CHARACTERIZATION OF PURE AND STRONTIUM-
SUBSTITUTED LANTHANUM COBALTTITES SYNTHESIZED
BY THE GLYCINE-NITRATE PROCESS.

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ABSTRACT

Various lanthanum cobaltite powders, $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$, with $x$ varying between 0 and .5, have been prepared by means of the glycine-
nitrate process. These powders were characterized by the usual means
like transmission electron microscopy, optical laser diffraction, X-ray
diffraction and BET analyses. They were then cold pressed and sintered
at temperatures between 1200 and 1500°C. An almost fully dense
material was obtained for pure cobaltite while strontium substitution led
to significant porosity. This is explained in terms of powder
morphology and residual, unreacted products. The glycine-nitrate
process is very convenient at the laboratory scale. Its extension to
various oxide systems depends on the heat balance that can be achieved
during the combustion synthesis.

1. INTRODUCTION

Lanthanum cobaltite is one of the most active electrode materials for the air
electrode in solid oxide fuel cells (1). Despite the fact that this material has an
exceedingly high expansion coefficient compared to stabilized zirconia, this
disadvantage can eventually be circumvented by gradated oxide layers (2). In order to
study the basic properties of lanthanum cobaltite, dense contamination-free samples
are preferred. In turn, the ability to attain full density products depends on the actual
properties of the initial powders. Like for many complex oxides, various processing
routes are available for synthesizing this material. The well-known Pechini process (3-
5) is quite commonly used for perovskites. It has progressively evolved through the
years, bearing also different names like the citrate process or the liquid mix polymer
precursor technique; this evolution is discussed at length in recent reviews (6-7).
 Basically, a polymeric gel is formed incorporating the various metal cations; this gel is
then charred or ignited, thereby producing a solid foam. The foam undergoes
additional calcination and grinding to finally lead to an ultrafine powder. A novel
route, named the glycine-nitrate process, has been described recently as an alternative
to the Pechini process (8-9). The main advantages claimed for this method are a
simplified procedure, a more complete reaction, a more homogeneous product and the
lack of extensive powder processing. The glycine-nitrate process consists in mixing
glycine as a fuel with nitrates forming the oxidizer. Water is evaporated from the
solution until ignition occurs. The initial product is loosely agglomerated; following
calcination, it is sonicated to lead to a final ultrafine powder. This method has been
applied successfully to the synthesis of lanthanum chromite and other complex oxide
materials (8-12).
In the present study, the combustion process has been applied to the synthesis of lanthanum cobaltite either pure or partly substituted by strontium. The main characteristics of the resulting powders were investigated in regard to the properties of the as-synthesized powders, the calcines and the sintered products. These properties are compared with previous results on other perovskites (8-9).

2. EXPERIMENTAL

Various La$_1-x$Sr$_x$CoO$_3$ powders with $0 \leq x \leq 0.5$ have been synthesized. The procedure used was basically that described in (9): one molar nitrate solutions were mixed in the appropriate proportions for the right cation stoichiometry to be achieved. Glycine was either added in a granular form or as a solution. The glycine/total cation molar ratio, while being varied, was maintained above one. The solution was heated up on a hot plate until the onset of combustion. Various conditioning procedures, including sonication, were used on both the as-synthesized and the calcined powders. Calcination was performed in dry air between 650 and 1200°C. Powders were pressed uniaxially into pellets at about 90 MPa. On some samples, additional isostatic pressing was also performed at 300 MPa. Sintering was conducted in a single isothermal stage between 1200 and 1500°C either in pure oxygen or in oxygen mixtures with most of the anneals at 1400°C in pure oxygen. The powders were characterized in regard to their crystal structure, their morphology, their particle size distribution, their specific surface area and their chemical content. Transmission electron microscopy (TEM) was performed with a 300 KeV Hitachi microscope, model H9000. X-ray diffraction was conducted on a Siemens D500 diffractometer with the monochromator on the incident beam for the copper K$_\alpha$ radiation, thereby resulting in the maximum resolution for the major structural peaks. The background peaks were analyzed with the molybdenum K$_\alpha$ radiation on a more conventional diffractometer set-up. Densities of the fired samples were determined by a liquid immersion technique in dibutyl phthalate with an estimated accuracy better than 0.1% for closed pore samples.

3. POWDER CHARACTERIZATION

Total combustion occurs in a matter of a few seconds for pure and strontium-substituted lanthanum cobaltites. When made visible through the appropriate set-up, yellow carburizing flames are seen to accompany this combustion process. The as-synthesized powders, with an initial specific volume of about 20 cc/g bear a fluffy aspect thereby indicating a high specific surface area. Fig. 1 and 2 are transmission electron micrographs of the as-synthesized powders. In the case of pure lanthanum cobaltite, primary grains are formed with an average diameter of approximately 0.4 μm. These primary grains are largely entangled and interconnected through ill-defined boundaries, leading to agglomerates of a few microns in diameter. In the case of strontium-substituted powders, agglomerates remain within about the same average size and also form primary grain networks. However, these primary grains, in Fig.2, look entirely different: they are much smaller in size and even less defined, being either hollow or with tiny holes through them.

Following calcination in dry air for 8 hours at 900°C, the initial cobaltite powder is significantly modified. Although the agglomerate size is more or less
preserved, the primary grains undergo specific changes: a well-crystallized structure becomes apparent in Fig. 3 with grain facetting and clearly delineated grain boundaries. On the other hand, strontium-substituted cobaltite requires a higher calcination temperature for significant changes to occur. In Fig. 4, calcination has been performed during 4 hours at 1000°C. Crystallization has occurred, but the primary grains are more scattered in size and well below .2 μm in diameter. The complexity of the initial morphology is partly maintained and so is the agglomerate size which is not significantly changed compared to the as-synthesized powder.

X-Ray diffraction analysis was also performed on the various powders synthesized within this study. In the case of pure lanthanum cobaltite in Fig. 5, the as-synthesized powder shows no signs of the specific orthorhombic structure. This structure becomes evident after high temperature annealing at 900°C; it is not significantly changed by further increasing the annealing temperature. For strontium-substituted cobaltite, the as-synthesized powder, in Fig. 6, shows no signs of the expected crystalline structure. At 900°C, the two most significant peaks of the rhombohedral structure are evidenced although the powder is not yet fully recrystallized. As the temperature increases, a new phenomenon comes into consideration: the structure slowly evolves towards the final cubic structure which is attained only at 1350°C. Fig. 7 is for the as-synthesized powders from a partly modified fabrication procedure. For the pure cobaltite synthesis, La2CoO4 is then the major resulting compound; a rhombohedral phase close to La₆Sr₄CoO₁₃ is found for the synthesis of La₅Sr₅CoO₃.

The particle size distributions were measured by means of optical laser diffraction. In Fig. 8, the results are shown for pure lanthanum cobaltite as a function of the calcination temperature. The peaks on these curves are in good agreement with the TEM observations for the agglomerates. The effect of calcination is, initially, to slightly shift these peaks towards lower values, roughly from 10 μm to 5-6 μm. A higher calcination temperature does not introduce any further significant change to the pure cobaltite particle distribution. In Fig. 9, corresponding to the strontium-substituted cobaltite, the peak of the as-synthesized powder is again close to 10 μm. Calcination then slightly increases the agglomerate size. High power sonication is one means of breaking out the agglomerates. It was applied quite systematically to calcines. However, no large significant changes were found for sonicated powders, either as-synthesized or calcined.

In addition to the preceding features, carbon is systematically detected in the as-synthesized powders, getting close to 3% for La₅Sr₅CoO₃ and being about 2% for LaCoO₃. These figures vary from one batch to another and have been lowered to about .6% for our best experiments. The as-synthesized powders undergo a reversible weight variation of about 3% while being heated in vacuum up to 250°C and brought back to ambient conditions. Pure cobaltite calcines are not prone to such weight losses while strontium-substituted powders calcined at 1000°C still present a slight sensitivity of about .5%. Calcination of the as-synthesized powders implies a very significant weight loss, generally above 10%. The specific surface areas of the as-synthesized powders by the BET method are 13.5 and 11 m²/g for LaCoO₃ and La₅Sr₅CoO₃, respectively; in the same successive order, they are 2.1 and 2.0 m²/g for the calcines.
4. SINTERING RESULTS

The main results on the sinterability of the synthesized powders are reported in Figs. 10 and 11. Sintering was performed for 4 hours at 1400°C in an atmosphere of pure oxygen. For pure lanthanum cobaltite, Fig. 10 relates the effect of the calcination temperature to the green density of the pellets and also to their final density. The green density increases steadily as the calcination temperature is raised. The final density also initially increases with the calcination temperature although a maximum is reached between about 900 and 1000°C. At 1400°C, the maximum sintered density achieved for pure cobaltite exceeds 98.5% of its theoretical density. On the other hand, the relative density obtained at 1200°C is close to 95% which indicates a good sinterability even at this significantly lower temperature. At the same temperature, La₅Sr₅CoO₁₉ reaches only 71% of its theoretical density. The main results for strontium-substituted cobaltite are shown in Fig. 11: the optimum calcination temperature for maximum green density is close to 1100°C. The maximum sintered density for samples from calcined and sonicated powders is slightly above 91% of the theoretical density. However, with an additional light grinding operation on the calcines, this density raises readily to 96% as also shown on Fig. 11. Fired densities, in this study, are not significantly changed by annealing at lower oxygen partial pressures close to 10⁻³ atm.

In Fig. 12, relatively few pores are found inside the pure cobaltite samples as expected from the previous density measurements; these pores are located mainly at grain boundaries and they are well distributed within the samples. The average grain size stands around 10μm. In strontium-substituted samples, Fig. 14, larger pores spreading over a larger portion of the sample surface area are found. Significant grain growth is also present with some grains reaching 30μm in diameter. Most of the pores are also located along grains boundaries although a few of them are found within the grains.

5. DISCUSSION

Most of the present results on La₁₋ₓSrₓCoO₃ are in agreement with the previous findings on chromites (8-9). Some results, however, are at variance and require further discussion. In addition, there is a very distinct behaviour between LaCoO₃ and La₅Sr₅CoO₁₉. In fact, the glycine-nitrate process is clearly a non equilibrium process. Non equilibrium occurs at two different stages, the first one being the water evaporation from the solution and the next one, the ignition-combustion stage. Evaporation is performed rapidly and may occur unevenly at the bottom of the beaker. Nonetheless, no actual crystallisation was found for lanthanum chromites (8). For the present oxide system, the process was found to operate just about as well for either 1) the solution rapidly evaporated and ignited in the prescribed manner on a hot plate or 1) totally evaporated under vacuum at 100°C and later ignited or, finally, evaporated on a hot plate in air at 120°C and also later ignited. Concerning the second stage, carbon has been evidenced systematically in the as-synthesized powders and residual nitrogen was also found thereby indicating incomplete combustion. La₅CoO₄ and CoO are formed which, according to the lanthanum phase diagram (12), tends to indicate a reducing atmosphere below that for the formation of LaCoO₃. There is then no such a thing as stoichiometric combustion.
for the present oxide system although the best glycine/total cation ratio for any composition was found close to the stoichiometric combustion ratio defined in (9).

The combustion synthesis is, of course, dependent upon the oxide system to be synthesized. Less heat is available for the synthesis of lanthanum cobaltite than for lanthanum chromite. Partially substituting strontium for lanthanum additionally acts in the same direction. As heat tends to become marginal, a more delicate heat balance has to be achieved. The overall quantity of reactants is also important. As mentioned above, evaporation up to a solid polymeric gel was also performed as an entirely separate stage. This was found effective in somewhat relieving the heat burden and lowering the total residual carbon content in the ashes. On the other hand, potential segregation may occur in the first stage although identical water losses were found for largely different evaporation conditions. Another mean of improving the reaction is the incorporation of ammonium nitrate with additional glycine both to increase the foaming action and the available heat (8-9). This has not been experienced in the present study. However, caution should be exerted in doing so since it has been found that these components form a specific compound when mixed together in any proportion and that this compound has blasting properties at a certain concentration level (13).

Powders made with the glycine-nitrate process are easily formed in both the as-synthesized and calcined states without the need for any binding agent. Pure cobaltite powders are readily sintered to almost full density. However, quantitative modelling of the sintering process is not attempted in this study due to the complexity of the particle morphologies. Calcination exerts a beneficial effect on the sintered density while the effect of high power sonication is only marginal. This can be mainly explained, in comparison to lanthanum chromites (8), by the consolidation of the agglomerates in the cobaltite powders due to the requirement for higher calcination temperatures. Strontium substitution results in a much higher porosity within the sintered samples. This may have to do with the vapor pressure of SrO at high temperature as mentioned before for manganites (14). There are however enough evidences in strontium-substituted cobaltites for the presence of microscopic heterogeneities resulting from relatively low combustion temperatures; solid state homogenization then becomes an additional part of the sintering process. Calcining at high temperature helps in homogenizing powders, but also leads to harder agglomerates; additional grinding cannot then be totally avoided as for the original glycine-nitrate process (8) in order to get higher fired densities.

To summarize, the present results are in satisfactory agreement with the previous findings on the glycine-nitrate process (8-9). This process is very convenient at the laboratory scale for the synthesis of pure lanthanum cobaltite and it leads to dense good-quality samples. On the other hand, there is a delicate heat balance to be achieved by substitution with strontium. Higher calcination temperatures and also additional grinding, which is inherently avoided in the original process, may become necessary for oxide systems where the available combustion heat is not totally sufficient to achieve the desired sintering properties.
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Fig. 1: TEM micrograph of as-synthesized LaCoO$_3$.

Fig. 2: TEM micrograph of as-synthesized La$_5$Sr$_5$CoO$_3$.

Fig. 3: TEM micrograph of LaCoO$_3$ powder calcined at 900°C for 8 hours.

Fig. 4: TEM micrograph of La$_5$Sr$_5$CoO$_3$ powder calcined at 1000°C for 4 hours.
Fig. 5: X-ray diffraction pattern of LaCoO₃ powder as-synthesized and calcined at three temperatures. Copper Kα radiation.

Fig. 6: X-ray diffraction pattern of La₅Sr₅CoO₃ powder as-synthesized and calcined at three temperatures. Copper Kα radiation.

Fig. 7: Compounds initially formed on as-synthesized powders. Molybdenum Kα radiation.
Fig. 8: Particle size distribution of the LaCoO₃ powder.

Fig. 9: Particle size distribution of the La₅Sr₅CoO₃ powder.

Fig. 10: Green and fired densities of LaCoO₃ samples as a function of the calcination temperature. RT (room temperature) stands for uncalcined samples.

Fig. 11: Green and fired densities of La₅Sr₅CoO₃ samples as a function of the calcination temperature.
Fig. 12: Fractography of a LaCoO$_3$ sample after calcination at 900°C and sintering at 1400°C.

Fig. 13: Metallographic cross-section of a La$_2$Sr$_5$CoO$_3$ sample after calcination at 1000°C and sintering at 1400°C.