Effects of high-energy kinetic milling conditions on the mechanochemically assisted synthesis of lanthanum cobalt oxide

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Abstract. This study presents an experimental investigation of the synthesis of perovskite-type lanthanum cobalt oxide (LaCoO3; LCO) powders using different mechanical milling approaches. The study explores the effects of processing parameters for planetary ball milling and attrition ball milling, including the employment of a wetting agent, milling rate, material of milling media and milling jar, and calcination temperature, on the resulting microstructure and phase composition of the obtained LCO powders. The main focus during the synthesis was to obtain a phase-pure powder with the minimum possible content of secondary phases. For planetary milling, dry milling conditions and calcination at 850 °C for 2 h turned out to be the most effective regime, yielding the highest LCO content and the lowest amounts of residual La_2O_3 and Co_3O_4 phases. In the case of attritor milling, phase-pure perovskite was successfully obtained using dry milling in a SiN-lined milling jar with ceramic balls and at a relatively low calcination temperature of 650 °C. Among the investigated mechanochemical milling approaches, attritor milling proved the most promising process, offering the greatest efficiency and scalability.

1. Background

Lanthanum cobalt oxide $LaCoO_3$ (LCO) is ABO_3-type perovskite well-known for its unique physical and chemical properties based on A-site and B-site atoms association. Being environmentally friendly, relatively accessible, and highly active in various redox reactions, LCO has proved its high application potential for environmental catalysis [1], [2], photocatalysis [3], catalytic oxidation [4], [5], [6], hydrogen purification [7], and cathode materials of oxide fuel cells [8], [9], [10]. As is well-known, the microstructure and physicochemical properties of perovskite powders are highly dependent on the synthesis method chosen. While traditional solvent-moderated synthesis routes, such as hydrothermal, sol-gel, or co-precipitation [11], [12], were widely used to prepare LCO perovskite powders, mechanically assisted synthesis routes based on high-energy kinetic milling have been rarely explored. Among the indirect mechanochemical synthesis, the report by Sompech et al. [13] can be mentioned, who used mechanochemically activated synthesis of LCO through planetary ball milling of $LaCl_3 \cdot 7H_2O$, $CoCl_2$, and Na_2CO_3 precursor powders. The mixture was milled at 300 rpm for 2 h in a Retsch PM 100 ball mill using a stainless-steel jar and stainless-steel balls. The obtained powder was subsequently calcinated at 600, 700, and 800 °C at a heating rate of 10 °C/min for 90 min. So far, only Ito et al. [14] reported a direct LCO synthesis in a planetary ball mill at 700 rpm, using zirconia balls and a zirconia pot.

Therefore, in this study, we aimed to fill the knowledge gap related to the preparation of LCO-based perovskites using the mechanochemical activation approaches. The main feature of the current work is the employment of two alternative grinding methods, namely planetary grinding and attrition milling, to clarify the effects of milling parameters on the resulting microstructure and phase composition of the obtained LCO powders. Among the studied milling parameters, the influence of wetting agent, milling rate, milling media and milling jar materials, and calcination temperature was considered in detail, with the focus on synthesizing phase-pure LCO.

2. Experimental

2.1. Initial materials

The rare-earth lanthanum oxide (La_2O_3; 99%; Nanoshel) and cobalt(II) hydroxide ($Co(OH)_2$; 99.9%; ThermoScientific) were used as initial precursors for mechanochemical syntheses. Prior to milling experiments, the precursors were homogeneously mixed at a molar La:Co ratio of 1:1.

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2.2. Mechanochemically activated synthesis

Two milling devices were employed for mechanochemical synthesis, namely (a) a planetary ball mill (Pulverisette 6, Fritsch) and (b) a horizontal attritor (Simoloyer CM-01, Zoz) (Figure 1). The planetary ball mill is a benchtop device used for milling and mixing of various materials as well as for mechanical alloying or reactive grinding of different powders, including LCO perovskite [14], [15]. At the same time, the horizontal attritor is considered the most advanced tool for lab-scale high-energy fine grinding, mixing, dispersing, mechanical alloying, or reactive grinding [16], especially designed for the preparation of nanostructured materials, which was not previously employed for the mechanochemical synthesis of LCO perovskite.

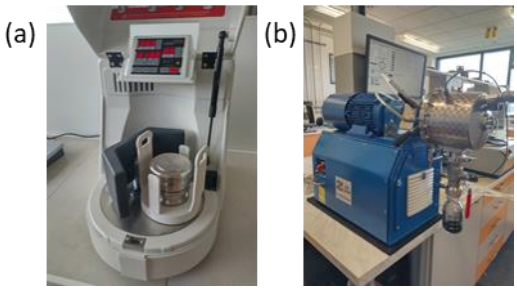

Figure 1. (a) The planetary ball mill Pulverisette 6 and (b) the horizontal attritor Simoloyer CM-01 used in the study.

The sample description and selected milling parameters are summarized in Table 1. As a wetting agent for wet planetary milling of the LCO-PW sample, the isopropyl alcohol (Penta, 99.5%) was used. After milling using both planetary and attritor mills, the powders were calcinated in a laboratory muffle furnace (LH 15/13, LAC) at temperatures of 550-850 °C for 2h in air.

Table 1. Sample designation and selected milling conditions.

Sample marking	*Milling type/ Condition*	*Milling jar/ media*	*Milling speed/ time*
LCO-PW	Planetary/ Wet	Steel balls / steel jar	350 rpm/2 h
LCO-PD	Planetary/ Dry	Steel balls / steel jar	350 rpm/2 h
LCO-A-Zr	Attritor/ Dry	ZrO_2 balls/SiN jar	1000 rpm/2h
LCO-A-S-1000	Attritor/ Dry	Steel balls / steel jar	1000 rpm/ 2h
LCO-A-S-1400	Attritor/ Dry	Steel balls / steel jar	1400 rpm/4h

2.3. Materials characterization

The diffraction patterns of initial powder precursors, as-milled and calcinated powders were obtained using the X-ray diffractometer (XRD; Rigaku 3kW) using Cu Kα radiation (λ = 0.15406 nm, 40 kV, 40 mA) in a 2θ range from 10 to 100 ° with a step size of 0.02° and a time per step of 1.5 s. The Rietveld refinement was performed using High Score Plus software supplemented with the ICDD Database. High-resolution scanning electron microscopy (SEM; Verios 460 L, FEI) coupled with energy dispersive X-ray spectroscopy (EDS) was used in back-scattered electron (BSE) mode to characterize powders' microstructure, elemental composition and elemental distribution of the powder samples. The specific surface area of the LCO samples was determined from the measured adsorption/desorption isotherms using a Micro 300 C1 surface area analyser (3P Instrument, BET-ANAMET). Prior to measurements, each calcined sample was degassed at 150 °C for 10 h under vacuum. Nitrogen served as the adsorbate gas, with the bath temperature maintained at liquid nitrogen temperature.

3. Results and discussion

3.1. Milling in the planetary mill

Both wet and dry planetary milling of La_2O_3 and $Co(OH)_2$ precursors produced well-homogenized mixtures consisting of La_2O_3, $La(OH)_3$ and $Co(OH)_2$ compounds (Figure 2). The formation of LCO perovskite with R3c rhombohedral structure was achieved in those mixtures after their following calcination at 750 °C for 2h. The sample LCO-PW contained 83.7 wt% of LCO, while the LCO-PD showed a higher LCO content of 87.5 wt.%. In addition to LCO, La_2O_3 and Co_3O_4 compounds were present as secondary phases in both calcinated powders, resulting from the unreacted fraction of precursors. The sample LCO-PW contained 10.7 wt% of La_2O_3 and 5.6 wt% of Co_3O_4, while the LCO-PD sample contained 10.7 wt% of La_2O_3 and 5.6 wt% of Co_3O_4, respectively. Although neither wet nor dry milling resulted in direct perovskite formation during milling, dry milling produced a larger amount of LCO in the calcinated powder, so the sample LCO-PD was chosen for further optimization of the calcination temperature.

Calcination studies (Figure 3) showed that the proportion of the secondary La_2O_3 and Co_3O_4 compounds relative to the desired $LaCoO_3$ decreased with the increase of calcination temperature. Within the investigated temperature range, the highest amount of LCO was formed at 850 °C, indicating that a higher temperature is required to obtain phase-pure LCO.

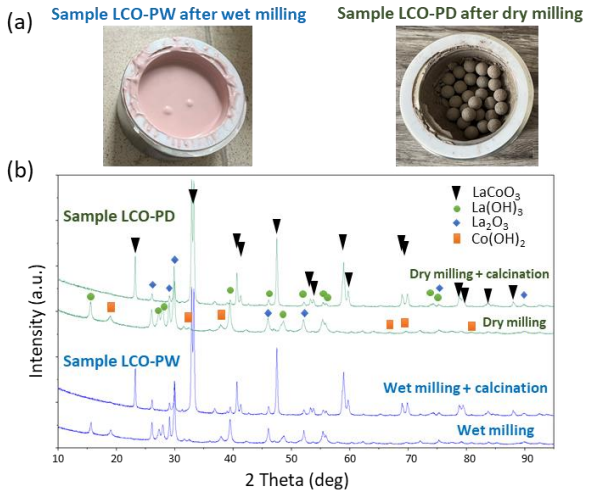

Figure 2. (a) The appearance of the milled products after wet and dry milling in the planetary mill, respectively, and (b) XRD patterns of LCO-PW and LCO-PD powders in the as-milled condition and after calcination at 750 °C for 2 h.

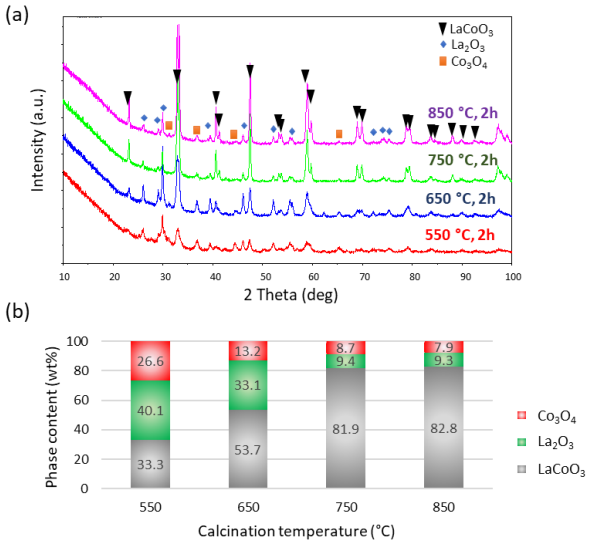

Figure 3. (a) XRD patterns of LCO-PD calcinated at 550, 650, 750, and 850 °C for 2 h and (b) the corresponding quantitative phase analysis of calcinated powders as a function of calcination temperature.

3.2. Milling in the attritor mill

In contrast to planetary ball milling, the attritor milling exhibited *in-situ* formation of 13.5 wt% of LCO in the LCO-AZ sample when using a mill configuration with a SiN-lined jar and ZrO_2 balls. In contrast, no LCO formation was detected for the mill configuration employing a stainless-steel jar and steel balls at 1000 rpm (sample LCO-A-S-1000), the formation of LCO was not detected. Only under more intensive high milling conditions used for the same mill configuration (milling speed of 1400 rpm and a longer milling time of 4h), *in-situ* LCO formation was achieved, although resulting in lower LCO content of 7.0 wt%. Based on these results, the LCO-AZ sample was selected for further optimization of the calcination temperature.

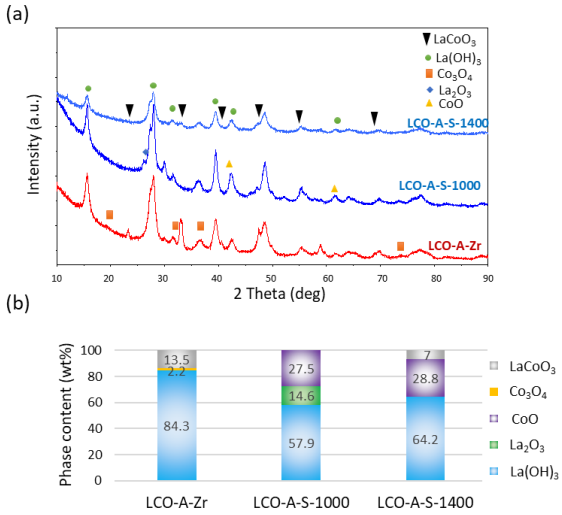

Figure 4. (a) XRD patterns of LCO-AZ, LCO-A-S-1000 and LCO-A-S-1400 powders milled at different conditions and (b) quantitative phase analysis of as-milled powders.

Study of the effect of calcination temperature on the phase composition of the as-milled LCO-AZ powder showed that the presence of secondary La_2O_3 and Co_3O_4 phases was only observed at 550 °C (Figure 5a-b). In contrast, at temperatures above 650 °C, LCO was a primary phase (>99.5wt%) with a minor admixture of secondary La_2O_3 oxide. After calcination, the sample had nanosized microstructure (Figure 5c) with the crystalline size of 22.7 nm and a surface area of 3.9 m^2/g.

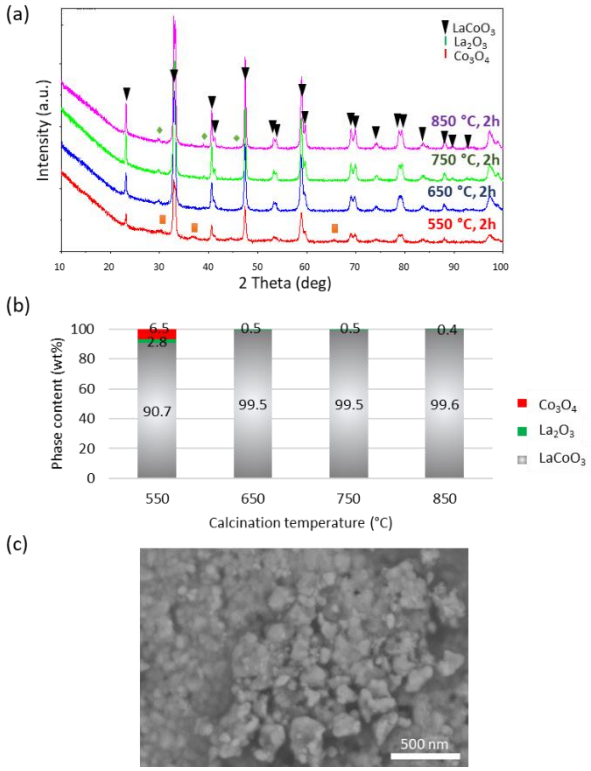

Figure 5. (a) XRD patterns of LCO-AZ powder calcinated at different temperatures and (b) quantitative phase analysis of calcinated LCO-AZ powder as a

function of calcination temperature, (c) and SEM BSE micrograph of LCO-AZ calcinated at 650 °C for 2h.

4. Summary

In this study, LCO perovskite was synthesized through mechanochemically assisted synthesis using different mechanical milling methods, including planetary ball milling and milling in the horizontal attritor, and varying synthesis parameters (wetting agent, milling rate, material of milling media and milling jar, and calcination temperature). The key findings are as follows:

- Milling in the planetary mill led to homogenization of the precursor mixture of initial $La(OH)_3$, La_2O_3 and $Co(OH)_2$ components, showing no substantial difference between wet and dry milling. The synthesis of LCO was achieved during subsequent calcination. Acquiring phase-pure LCO requires calcination temperatures above 850 °C.
- Direct mechanochemical synthesis of $LaCoO_3$ perovskite was achieved using a horizontal attritor due to its higher mechanical energy input in comparison with planetary milling. The mill configuration with SiN-lined jar and ZrO_2 balls produced the highest proportion of synthesized LCO in the powder's structure of 13.5 wt%, while the rest consisted of $La(OH)_3$ and Co_3O_4 compounds. Calcination of the milled powder in the temperature range 550-850 °C prompted subsequent LCO formation, with a purity of 99.5 wt%, achieved already at temperatures as low as 650 °C.

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