C is registered. This feature is attributed to the ongoing dehydration of LaO(OH) and formation of LaCoO_3 from a solid state reaction of lanthanum and cobalt oxides, as the following equation states:

\[
3\text{La}_2\text{O}_3 (s) + 2\text{Co}_3\text{O}_4 (s) + \frac{1}{2} \text{O}_2 (g) \xrightarrow{\Delta} 6\text{LaCoO}_3 (s) \quad (8)
\]

Finally, a weight loss of 0.4% associated with an endothermic reaction is detected at 802°C. Ozawa et al. [55] agree with the proposed two-step decomposition of La(OH)_3; nevertheless, they also found a third weight loss steep associated with an endothermic event at around 800°C during the thermal decomposition of a pure La(OH)_3 sample. These authors attributed this event to the decomposition of a lanthanum carbonate, possibly LaCO_3OH produced by exposition of La_2O_3 to atmospheric CO_2. Since La_2O_3 is present in the reaction mixture below 800°C according to the X-ray results, we attribute the same origin to this endothermic event. No significant thermic effect was registered at higher temperatures.

4. Conclusions

The microstructure and formation mechanism of LaCoO_3 crystals prepared from calcination of a powder precursor (CoO_4 + La(OH)_3) synthesized by a hydrothermal route were studied. It was found that the morphology of the sample progressively turns from a mix of fibers and rods to interconnected nanograins when the calcination temperature is set at 850°C. However, if the calcination temperature is increased microgains are obtained instead. It is determined that LaCoO_3 phase is produced by a reaction of cobalt and lanthanum oxides, the latter produced by a two-step dehydration
process of \( \text{La(OH)}_3 \). Although the X-ray measurements suggest the formation of well-crystalized \( \text{LaCoO}_3 \) phase at calcination temperatures above 900°C, the Raman spectroscopy and the elemental analysis indicate that the resulting \( \text{LaCoO}_3 \) contains a high density of point defects. It is proposed that nanosized stoichiometric \( \text{LaCoO}_3 \) can be produced by calcination of a mixture of \( \text{Co}_3 \text{O}_4 \) and \( \text{La(OH)}_3 \) powders at temperatures as low as 850°C. Nevertheless, an appropriate reaction time and an oxygen-rich atmosphere are required, in order to avoid reduction by molecular nitrogen and formation of lanthanum carbonates.

**Competing Interests**

The authors declare that they have no competing interests.

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**References**

[1] S. Ghosh, S. Dasgupta, A. Sen, and H. S. Maiti, “Low-temperature synthesis of nanosized bismuth ferrite by soft chemical route,” *Journal of the American Ceramic Society*, vol. 88, no. 5, pp. 1349–1352, 2005.

[2] N. Q. Minh, “Ceramic fuel cells,” *Journal of the American Ceramic Society*, vol. 76, no. 3, pp. 563–588, 1993.

[3] A. E. Giannakas, A. K. Ladavos, and P. J. Pomonis, “Preparation, characterization and investigation of catalytic activity for NO + CO reaction of \( \text{LaMnO}_3 \) and \( \text{LaFeO}_3 \) perovskites prepared via microemulsion method,” *Applied Catalysis B: Environmental*, vol. 49, no. 3, pp. 147–148, 2004.

[4] M. Popa, J. Frantti, and M. Kakihana, “Characterization of \( \text{LaMeO}_3 \) (Me: Mn, Co, Fe) perovskite powders obtained by polymerizable complex method,” *Solid State Ionics*, vol. 154-155, pp. 135–141, 2002.

[5] X. Qi, J. Zhou, Z. Yue, Z. Gui, and L. Li, “Auto-combustion synthesis of nanocrystalline \( \text{LaFeO}_3 \),” *Materials Chemistry and Physics*, vol. 78, no. 1, pp. 25–29, 2003.

[6] M. B. Phillipps, N. M. Sammes, and O. Yamamoto, “The structure and conductivity of \( \text{LaMn}_{1−x}\text{Cr}_x\text{O}_3 \) and (\( \text{La}, \text{A}\) )\(_{1−x}\text{Mn}_{1−x}\text{Cr}_x\text{O}_3 \) (\( \text{A} = \text{Sr, Ca} \)) as air cathodes in solid oxide fuel cells,” *Journal of Materials Science*, vol. 31, no. 7, pp. 1689–1692, 1996.

[7] S. P. Jiang, L. Liu, K. P. Ong, P. Wu, J. Li, and J. Pu, “Electrical conductivity and performance of doped \( \text{LaCrO}_3 \) perovskite oxides for solid oxide fuel cells,” *Journal of Power Sources*, vol. 176, no. 1, pp. 82–89, 2008.

[8] X. F. Ding, Y. Liu, L. Gao, and L. Guo, “Effects of cation substitution on thermal expansion and electrical properties of lanthanum chromites,” *Journal of Alloys and Compounds*, vol. 425, no. 1-2, pp. 318–322, 2006.

[9] S. Srinivasan, B. B. Davé, K. A. Murugesamoothi, A. Par tasarathy, and A. J. Appleby, “Overview of fuel cell technology,” in *Fuel Cell Systems*, L. J. M. J. Blomen and M. N. Mugerwa, Eds., pp. 57–72, Plenum Press, New York, NY, USA, 1993.

[10] M. Shiono, K. Kobayashi, T. L. Nguyen et al., “Effect of \( \text{CeO}_2 \) interlayer on \( \text{ZrO}_2 \) electrolyte/\( \text{La(Sr)}\text{CoO}_3 \) cathode for low-temperature SOFCs,” *Solid State Ionics*, vol. 170, no. 1-2, pp. 1–7, 2004.

[11] M. A. Peña and J. L. G. Fierro, “Chemical structures and performance of perovskite oxides,” *Chemical Reviews*, vol. 101, no. 7, pp. 1981–2017, 2001.

[12] D. T. V. Anh, W. Othilus, and P. Bergved, “Sensing properties of perovskite oxide \( \text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3 \) obtained by using pulsed laser deposition,” *Sensors and Actuators, B: Chemical*, vol. 103, no. 1-2, pp. 165–168, 2004.

[13] X. Liu, B. Cheng, J. F. Hu, H. W. Qin, and M. H. Jiang, “Semi-conducting gas sensor for ethanol based on \( \text{LaMg}_{0.9}\text{Fe}_{0.1}\text{O}_3 \) nanocrystals,” *Sensors and Actuators, B: Chemical*, vol. 129, no. 1, pp. 53–58, 2008.

[14] L.-B. Kong and Y.-S. Shen, “Gas-sensing property and mechanism of \( \text{Ca}_{1−x}\text{La}_{x}\text{FeO}_3 \) crystals,” *Sensors and Actuators, B: Chemical*, vol. 30, no. 3, pp. 217–221, 1996.

[15] Y. Teraoka, H. M. Zhang, S. Furukawa, and N. Yamazoe, “Oxygen permeation through perovskite-type oxides,” *Chemistry Letters*, vol. 14, no. 11, pp. 1743–1746, 1985.

[16] A. Weidenkaff, R. Robert, M. Aguirre, L. Bocher, T. Lippert, and S. Canuelceu, “Development of thermonoelectric oxides for renewable energy conversion technologies,” *Renewable Energy*, vol. 33, no. 2, pp. 342–347, 2008.

[17] K.-S. Song, H. X. Cui, S. D. Kim, and S.-K. Kang, “Catalytic combustion of \( \text{CH}_4 \) and \( \text{CO} \) on \( \text{La}_{1−x}\text{Sr}_x\text{MnO}_3 \) perovskites,” *Catalysis Today*, vol. 47, no. 1–4, pp. 155–160, 1999.

[18] M. O’Connell, A. K. Norman, C. F. Hüttermann, and M. A. Morris, “Catalytic oxidation over lanthanum-transition metal perovskite materials,” *Catalysis Today*, vol. 47, no. 1–4, pp. 123–132, 1999.

[19] R. Doshi, C. B. Acock, and J. J. Carberry, “Effect of surface area on \( \text{CO} \) oxidation by the perovskite catalysts \( \text{La}_{1−x}\text{Sr}_x\text{MnO}_3 \) (\( \text{M} = \text{Co, Cr} \)),” *Catalysis Letters*, vol. 18, no. 4, pp. 337–343, 1993.

[20] R. J. H. Voorhoeve, J. P. Remelika, L. E. Trimble, A. S. Cooper, F. J. Disalvo, and P. K. Gallagher, “Perovskite-like \( \text{La}_{1−x}\text{K}_x\text{MnO}_3 \) and related compounds: Solid state chemistry and the catalysis of the reduction of \( \text{NO} \) by \( \text{CO} \),” *Journal of Solid State Chemistry*, vol. 14, no. 4, pp. 395–406, 1975.

[21] F. Gaillard, X. Li, M. Uray, and P. Vernoux, “Electrochemical promotion of propene combustion in air excess on perovskite catalyst,” *Catalysis Letters*, vol. 96, no. 3–4, pp. 177–183, 2003.

[22] L. Radev, L. Pavlova, B. Samunewa et al., “Sol-gel synthesis and structure of \( \text{La}_2\text{O}_3–\text{CoO-SiO}_2 \) powders,” *Processing and Application of Ceramics*, vol. 2, no. 2, pp. 103–108, 2008.

[23] F. M. Figueiredo, J. R. Frade, and F. M. B. Marques, “Electrical and electrochemical behaviour of \( \text{LaCoO}_3+x\text{La}_x\text{Zr}_y\text{Y}_3 \text{O}_{3+x} \)-based electrode materials,” *Solid State Ionics*, vol. 118, no. 1-2, pp. 81–87, 1999.

[24] G. Thornton, B. C. Tofield, and A. W. Hewat, “A neutron diffraction study of \( \text{LaCoO}_3 \) in the temperature range 4.2<\( T \)<1248 K,” *Journal of Solid State Chemistry*, vol. 61, no. 3, pp. 301–307, 1986.

[25] Y. Wang, Y. Sui, P. Ren et al., “Correlation between the structural distortions and thermochemical characteristics in \( \text{La}_{1−x}\text{A}_x\text{CoO}_3 \) (\( \text{A} = \text{Ca and Sr} \)),” *Inorganic Chemistry*, vol. 49, no. 7, pp. 3216–3223, 2010.

[26] M. Anzai, H. Kawakami, M. Saito, and H. Yamamura, “Thermoelectric properties of \( p \)-type perovskite compounds \( \text{LaCoO}_3 \) systems containing the \( A \)-site vacancy,” *IOP Conference Series: Materials Science and Engineering*, vol. 18, Article ID 142005, 2011.
[27] A. D. Jadhav, A. B. Gaikwad, V. Samuel, and V. Ravi, "A low temperature route to prepare LaFeO$_3$ and LaCoO$_3$,“ Materials Letters, vol. 61, no. 10, pp. 2030–2032, 2007.

[28] S. Nakayama, M. Okazaki, Y. L. Aung, and M. Sakamoto, “Preparations of perovskite-type oxides LaCoO$_3$ from different methods and their evaluation by homogeneity, sinterability and conductivity,” Solid State Ionics, vol. 158, no. 1-2, pp. 133–139, 2003.

[29] Y. Zhu, R. Tan, T. Yi, S. Ji, X. Ye, and L. Cao, “Preparation of nanosized LaCoO$_3$ perovskite oxide using amorphous heteronuclear complex as a precursor at low temperature,” Journal of Materials Science, vol. 35, no. 21, pp. 5415–5420, 2000.

[30] D. Berger, V. Fruth, I. Jitaru, and J. Schoonman, “Synthesis and characterization of La$_{1-x}$Sr$_{x}$CoO$_3$ with large surface area,” Materials Letters, vol. 58, no. 19, pp. 2418–2422, 2004.

[31] Y. Sadaoka, E. Traversa, and M. Sakamoto, “Preparation and structural characterization of perovskite-type La$_{1-x}$Ln$_{x}$CoO$_3$ by the thermal decomposition of heteronuclear complexes, La$_{1-x}$Ln$_{x}$(Co$_{1-y}$Ni$_y$)$_3$O$_7$: Sm and Ho,” Journal of Alloys and Compounds, vol. 240, no. 1-2, pp. 51–59, 1996.

[32] V. Szabo, M. Bassir, A. Van Neste, and S. Kaliaguine, “Perovskite-type oxides synthesized by reactive grinding: part II: catalytic properties of La$_{1-x}$Fe$_x$O$_3$ in VOC oxidation,” Applied Catalysis B, vol. 37, pp. 175–180, 2002.

[33] L. Armelao, G. Bandoli, D. Barreca, M. Bettinelli, G. Bottaro, and A. Caneschi, “Synthesis and characterization of nanohydrated LaCoO$_3$ powders,” Surface and Interface Analysis, vol. 34, no. 1, pp. 112–115, 2002.

[34] G. Sinquin, C. Petit, J. P. Hindermann, and A. Kiennemann, “Study of the formation of LaMO$_3$ (M=Co, Mn) perovskites by propionates precursors: application to the catalytic destruction of chlorinated VOCs," Catalysis Today, vol. 70, no. 1–3, pp. 183–196, 2001.

[35] M. Popa, L. V. Hong, and M. Kakihana, “Nanopowders of LaMeO$_3$ perovskites obtained by a solution-based ceramic processing technique,” Physica B: Condensed Matter, vol. 327, no. 2–4, pp. 233–236, 2003.

[36] S. Farhadi and S. Sepahvand, “Microwave-assisted solid-state decomposition of La[Co(CN)$_6$]-5H$_2$O precursor: a simple and fast route for the synthesis of single-phase perovskite-type LaCoO$_3$ nanoparticles,” Journal of Alloys and Compounds, vol. 489, no. 2, pp. 586–591, 2010.

[37] K. Yamashita, K. V. Ramanujachary, and M. Greenblatt, “Hydrothermal synthesis and low temperature conduction properties of substituted ceria ceramics,” Solid State Ionics, vol. 81, no. 1-2, pp. 53–60, 1995.

[38] I. Rodriguez-Iznaga, A. Gómez, G. Rodríguez-Fuentes, A. Benítez-Aguilar, and J. Serrano-Ballán, “Natural clinoptilolite as an exchanger of Ni$^{2+}$ and NH$^{4+}$ ions under hydrothermal conditions and high ammonia concentration,” Microporous and Mesoporous Materials, vol. 53, no. 1–3, pp. 71–80, 2002.

[39] F. Fu and Q. Wang, “Removal of heavy metal ions from wastewaters: a review,” Journal of Environmental Management, vol. 92, no. 3, pp. 407–418, 2011.

[40] D. Ghosh, S. Giri, and C. K. Das, “Hydrothermal synthesis of platelet β-Co(OH)$_2$ and Co$_3$O$_4$: Smart electrode material for energy storage application,” Environmental Progress and Sustainable Energy, vol. 33, no. 3, pp. 1059–1064, 2014.

[41] X. Li, G.-L. Xu, F. Fu et al., “Room-temperature synthesis of Co(OH)$_2$ hexagonal sheets and their topotactic transformation into Co$_3$O$_4$: A new porous structure with enhanced lithium-ion storage properties,” Electrochimica Acta, vol. 96, pp. 134–140, 2013.
