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Synthesis and characterization of $LaFeO_3$ powders prepared by a mixed mechanical/thermal processing route

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Abstract

Lanthanum ferrite, $LaFeO_3$ (LF), has raised considerable interest since it can be used in many applications such as solid-oxide fuel cell electrode, sensor material (H_2O and ethanol) and catalyst. Since the conventional ceramic route of synthesis has some disadvantages, mainly related to an exaggerated grain growth, LF has been prepared by different methods including combustion synthesis, sol–gel, hydrothermal processes, polymerizable complex method and mechanochemistry. As concerns this last method, a problem occurs due to the moisture sensitivity of $La2O_3$. To overcome the problem, we used lanthanum acetate sesquihydrate [$La(CH_3COO)_3 \cdot 1.5H_2O$] and iron (II) oxalate dehydrate [$FeC_2O_4 \cdot 2H_2O$] as precursors. The mechanism of the solid-state reactions in the mixtures has been studied by TG–DSC and XRPD. Synthesis of $LaFeO_3$ has been realized by annealing the mechanically activated mixtures for 3 h at temperatures between 500 and 800 °C. While LF prepared at $500\ °C < T < 600\ °C$ has an amorphous character, LF obtained at $T \geq 600\ °C$ is free from carbonaceous impurities as it is shown by FT-IR and TG measurements. The specific area of the $LaFeO_3$ powders obtained starting from the mechanically activated mixture is decreasing by increasing the annealing temperature. On the contrary, the annealing on samples of physical mixture at temperatures up to 800 °C only yields a mixture of $LaFeO_3$, La_2O_3 and Fe_2O_3.

Keywords Lanthanum ferrite · Mechanochemistry · Thermal analysis · Specific surface area

Introduction

Among the perovskite oxides (general formula ABO_3), the lanthanum ferrite, $LaFeO_3$ (LF), has raised considerable interest since it can be used in many applications due to its resistance to high temperatures. So, for example, $LaFeO_3$ can be employed as solid-oxide fuel cell electrode [1], as sensor material for the detection of humidity and alcohol [2] and as catalyst [3, 4].

Several methods have been worked out for LF synthesis. The conventional ceramic route has some disadvantages mainly related to an exaggerated grain growth [5, 6].

Therefore, LF has been prepared by different methods including combustion synthesis [7], sol–gel [8], hydrothermal processes [9] and polymerizable complex method [10, 11].

Such "Soft Chemistry" approaches present some problems essentially linked to the use of expensive and oft not environment-friendly, starting reagents. Besides, another considerable issue lies with experimental conditions such as temperature, pH and chemical composition of the reacting system that have to be carefully and continuously monitored.

Mechanochemical activation has been used during the last decades as a powerful tool for the preparation of metastable crystalline and amorphous phases, and nanostructured materials that cannot be obtained through conventional methods [12, 13]. The effect of conveying mechanical energy to a sample powder can be described under three fundamental reasons: (1) shortening of reaction times; (2) reduction in the high temperatures usually required for developing solid-state reactions; (3) possibility of preparing materials with special properties.

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In previous works [14–17], we studied the formation of different ternary oxides ($BaTiO_3$, $YFeO_3$, $CaSnO_3$ and $NiFe_2O_4$) from a combination of mechanical and thermal treatment.

In the present work, we report on a further study of the mechanothermal synthesis of $LaFeO_3$. As lanthanum and iron precursors, we used, respectively, lanthanum acetate sesquihydrate [$La(CH_3COO)_3 \cdot 1.5H_2O$], that has a hedge over lanthanum oxide since it is not hygroscopic, and iron (II) oxalate dehydrate [$FeC_2O_4 \cdot 2H_2O$]. By studying the reactions taking place in the mixtures during heating, we set up a synthesis procedure that combines mechanical and thermal treatment of the mixtures. Finally, we characterized the products formed in the mixtures annealed at different temperatures with different techniques (XRPD, TG, FT-IR, SEM and nitrogen porosimetry).

Experimental

The starting chemicals used were $FeC_2O_4 \cdot 2H_2O$ (purity 99.9%—Aldrich Chimica, Italy) and $La(CH_3COO)_3 \cdot 1.5 H_2O$ (purity 99.9%—Alfa Aesar–Germany).

Physical mixtures of composition ratio La/Fe = 1.0 were prepared by weighing the appropriate amounts of the two precursors and by stirring them in acetone suspension for 3 h. Then, the solvent was allowed to evaporate at room temperature overnight.

The mechanically activated mixtures were prepared by dry milling lots of 1 g of physical mixtures: the powders were put into zirconia jars (12.5 ml) of a planetary mill (Pulverisette 7 by Fritsch, Germany) with 5 zirconia balls (12 mm diameter; the mass ratio between the milling balls and the sample powder was 11:1). The mill was operated at 650 rpm rotation speed for 6 h.

TG/DSC measurements were performed with a TG/DSC simultaneous analyser (Q600, TA Instruments Inc. USA) connected to a computer fitted with an appropriate software. Samples of ≈ 50 mg of both physical and milled mixtures were placed in an alumina pan and heated at 10 K min^{-1} (under air flow of 100 mL/min) from 25 up to 800 °C where a constant mass value is reached.

Samples of both milled and physical mixture have been heated in tube furnace (static air, 10 K min^{-1}) up to temperatures between 500 and 800 °C in steps of 50 °C with isothermal stage of 3 h at the end of each heating ramp.

X-ray powder diffraction (XRPD) patterns have been taken to determine the phases that were formed during the annealing. The relevant patterns were recorded with an X-ray powder diffractometer (Bruker D5005) in step-scan mode (CuKα radiation, step width 0.015°, 2 s/step, 40 kV, 40 mA, $2\vartheta° = 15–50$).

Diffuse reflectance (DR) FT-IR spectra have been recorded on samples of milled mixture heated up to different temperatures by a Nicolet spectrometer (iS10, Nicolet, USA). The spectra collected with DR have been recorded on samples dispersed in KBr (≈ 5% by mass in KBr): 128 scans have been coadded at 4 cm^{-1} resolution and ratioed against 128 scans collected on samples of pure KBr (99+%, Sigma-Aldrich, Italy).

The specific surface area of the milled mixtures after annealing under different conditions was determined by N_2 adsorption (BET method). The nitrogen adsorption curve was recorded by a Sorptomatic 1990 (Thermo Electron Corporation, operating with the static volumetric principle). The correction for the volume of the sample was introduced by measuring the He sorption.

SEM measurements were taken using a Zeiss EVO MA10 (Carl Zeiss, Oberkochen, Germany) at an acceleration voltage of 20 kV and 8.5-mm working distance on gold-sputtered samples.

Results and discussion

Thermal behaviour of the mixtures

Figure 1 shows the XRPD patterns of both the physical and the activated mixture. As it can be seen, the peaks of the two precursors disappear in the activated mixture as a result of the mechanical treatment that induces amorphization.

Figure 2 shows the TG–DSC–DTG signals recorded on a sample of the milled mixture.

The first stage of mass loss process ends (≈ 175 °C) at a residual mass of 87.46 ± 0.19% (mean value from 5 independent measurements) that is in a reasonable agreement

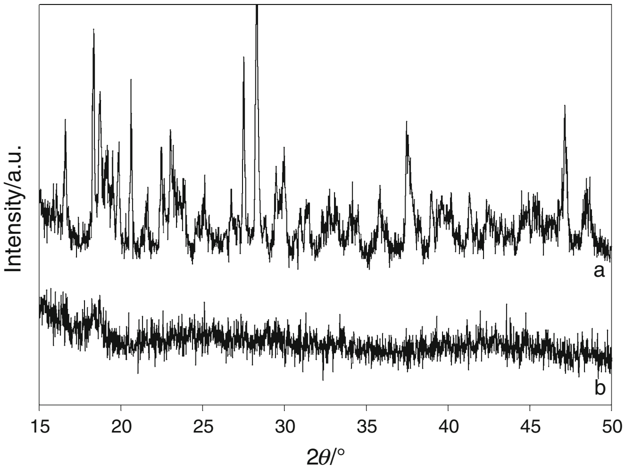


Fig. 1 XRPD patterns on samples of **a** physical mixture and **b** mechanically activated mixture

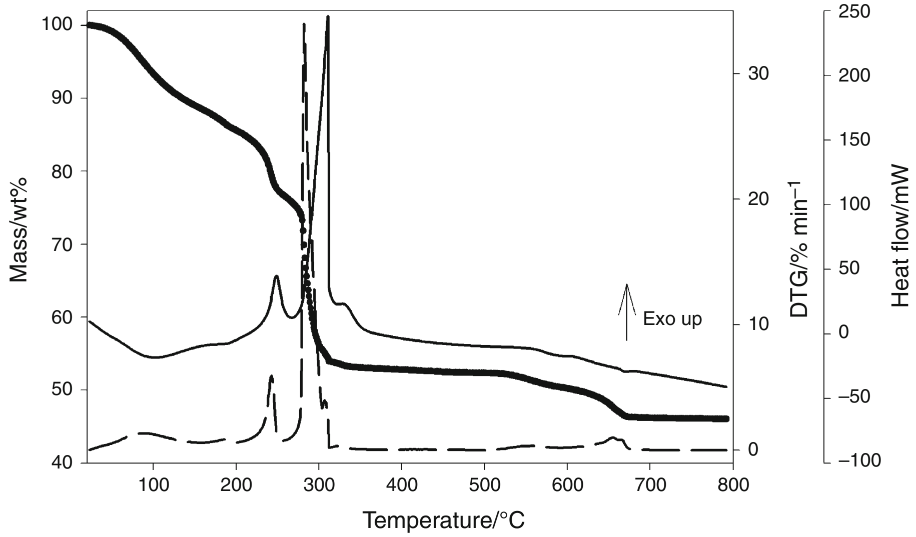


Fig. 2 TG (bold line), DSC (full line), DTG (dashed line) curves recorded on a sample of activated mixture

with the value of residual mass expected for the total dehydration of the mixture (87.94%). Under the first stage of mass loss, an endothermic DSC peak is present that corresponds to the endothermic dehydration process. The DTG curve shows two peaks: the first one ends at ≈ 260 °C and corresponds to a residual mass value (76.93 ± 0.36%) that is ≈ 1% higher than the value expected for the formation of the mixture $La(CH_3COO)_3 + (1/2)Fe_2O_3$(75.70%). The DSC counterpart is an exothermic peak whose enthalpy cannot be evaluated as such a peak is not well separated from the subsequent one much more intense exothermic DSC peak. The following DTG peak is much more intense than the previous one, and it is accompanied by a strong exothermic DSC peak. The mass value at the end of this peak is 52.39 ± 0.55% ($T \approx 500$ °C). Such a value is sensibly lower than the value of the residual mass expected (54.83%) at the end of reaction (1):

$$\begin{aligned} &FeC_2O_{4(s)} + La(CH_3COO)_{3(g)} + (25/4)O_{2(g)} \\ &\quad \rightarrow (1/2)Fe_2O_{3(s)} + (1/2)La_2O(CO_3)_{2(s)} + CO_{(g)} \\ &\qquad + 6\ CO_{2(g)} + (9/2)H_2O_{(g)} \end{aligned} \qquad (1)$$

Clearly, the two stages of the mass loss process involve, besides Fe(II) oxalate decomposition and La acetate combustion, a partial decomposition of La oxycarbonate to La oxide. The total enthalpy under the two exothermic DSC peak is $\Delta_{exo}H = -\ 1512 \pm 78\ J\ g^{-1}$.

The last stage of mass loss ends at ≈ 700 °C at a residual mass of 46.08 ± 0.32% that shows a good agreement with the value expected for the formation of a mixture (1/2) La_2O_3–(1/2) Fe_2O_3 (46.41%).

For the sake of comparison, a TG–DSC run has also been performed on a sample of physical mixture. Figure 3 shows the TG–DSC–DTG signals recorded on this sample.

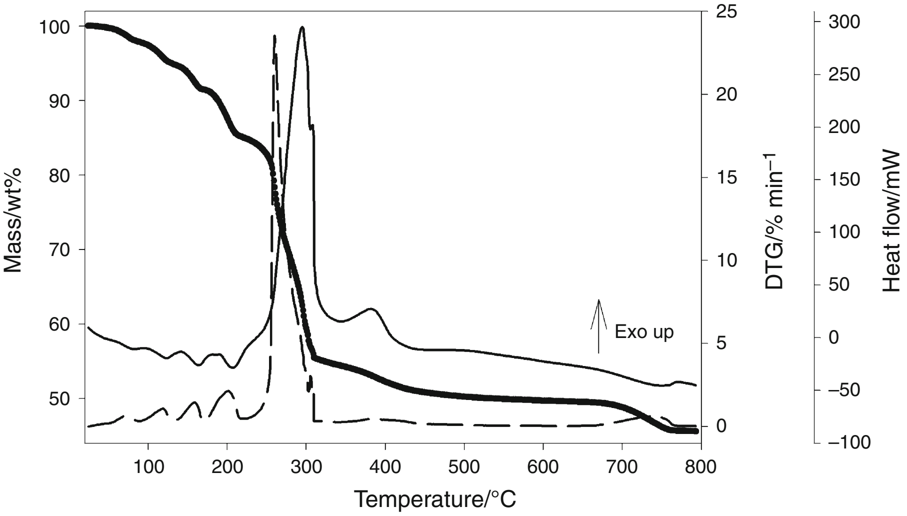
The first stage of mass loss shows a final mass value at the end of the first stage (86.00 ± 0.25%) that is sensibly lower than that expected (87.94%) for the complete dehydration of the mixture. Clearly, the first stage of mass loss contains, besides the dehydration of the precursors, a share of the FeC_2O_4 decomposition. The DSC counterpart under these stages is an endothermic peak.

By higher temperature, only a DTG peak is present, contrarily to what happens in the activated mixture. At the end of such a peak (≈ 350 °C), the residual mass value is 50.42 ± 0.32% that is sensibly lower than the value expected for reaction (1). In the case of the physical mixture too, the process of combustion includes the oxycarbonate decomposition to La(III) oxide and to a larger extent than it is the case with milled mixture. The DSC counterpart under such a stage of mass loss is, as with the milled mixture, a double exothermic peak, but with inverted relative intensities. Moreover, it can be observed that the heat released under such a double exothermic peak is much higher ($\Delta_{exo}H = -\ 3000 \pm 97\ J\ g^{-1}$). This points out to the fact that different processes are going on within the two types of mixture. The final stage of mass loss ends at ≈ 780 °C with a residual mass of 45.83 ± 0.22% that shows a fair agreement with the value expected for the formation of a mixture (1/2)La_2O_3–(1/2) Fe_2O_3 (46.41%).

It seems that the main difference between the TG–DSC runs on the mixtures is observed in the enthalpy of the exothermic DSC peak under the main mass loss stage. However, the most striking difference on what happens by heating the two types of mixture can be observed in Fig. 4, which shows the XRPD patterns of the residual of both physical and mechanically activated mixtures recovered at the end of the runs performed up to 800 °C.

The only diffraction peaks of the residual of the mechanically activated mixture (a) are those characteristic of lanthanum ferrite $LaFeO_3$ (orthorhombic JCPDS-00-037-1493). The situation is completely different as

Fig. 3 TG (bold line), DSC (full line), DTG (dashed line) curves recorded on a sample of physical mixture



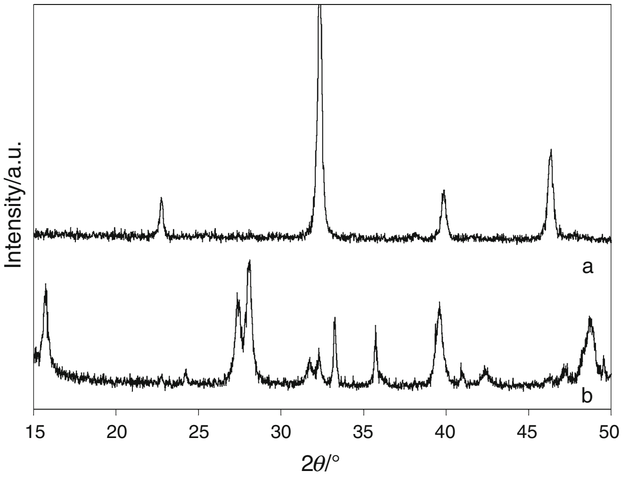


Fig. 4 XRPD patterns of the residual recovered at the end of TG/DSC runs on sample of **a** activated mixture, **b** physical mixture

concerns the residual of the physical mixture (b) that, besides some less intense peaks of $LaFeO_3$, shows the peaks characteristic of Fe_2O_3 and of $La(OH)_3$ that forms by the interaction between unreacted La_2O_3 and air moisture.

Synthesis of $LaFeO_3$

Figure 5 shows the XRPD patterns of samples of milled mixtures heated up to different temperatures (from 500 to 800 °C in steps of 50 °C; isothermal stage of 3 h).

In all the samples, but that heated up to 500 °C, only the peaks of $LaFeO_3$ are present. In the sample heated up to 500 °C, the peaks are very broad and point out to the formation of amorphous $LaFeO_3$. The collected experimental evidence shows that $LaFeO_3$ can be obtained by short annealing (3 h) of the mechanically activated mixture at temperatures as low as 550 °C.

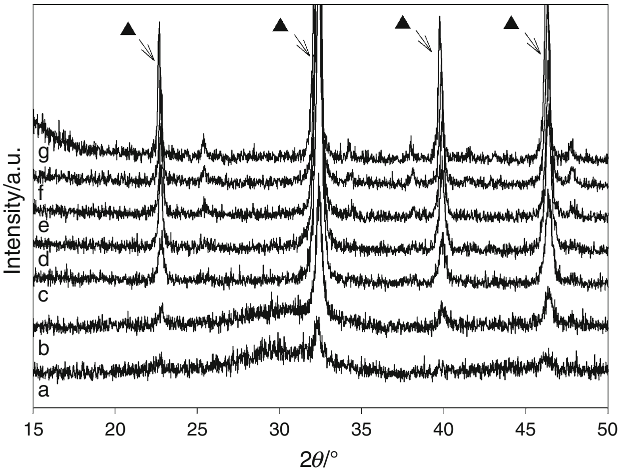


Fig. 5 XRPD patterns recorded on samples of the activated mixture annealed for 3 h at **a** 500 °C, **b** 550 °C, **c** 600 °C, **d** 650 °C, **e** 700 °C, **f** 750 °C, **g** 800 °C

The same thermal schedule (with isothermal stages of 3 h at 550–800 °C in steps of 50 °C) has been applied to samples of physical mixture. The XRPD patterns of the different samples after the annealing are shown in Fig. 6. It can be seen that, although the peaks of $LaFeO_3$ are present starting from the patterns of the mixture annealed at 600 °C, the most intense peaks up to temperatures as high as 800 °C are those characteristic of the two component oxides (La_2O_3 and Fe_2O_3). The obtained results suggest that, starting from the activated mixture, $LaFeO_3$ forms directly as the precursors thermally decompose, while the situation is different when the synthesis is attempted starting from a physical mixture. In this case, the oxide mixture forms from the thermal decomposition of the precursors in the same temperature range as it is the case with the milled mixtures, but it reacts slowly, leading to a final product that is a mixture La_2O_3-Fe_2O_3-$LaFeO_3$.

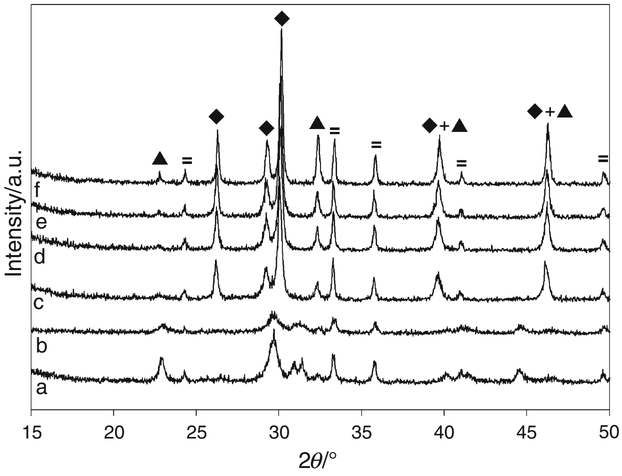


Fig. 6 XRPD patterns recorded on samples of the physical mixture annealed for 3 h at **a** 550 °C, **b** 600 °C, **c** 650 °C, **d** 700 °C, **e** 750 °C, **f** 800 °C. Filled triangle: $LaFeO_3$; = : Fe_2O_3; filled diamond: La_2O_3

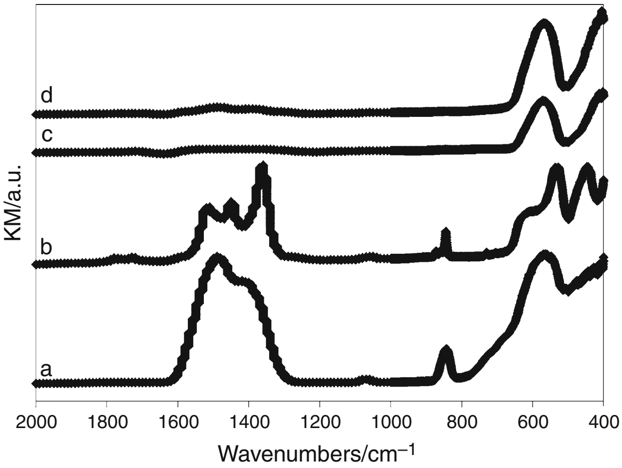


Fig. 7 FT-IR spectra recorded on samples of the activated mixture annealed for 3 h at **a** 500 °C, **b** 550 °C, **c** 600 °C, **d** 650 °C

Characterization of $LaFeO_3$ synthesized from mechanically activated mixtures

It is reported in the literature [18] that the samples of $LaFeO_3$ prepared by different routes can be contaminated by carbonate which likely forms from the interaction of unreacted La oxide with atmospheric carbon dioxide or with the presence of undecomposed La oxycarbonate formed during the combustion process of the acetate.

To assess whether such a contamination is present in the samples obtained by annealing the milled mixture, the IR spectra of these very same samples have been recorded. The spectra of the samples annealed at temperatures up 650 °C are shown in Fig. 7.

It can be observed that bands at 1600–1300, 1059 and 844 cm^{-1}, suggesting the presence of $La_2O(CO_3)_2$ [18], are present only in the IR spectra of the activated mixture annealed for 3 h at 500 and 550 °C. The spectra of the sample annealed at $T \geq 600$ °C do not longer show these peak but only the doublet at 570 and 430 cm^{-1} that is due to the stretching of Fe–O bonds in $LaFeO_3$ [18]. Therefore, according to the IR evidence, a thermal treatment of 3 h at 600 °C it is enough to yield carbonate-free $LaFeO_3$ powder when starting from the mechanically activated mixture.

Such information has been checked by TG measurements performed on the samples of milled mixture annealed for different times at different temperatures. The samples, after the annealing, have been heated up to 900 °C, and the residual mass values attained at the end of the runs are reported in Table 1.

From the obtained results, it can be concluded that the reaction has not been completed yet after the 3-h annealing at 500 and 550 °C: indeed the relevant samples show a larger mass loss in the TG runs performed on them. The opposite is true by higher annealing temperatures ($T \geq 600$ °C): the relevant samples show a negligible mass loss in the TG runs performed on them after they have been annealed. However, it has to be noted that the reaction can be completed also at lower temperatures provided that the mixture is kept at these temperatures (500 and 550 °C) for longer times. Indeed, 83 h (at 500 °C) and 24 h (at 550 °C) are needed to yield samples that in the relevant TG run

Table 2 Specific surface area data (A, m^2 g^{-1}) of samples of mechanical milling prepared $LaFeO_3$ after annealing under different time (h)/temperature (°C) conditions

T_{anneal}/°C/t(h)	A/m^2 g^{-1}
500/83	19.75
550/24	8.14
600/3	7.04
700/3	6.15
800/3	2.13

Table 1 Residual mass (%) attained on samples annealed for different times at the temperatures reported (see text)

T_{anneal}/°C/time/h	$M_{residual,900\ °C}$/%	T_{anneal}/°C/time/h	$M_{residual,900\ °C}$/%
500/3	89.97	550/24	98.61
500/9	93.12	600/3	98.19
500/12	92.62	650/3	99.36
500/50	96.99	700/3	99.49
500/83	98.15	750/3	99.43
550/3	95.10	800/3	99.47

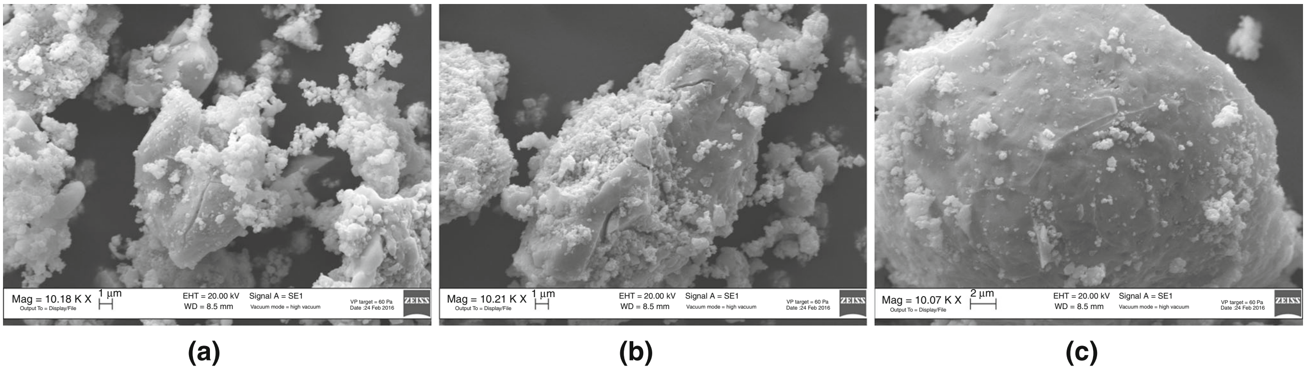


Fig. 8 SEM micrographs recorded on samples of the activated mixture annealed for 3 h at **a** 600 °C, **b** 700 °C and **c** 800 °C

show residual masses near to those obtained after the annealing performed at $T \geq 600$ °C. The XRD patterns of these mixtures confirm that $LaFeO_3$ is the only phase present in the mixtures annealed for 3 h at $T \geq 600$ °C and for 83 h (500 °C) and 24 h (550 °C).

The specific surface area has been determined on samples of $LaFeO_3$ obtained from the milled mixture annealed at 500 °C (83 h), 550 °C (24 h), and at all the temperatures from 600 up to 800 °C (3 h annealing).The results are reported in Table 2, showing that the specific surface area decreases by increasing the annealing temperature.

This result is confirmed by SEM micrographs taken on samples of milled mixture annealed for 3 h at 600 °C (Fig. 8a), 700 °C (8b) and 800 °C (8c). They show that, by increasing the annealing temperature, the share of the fine grains present in the annealed mixtures decreases.

Conclusions

1. The mechanism of the solid-state reactions in the $La(CH_3COO)_3 \cdot 1.5H_2O–FeC_2O_4 \cdot 2H_2O$ mixtures has been studied by TG–DSC. The mass loss processes taking place in the milled and in the physical mixture are quite similar. What is different is the exothermic enthalpy change under the main mass loss process. Furthermore, XRPD shows that $LaFeO_3$ is the product formed when starting from milled mixtures, while a mixture of $LaFeO_3$ and the forming oxides (La_2O_3–Fe_2O_3) is the product obtained when starting from a physically prepared mixture;
2. The synthesis of $LaFeO_3$ can be accomplished from reaction between La_2O_3 and Fe_2O_3 formed by the thermal decomposition of the milled mixture of the precursors. Such a decomposition/solid -state reaction is realized by 3-h annealing at temperatures as low as 600 °C;
3. The $LaFeO_3$ is free from carbonaceous impurities when synthesized at $T \geq 600$ °C. However, the compound can be synthesized at temperatures as low as 500 °C provided it is maintained at these temperatures for longer times. The specific surface area of the samples decreases with increasing temperature.

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