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COMPARATIVE STUDY ON SINTERING BEHAVIOUR OF $LaCoO_3$ CERAMICS OBTAINED BY MECHANICAL ACTIVATION WITH SINGLE-AND TWO-STEP FIRING

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In this paper the sintering behavior of $LaCoO_3$ prepared by mechanical activation followed by single and two-step firing was studied. All kinds of $LaCoO_3$ obtained were investigated in terms of the particle size distribution. In both situations, the highest degree of uniformity was obtained after 10 hours of milling. The samples were thermally treated for the synthesis and sintering at temperatures of 1225 and 1275°C, respectively. To determine the sinterability, the apparent density and porosity of the samples were measured by the Archimedes' method. Irrespective of the number of firing steps, samples with relative density higher than 90% were obtained. The morphology of the ceramic samples resulted after single and double firing was analysed by scanning electron microscopy (SEM).

Keywords: $LaCoO_3$, single and double firing, grain size distribution, XRD, SEM

1. Introduction

Lanthanum cobaltite ($LaCoO_3$) based ceramics show a special interest, because of their both ionic and electronic conductivity, which recommends the use of these materials as cathode for fuel cells with solid electrolyte, membrane permeable to oxygen, or as a catalyst for the oxidation of carbon monoxide [1-5]. The powdery mixtures obtained by homogenizing of raw materials in proper proportions are shaped. Afterwards, the green samples are thermally treated in order to promote densification by sintering, to achieve the desired phase

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composition and, therefore, to obtain the specific properties, required by the domain of use [6]. Sintering takes place at lower temperatures than those ones which correspond to the liquid phase formation, so that all the physicochemical processes occur in solid phase. Sintering is conducted primarily through diffusion processes determined by the gradient of chemical potential and it takes place through various mechanisms, which depend on the characteristics and preparation procedure of the precursor powders. Sintering is accompanied by increasing the density of products, which tends to get closer to the theoretical one, as well as by a normal or abnormal grain growth process. The overall porosity is reduced until its complete removal. In the case of multicomponent ceramics, beside densification and formation of microstructure, sintering also involves appropriate phase composition by solid state reaction processes [7].

The mechanical activation process determines significant changes of characteristics of the precursor powders, by modifying morphology, size distribution and agglomeration tendency of particles, as well as by inducing many deformations and structural flaws [8-15]. Low particle size and high degree of mixing achieved by applying mechanical activation may result in the decrease of temperatures corresponding to both synthesis and sintering processes [7].

The purpose of this paper is to study the sintering behaviour of lanthanum cobaltite prepared by mechanical activation, starting from precursor oxide powders, in two distinct cases: (a) sintering taking place concurrently with the synthesis of $LaCoO_3$ from oxide raw materials by a single-step thermal treatment (single firing process) and (b) a second-step sintering of the lanthanum cobaltite powder synthesized beforehand (double firing process).

2. Experimental Procedure

The binary compound corresponding to the nominal $LaCoO_3$ formula was synthesized starting from oxide raw materials of high purity, *i.e.* La_2O_3 and Co_3O_4 dosed in the stoichiometric molar ratio of 3:2, required for the formation of lanthanum cobaltite.

The mixture of the two oxides has been mechanically activated in ethanol in a planetary mill Pulverisette 5. Grinding times of 2, 10 and 20 hours were used, maintaining constant balls: material weight ratio of 10:1.

In the case of the first procedure, involving a single-step firing, from this raw materials mixture the discs with a diameter of 10 mm and a thickness of ~2.5 mm was uniaxially pressed at a pressure of 100 daN/cm². The green samples were then thermally treated in air, in order to synthesize $LaCrO_3$ and to obtain consolidated ceramic bodies by sintering at 1225 and 1275 °C, with a soaking time of 2 hours at the mentioned temperatures.

For the second procedure involving double firing, in order to accomplish the solid-state reaction process, the samples were thermally treated in a first stage (presintering) at a temperature of 1000 °C with a plateau of 2 hours.

After presintering, the samples were ground in planetary mill Pulverisette for 2, 5, 10 and 20 hours. The particle size distribution for these powders was determined with a Brookhaven 90 Plus particle size analyzer. The modal diameter (MD), as well as and the full width at half maximum (FWHM) for the differential distribution curves were also estimated. Using the values of these two parameters the relative width was calculated (FWHM/2MD) × 100 [16]. These powders were then pressed in similar conditions as the samples obtained through single-step firing. After presintering and reshaping, the samples were sintered in air, at temperatures of 1225 and 1275 °C, respectively, with a soaking time of 2 hours at each of these temperatures.

Regardless of thermal processing strategy, firing was carried out in an electric oven, with a heating rate of 5 °C/min. After sintering, the samples were slowly cooled at the normal cooling rate of the furnace.

The sinterability of the ceramic pellets has been assessed through the relative density values, calculated as ratio between the apparent density measured by Archimedes' principle and crystallographic (theoretical) density. The phase composition of the ceramics has been investigated by X-ray diffraction (XRD), using a Shimadzu 6000 diffractometer. The XRD patterns have been recorded at room temperature, using Ni-filtered Cu-Kα radiation (λ = 1.5418 Å), with a scan step increment of 0.02° and a counting time of 1 s/step, for 2θ ranged between (20 – 80)°. The morphology of the sintered samples was examined by scanning electron microscopy (SEM), by means of a FESEM-FIB Auriga Workstation microscope.

3. Results and discussion

3.1. Single-step firing

3.1.1. Sintering characteristics

The particle size distribution for all the powdery mixtures of La_2O_3 and Co_3O_4 resulted after mechanical activation was discussed in detail in a previous paper [16]. In the mentioned work the variation of the particle size against the milling time was presented. The milling time of 10 hours was considered the optimal one, because in this case, the lowest value of the modal diameter (MD) was obtained. For ceramic samples derived from powders mechanically activated by grinding for 2 and 10 hours (denoted as LC2 and LC10), pressed and then thermally treated at 1225 and 1275 °C the apparent density and porosity were determined. The values of these properties are presented in Table 1.

Table 1

Sintering characteristics of the $LaCoO_3$ ceramics obtained through single-step firing

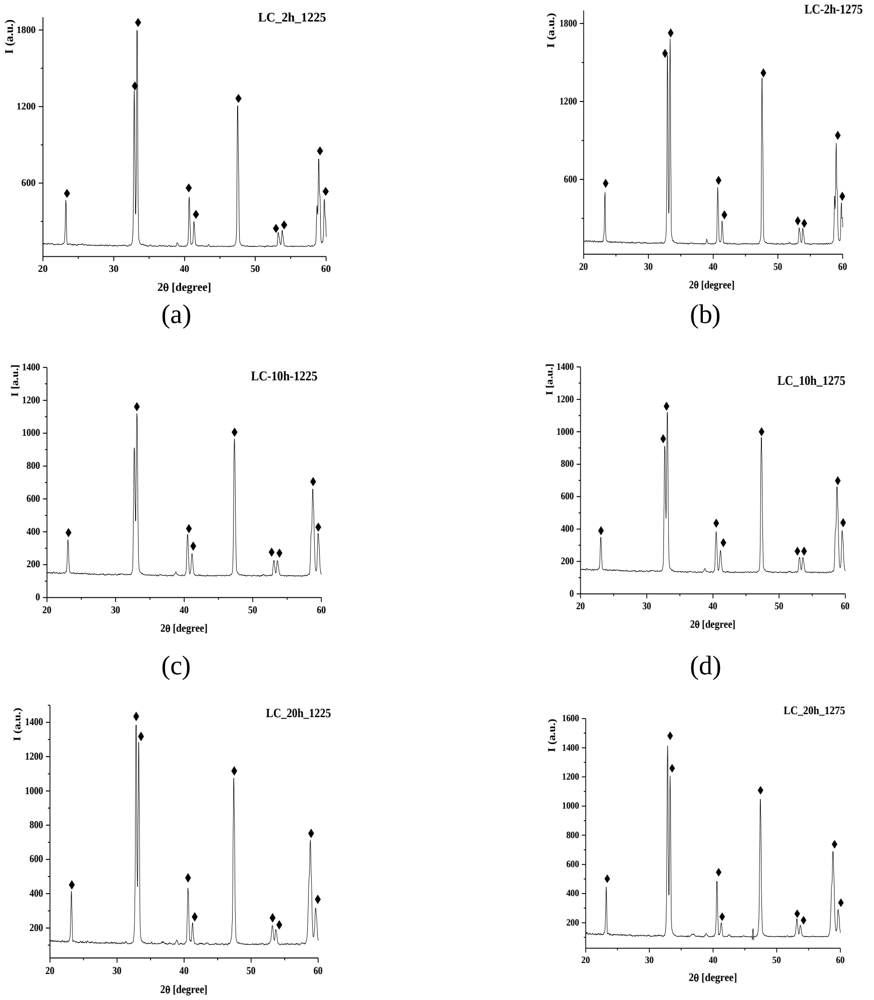
Sample	Temperature [^{0}C]					
	1225			1275		
	Apparent density [g/cm^3]	Relative density [%]	Apparent porosity [%]	Apparent density [g/cm^3]	Relative density [%]	Apparent porosity [%]
LC2	5.64	77	14.07	6.44	88	1.70
LC10	6.18	85	8.73	6.81	93	0.22

It was noticed that for both sintering temperatures, increasing the milling time from 2 to 10 hours contributed to a better densification. The density of the sample mechanically activated for 10 hours and sintered at a temperature of 1275 ^oC, exceeds the value of 90% of theoretical density. It is worthy to mention that, in the case of the samples derived from the powder mechanically activated by milling for 20 hours, the single-step firing leads to a certain volume inconstancy, so that their sintering properties were considered as non-relevant and, therefore, they were not indicated in Table 1. This shows that, in the mentioned samples, some residual amounts of La_2O_3, highly sensitive towards the environmental moisture, were responsible for their disintegration [17]. This can be explained taking into account that a higher grinding time determines an increase in the particle size by depositing small particles onto the larger ones [16], which causes a certain degree of morphological inhomogeneity.

3.1.2. Phase composition

The phase composition of samples mechanically activated for 2, 10 and 20 hours and thermally treated at temperatures of 1225 ^oC and 1275 °C examined by X-ray diffraction is presented in Figs.1 (a-f).

The X-ray diffraction patterns presented in Fig.1 (a-f). that, in all cases, the investigated ceramics tends to exhibit a single-phase composition. Thus, regardless of the grinding time related to mechanical activation of the precursor powdery mixtures, one can notice that, even after sintering at the lower temperature of 1225 °C, the major $LaCoO_3$ phase with rhombohedral structure is already well crystallized. Increasing the sintering temperature at 1275 °C leads to the increase of the crystallinity degree reflected in the intensity enhancement of the main diffraction peaks corresponding to the lanthanum cobaltite.



(a) (b)

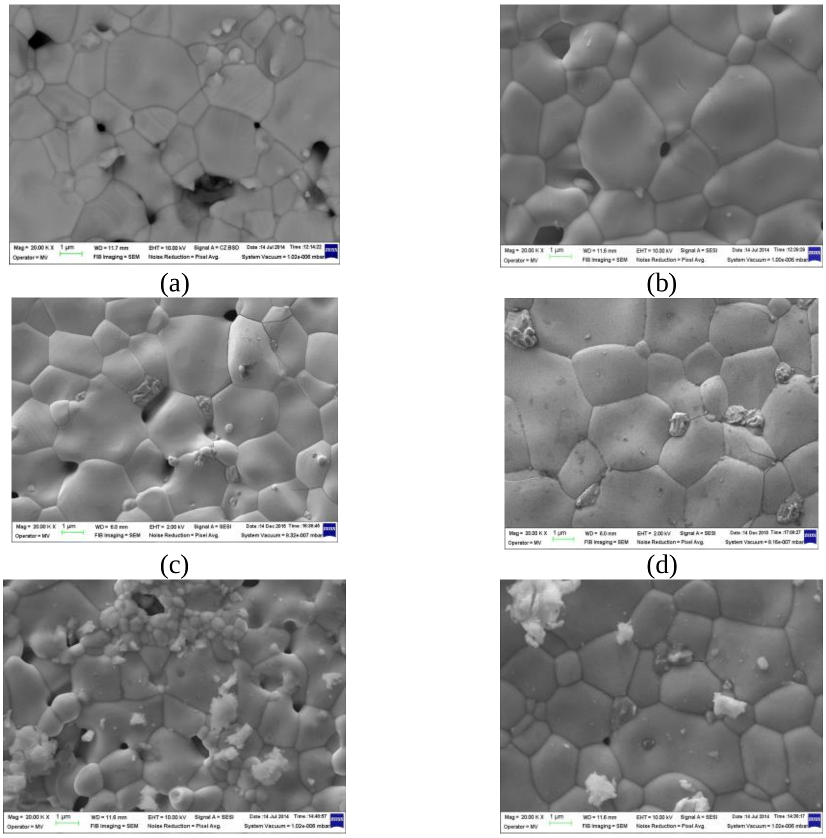
(c) (d)

(e) (f)

Fig. 1. XRD patterns of $LaCoO_3$ ceramics obtained by single-step sintering for 2 hours at temperatures of 1225°C (a), (c), (e) and 1275°C (b), (d), (f), from powdery mixtures resulted after mechanical activation: (a), (b) for 2 hours, (c), (d) for 10 hours and (e), (d) for 20 hours

3.1.3. Microstructure

SEM images for ceramics derived from the powdery mixture mechanically activated are presented in Fig. 2 (a-f) In Figs (a) and (b) the ceramics were mecanically activated for two hours and sintered for 2 hours at temperatures of 1225 °C and 1275 °C, respectively. For the ceramics sintered at 1225 ^{o}C, a microstructure consisting of polyhedral, uneven grains, with sizes of ~ 3 μm was noticed. One can also observe the presence of the pores in the grain boundary regions, which is in agreement with the porosity measurements, showing that this sample is not yet completely densified (Fig. 2 (a)).


(a) (b)

(c) (d)

(e) (f)

Fig. 2. SEM images for ceramic samples derived from powdery mixture activated mechanically for 2,10, 20 hours and single-step sintering for 2 hours at temperatures of: 1225 °C (a), (c), (e) and 1275 °C (b), (d), (f)

In the case of the ceramic sample derived from the same powder, but sintered at 1275 ^{o}C, the increase of the sintering temperature induces the decrease of the number of intergranular pores. This observation is supported by both a higher value of relative density and a lower value of apparent porosity, relative to the sample sintered at 1225 ^{o}C, as already shown in Table 1. However, the relative density value of 88%, correlated with the apparent porosity value of only 1.70% seems to indicate the presence of a certain amount of closed pores inside the ceramics (Fig. 2 (b)). Besides, one can notice that an increase of the sintering temperature of 50 °C determines a slight increase of the average grain size (~ 4.5 μm) and an increase of microstructural uniformity, with an obvious tendency toward an unimodal grain size distribution. In this case, the grains also present a polyhedral shape, with well-defined grain boundaries and almost perfect triple junction points (Fig. 2 (b)). Figs. 2 (c) and (d) show the SEM images of the samples derived from a powdery mixture ground for 10 hours and then sintered in similar conditions, as the ceramics previously discussed. In the case of sintering at 1225 °C, the microstructure is fairly uniform, consisting of polyhedral grains of 2 - 3 μm and a certain proportion of intergranular porosity, somewhat lower than that one observed in the case of the ceramics sintered at the same temperature, but derived from the powder mechanically activated by grinding for 2 hours (Fig. 2 (a)).

As in the previous case, increasing the sintering temperature at 1275°C promotes densification, accompanied by the increase in average grain size, as well as significant decrease in intergranular porosity (Fig. 2 (d)). This indicates a better sinterability than that one corresponding to the ceramic sample sintered at the same temperature, but coming from powder mechanically activated by grinding for 2 hours. These observations are consistent with the values determined for relative density, which in this case is higher (of 93%) than that of 88%, obtained for the ceramic sample mentioned previously.

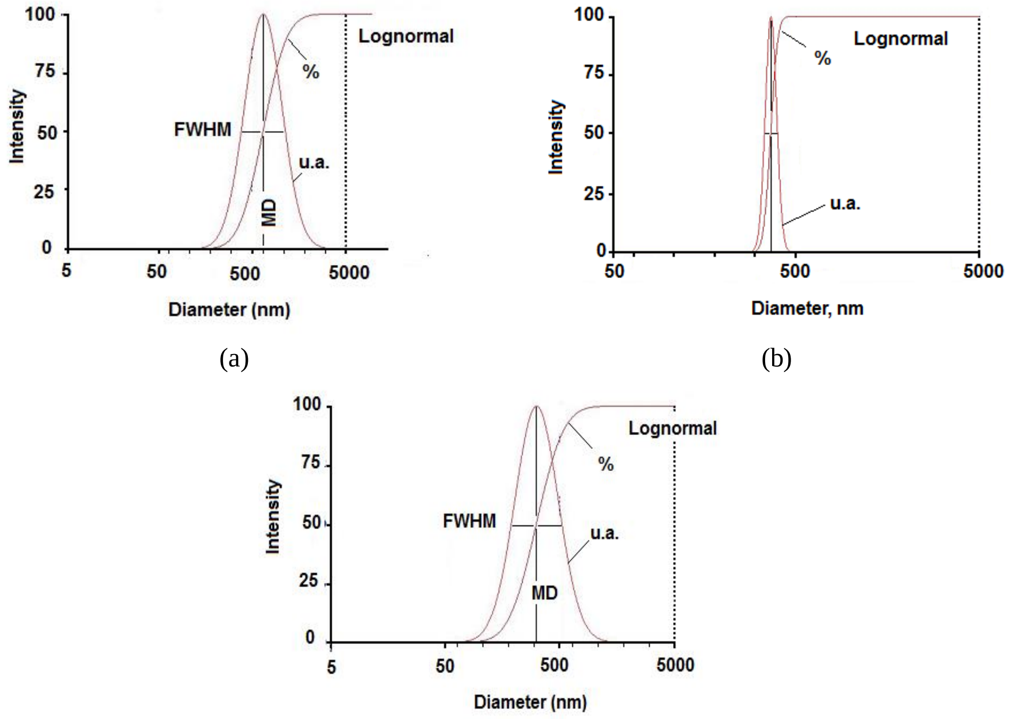
In the case of the sample resulting from powder mechanically activated by grinding for 20 hours and sintered at 1225 °C, a less uniform microstructure, consisting of polyhedral grains with variable sizes was noticed. Thus, larger grains of ~ 3 μm, coexist with smaller ones with sizes in the submicron range, which determines a rather bimodal grain size distribution. A significant amount of pores of irregular shape, located in the grain boundary regions, indicates a lower sinterability (Fig. 2 (e)). The increase of the sintering temperature at 1275 ^{o}C has the same beneficial effect on the densification, as already discussed, so that the intergranular pores are almost missing (Fig. 2 (f)). However, even under these conditions, the microstructural inhomogeneity still persists, the submicron sized grains coexisting with larger grains of (1- 6) μm. Regardless of the sintering temperature, on the surface of the grains of $LaCoO_3$ major phase, the presence of some small grains belonging to the secondary phase of La_2O_3, was noticed. Hydration of La_2O_3 grains determines volume inconstancy, as previously mentioned. Based on these observations, one can conclude that an optimal grinding time of 10 hours is required for the mechanical activation of the powdery mixture of raw materials, in order to obtain homogeneous and pore free microstructures for the related $LaCoO_3$ ceramics, resulted by a single-step firing.

3.2. Two-step firing

3.2.1. Preparation and characterization of the precursor $LaCoO_3$ powder

The mixture of raw materials, mechanically activated under the same conditions as in the case of samples previously discussed, was subjected to a preliminary thermal treatment of presintering at 1000 °C with a plateau of two hours, required for finalizing the solid state reactions and to obtain single phase $LaCoO_3$ [16]. After presintering, the samples were milled in the same conditions as in the case of the mechanical activation applied on the raw materials mixture. On the as-prepared powders the particle size distribution was determined. The results of the measurements are presented in Fig. 3.

Thus, for a grinding time of 2 hours a unimodal particle size distribution was obtained. Taking into account the values determined for the characteristic parameters, *i.e.* modal diameter, MD = 1000 nm and FWHM = 1465 nm, a relative width H_l of 34% was calculated, this showing a wide particle size distribution (Fig. 3(a)). When a grinding of 10 hours was performed, also a unimodal particle size distribution was obtained. In this case, a significantly lower value of modal diameter, of 450 nm, and a relative width of only 3.9% indicate a narrow range of particle size distribution (Fig. 3 (b)). For a grinding time of 20 hours, the value of the modal diameter is slightly lower (~ 400 nm) than that one corresponding to a grinding time of 10 hours, but the relative width value, H_l reached 28%, which shows a much wider particle size distribution, most likely due to an incipient agglomeration process (Fig. 3 (c)).



(a) (b)

(c)

Fig. 3. Particle size distribution for $LaCoO_3$ powders resulted by grinding the presintered (at 1000 ^{o}C) samples for: (a) 2 hours; (b) 10 hours and (c) 20 hours

3.2.2. Sintering characteristics

From the milled $LaCoO_3$ powders the samples were pressed and sintered under similar conditions as those used in the case of single-step fired ceramics. The characteristics of the ceramic samples prepared through the two-step firing procedure and denoted as LCD2, LCD10 and LCD20 are given in Table 2.

Table 2

Sintering characteristics of the $LaCoO_3$ ceramics obtained by two-step firing, involving a first stage of presintering at 1000 °C

Sample	Temperature [^{0}C]					
	1225			1275		
	Apparent density [g/cm^3]	Relative density [%]	Apparent porosity [%]	Apparent density [g/cm^3]	Relative density [%]	Apparent porosity [%]
LCD2	6.73	92	1.14	6.97	96	0.44
LCD10	6.79	93	1.25	6.91	95	0.23
LCD20	6.43	88	0.47	6.64	91	0.04

In comparison with the $LaCoO_3$ ceramics obtained by single-step firing at 1225°C, the ceramics resulted after the two-step firing, involving presintering at 1000°C followed by sintering at 1225°C, present a significant decrease of apparent porosity and an increase of relative density, especially for the samples labelled LCD2 and LCD10, which show relative density values above 90%. For the sample derived from $LaCoO_3$ powder milled for 20 hours, the relative density decreases, although its apparent porosity is lower than those corresponding to the ceramic samples sintered in similar conditions, but derived from $LaCoO_3$ powders obtained by using of lower durations of mechanical activation (2 and 10 hours, respectively). This can be explained in terms of a likely increase of closed porosity which occurs inside the ceramic body. Irrespective of the milling time of the precursor oxide powder, in the case of all the samples sintered at 1275 °C, densification obviously progresses, relative to the ceramics sintered at lower temperature. Thus, the relative density reached values above 90%, indicating a high sinterability of the ceramics. Even in this case, for the ceramics derived from $LaCoO_3$ powders milled for 10 and 20 hours, the slight decrease of relative density, concurrently with the decrease of the apparent porosity, might indicate the presence of closed pores.

3.2.3. Microstructure

SEM images of the ceramics derived from mechanically activated $LaCoO_3$ powders and obtained by a two-step firing procedure were presented in Fig. 4.

The microstructure of the ceramic sample obtained after sintering at 1225°C and derived from oxide powder mechanically activated for 2 hours consists of polyhedral grains, nonuniform as shape and size and a low amount of intergranular porosity (Fig. 4 (a)).

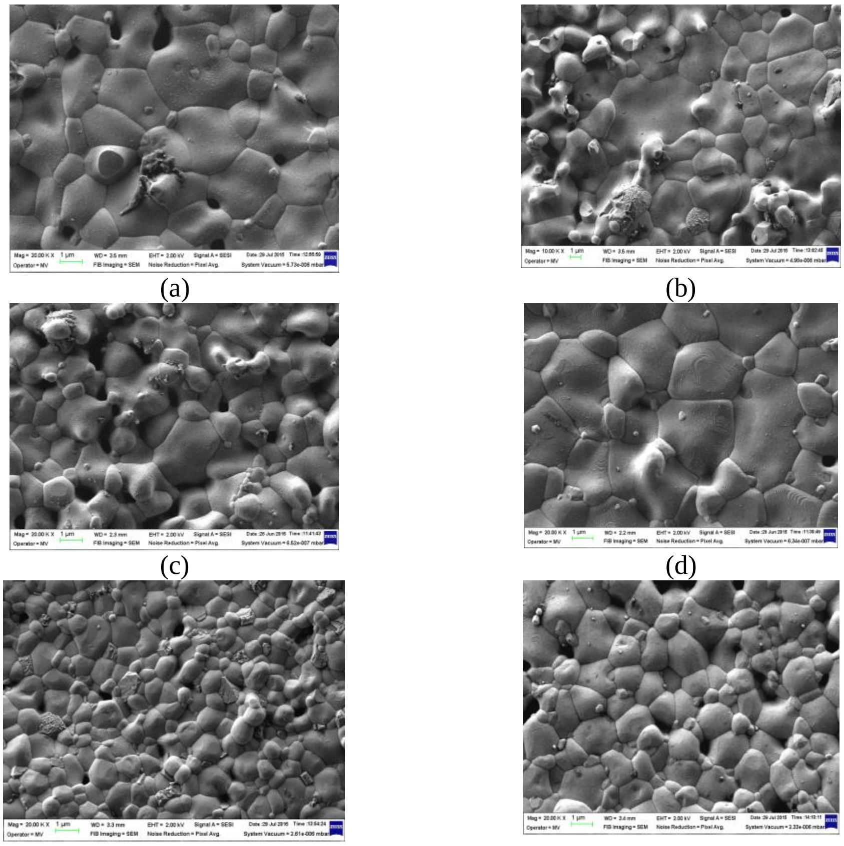

(a) (b)
(c) (d)
(e) (f)

Fig. 4. SEM images of the ceramic samples obtained by two-step firing (presintering at 1000 °C, followed by sintering) and derived from $LaCoO_3$ powders mechanically activated by milling for: (a), (b) 2 hours; (c), (d) 10 hours; (e), (f) 20 hours and sintered. Sintering was carried out at temperatures of: (a), (c), (e) 1225 °C and (b), (d), (f) 1275 °C

The microstructural inhomogeneity might be determined by the wide particle size distribution of the precursor $LaCoO_3$ powder resulted after milling. The increase of the sintering temperature leads to a well-densified, pore-free microstructure, but also induces a discontinuous grain growth, so that, for the sample obtained after sintering at 1275°C, the size nonuniformity of the ceramic grains increases obviously (Fig. 4 (b)).

In the case of the sample derived from $LaCoO_3$ powders, mechanically activated by milling for 10 hours, the sintering at 1225°C leads to a microstructure characterized by the presence of polyhedral grains, with well-defined boundaries and a few small, isolated, intergranular pores (Fig. 4 (c)). A certain microsturctural inhomogeneity still persists, but this almost disappears in the ceramic body sintered at 1275°C, which shows a unimodal size distribution and an average grain size of ~ 4 µm (Fig. 4 (d)).

The effect of an advanced mechanical activation is clearly emphasized for the samples derived from the oxide powder resulted after a prolonged milling time of 20 hours. These ceramics show uniform and fine-grained microstructures relative to those previously discussed, regardless of the sintering temperature. However, the microstructural refinement induces the increase of the amount of intergranular porosity, which is in agreement with the relative density data (Fig. 4 (e), (f)).

4. Conclusions

In this study, the sintering behaviour of $LaCoO_3$ ceramics obtained by mechanical activation coupled with single- and two-step firing was investigated. In both cases, the increase of sintering temperature from 1225 to 1275 °C promotes densification of the ceramic samples. However, irrespective of the sintering temperature, a better sinterability reflected in higher values of relative density and lower values of apparent porosity was obtained for the ceramics resulted after a two-step firing procedure, involving a prior presintering stage at 1000°C.

In the case of a single-step firing procedure, an optimal grinding time of 10 hours was determined for the mechanical activation of the raw materials mixture, in order to achieve single phase and dense ceramics.

Regarding the two-step firing procedure, it was found that the prior presintering stage, ensuring $LaCoO_3$ formation, followed the second mechanical activation of the as-obtained oxide powder, has a beneficial effect on the microstructure of ceramics in the second sintering stage. Thus, pore-free ceramic samples presenting relative density values above 90% were obtained. In this case, the particle size and, especially, the characteristics of the particle size distribution of $LaCoO_3$ powders resulted after presintering played a key-role on the microstructural features of the sintered ceramics. Thereby, the $LaCoO_3$ powder resulted after milling for 10 hours and showing the narrowest unimodal particle size distribution, with an average particle size of 450 nm, was found to be the most suitable, in order to obtain a dense and uniform ceramic microstructure after sintering.

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