

Synthesis and Characterization of LaFeO₃ powders by a mixed Mechanical/Thermal processing route

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Among the perovskite oxides (general formula ABO₃), the lanthanum ferrite, LaFeO₃ (LF), has raised considerable interest since it can be used in many applications due to its resistance to high temperatures. So for example LaFeO₃ 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, sometimes not very environment-friendly, starting reagents. Besides, another considerable issue lays 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 of the high temperatures usually required for developing solid-state reactions; 3) possibility of preparing materials with special properties.

In previous works [14,15,16,17] we studied the formation of different ternary oxides (BaTiO₃, YFeO₃, CaSnO₃ and NiFe₂O₄) from a combination of mechanical and thermal treatment.

In the present work we report on a further study of the mechanochemical synthesis of LaFeO₃. As lanthanum and iron precursors we used respectively lanthanum acetate sesquihydrate [La(CH₃COO)₃·1.5H₂O], that has an edge over lanthanum oxide in not being hygroscopic, and iron (II) oxalate dehydrate [FeC₂O₄·2H₂O].

We studied the reactions taking place in the mixtures during heating and also characterized the products formed in the mixtures by annealing them at different temperatures with different techniques (XRPD, TG, FT-IR, DSC, nitrogen porosimetry).

EXPERIMENTAL SECTION

The starting chemicals used were FeC₂O₄·2H₂O (purity 99.9% - Aldrich Chimica, Italy) and La(CH₃COO)₃·1.5 H₂O (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 (under air flow of 100 mL/min) from 25 °C 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 hours 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 ($\text{CuK}\alpha$ radiation, step width 0.015° , 2s/step, 40 kV, 40 mA, $2\theta = 15-50$).

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 ($\approx 5\%$ 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.

RESULTS AND DISCUSSION

a. 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.

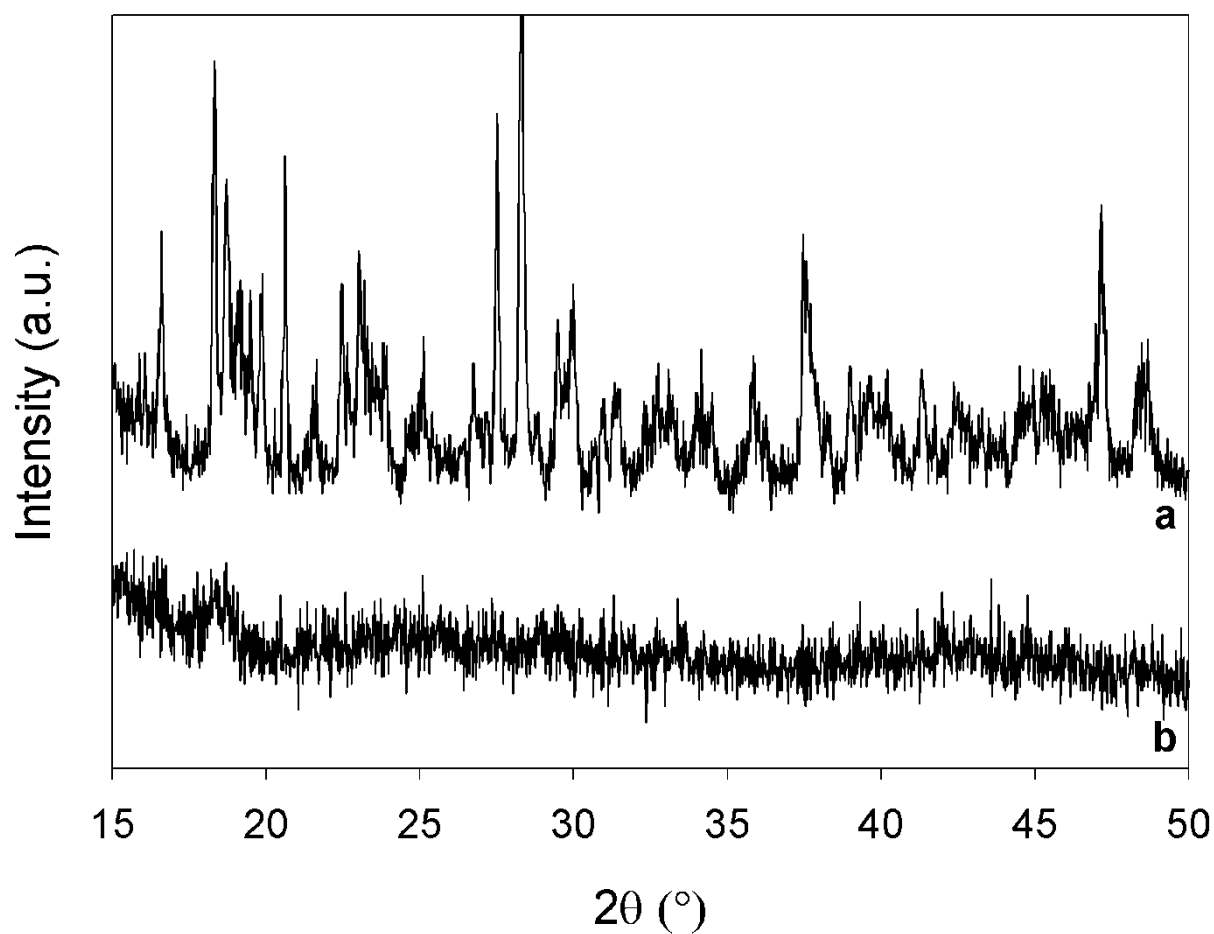


Figure 1 – XRPD patterns on samples of (a) physical mixture and (b) mechanically activated mixture

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

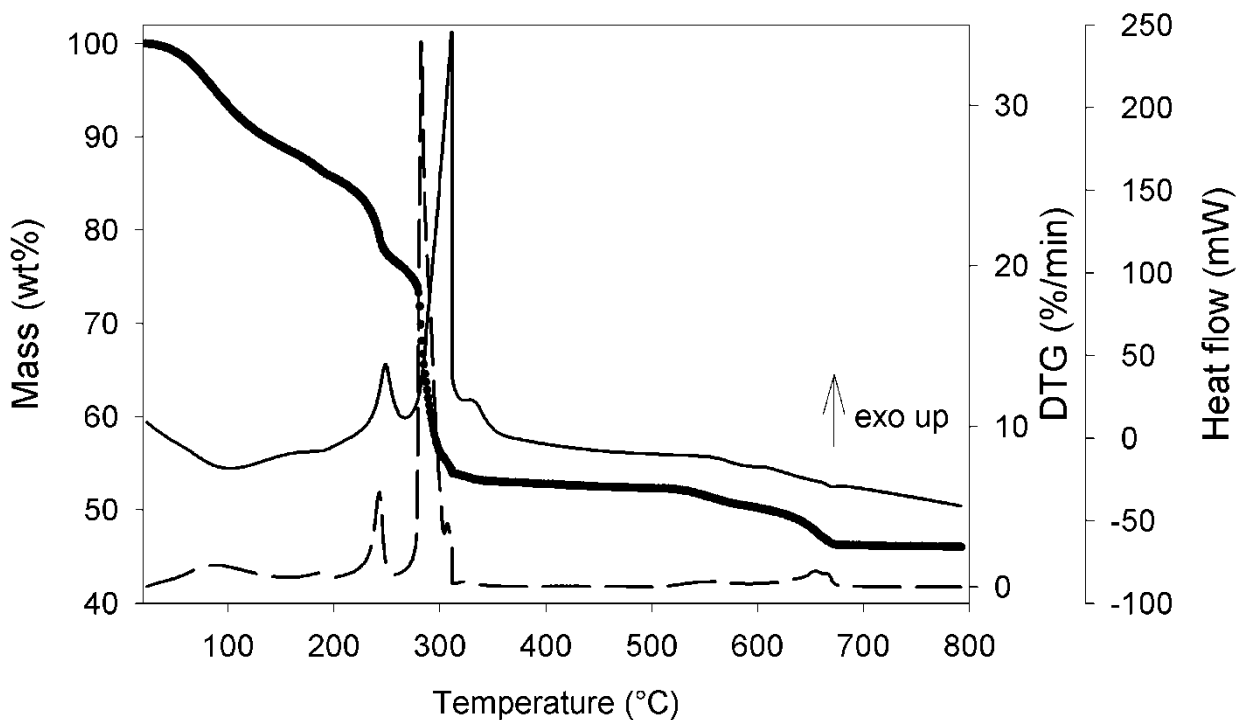
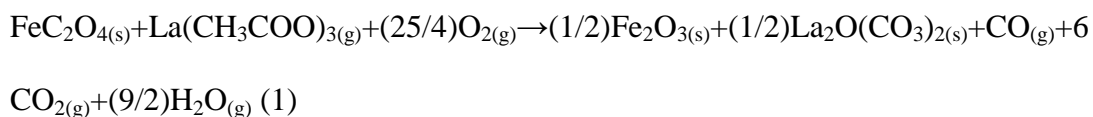


Figure 2 – TG (Full line), DSC (Full thinner line), DTG (dashed line) curves recorded on a sample of activated mixture

The first stage of mass loss process ends ($\approx 175^{\circ}\text{C}$) at a residual mass of $87.46 \pm 0.19\%$ (mean value from 5 independent measurements) that is in a reasonable agreement 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, originating from the dehydration process.

The DTG curve shows two peaks: the first one ends at $\approx 260^{\circ}\text{C}$ and corresponds to a residual mass value ($76.93 \pm 0.36\%$) $\approx 1\%$ higher than the value expected for the formation of the mixture $\text{La}(\text{CH}_3\text{COO})_3 + (1/2)\text{Fe}_2\text{O}_3$ (75.70%). The DSC counterpart is an exothermic peak whose enthalpy cannot be evaluated as stage 2 is not well separated from the subsequent stage 3.

Stage 3 is characterized by a very high rate of reaction (see the very intense DTG peak) and it is accompanied by a very intense exothermic DSC peak. The mass value at the end of stage 3 is $52.39 \pm 0.55\%$ ($T \approx 500^{\circ}\text{C}$), that is sensibly lower than the value of the residual mass expected (54.83%) at the end of reaction (1):



Clearly stages (2+3) 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 enthalpy of the double exothermic DSC peak accompanying stages (2+3) of the process is $\Delta_{\text{exo}}H = -1512 \pm 78 \text{ Jg}^{-1}$. The last stage of mass loss (stage 4) ends at $\approx 700^\circ\text{C}$ at a residual mass of $46.08 \pm 0.32\%$ that shows a good agreement with the value expected for the formation of a mixture $(1/2)\text{La}_2\text{O}_3 - (1/2)\text{Fe}_2\text{O}_3$ (46.41%).

For 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.

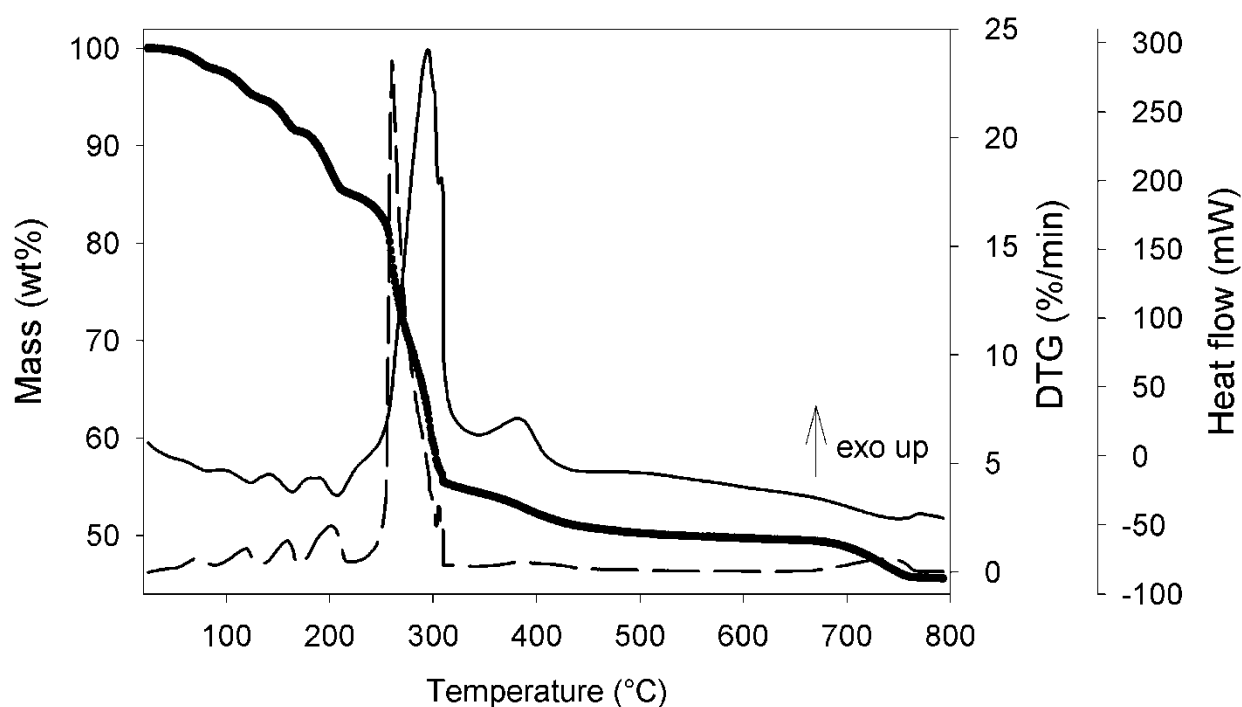


Figure 3 – TG (Full line), DSC (Full thinner line), DTG (dashed line) curves recorded on a sample of physical mixture

The first stage of mass loss shows a final mass value at the end of the first stage ($86.00 \pm 0.25\%$) 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 ($\approx 350^\circ\text{C}$) the residual mass value is $50.42 \pm 0.32\%$ that is sensibly lower than that expected for the combustion of La acetate leading to the formation of $\text{La}_2\text{O}(\text{CO}_3)_2$. In the case of the physical mixture too the process of combustion includes also 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 with respect to what happened with the milled mixtures. Moreover, it can be observed that the heat released under such a double exothermic peak is much higher ($\Delta_{\text{exo}}H = -3000 \pm 97 \text{ Jg}^{-1}$). 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 $\approx 780^\circ\text{C}$ with a residual mass of $45.83 \pm 0.22\%$ that shows a fair agreement with the value expected for the formation of a mixture $(1/2)\text{La}_2\text{O}_3 - (1/2)\text{Fe}_2\text{O}_3$ (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 mass loss stage (2+3).

However the most striking difference on what happens by heating the two types of mixture can be observed in Figure 4, that 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 .

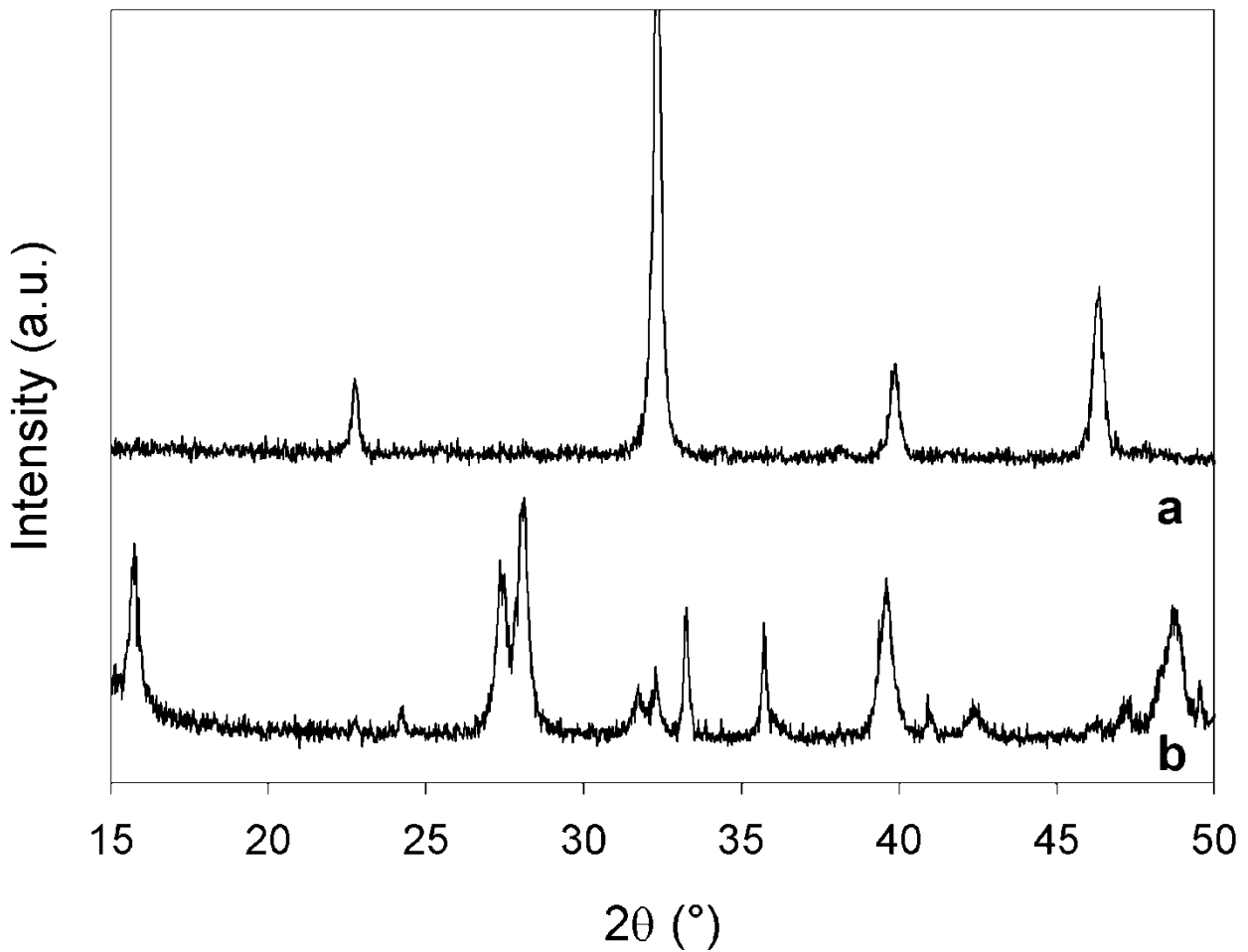


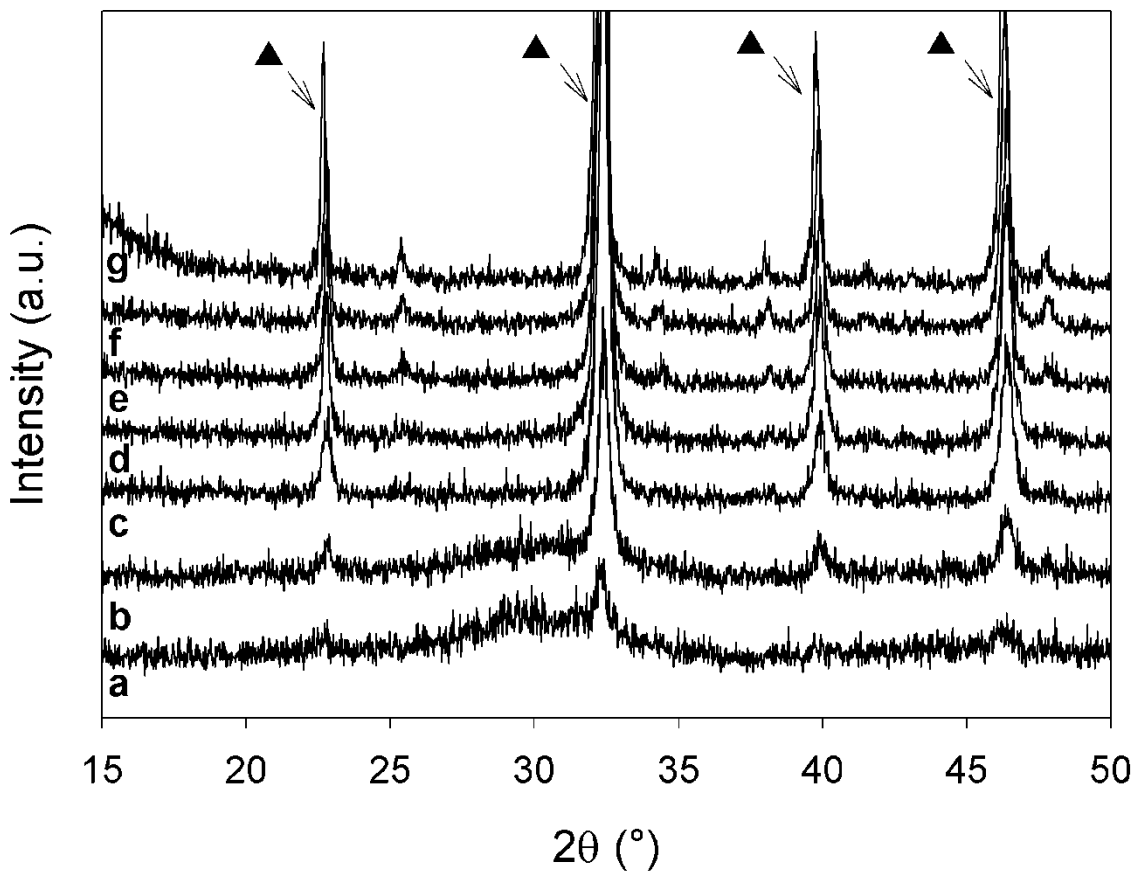
Figure 4 – XRPD patterns of the residual recovered at the end of TG/DSC runs on sample of (a) activated mixture (b) physical mixture

The only diffraction peaks of the residual of the mechanically activated mixture are those characteristic of lanthanum ferrite LaFeO_3 (orthorhombic JCPDS-00-037-1493). The situation is completely different as concerns the residual of the physical mixture that, besides some less intense peaks of LaFeO_3 , shows the peaks characteristic of Fe_2O_3 and of $\text{La}(\text{OH})_3$ that forms by the interaction between unreacted La_2O_3 and air moisture.

b. Synthesis of LaFeO₃

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

Figure 5 – XRPD patterns recorded on samples of the activated mixture annealed 3h at (a) 500°C; (b) 550°C; (c) 600°C; (d) 650°C; (e) 700°C; (f) 750°C; (g) 800°C.



In all the samples, but that heated up to 500°C, only the peaks of LaFeO₃ are present. In the sample heated up to 500°C, the peak are very broad and point out to the formation of amorphous LaFeO₃. The collected experimental evidence shows that LaFeO₃ can be obtained by short-annealing (3h) of the mechanically activated mixture at temperatures as low as 550°C.

The same thermal schedule (with isothermal stages of 3h 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 Figure 6.

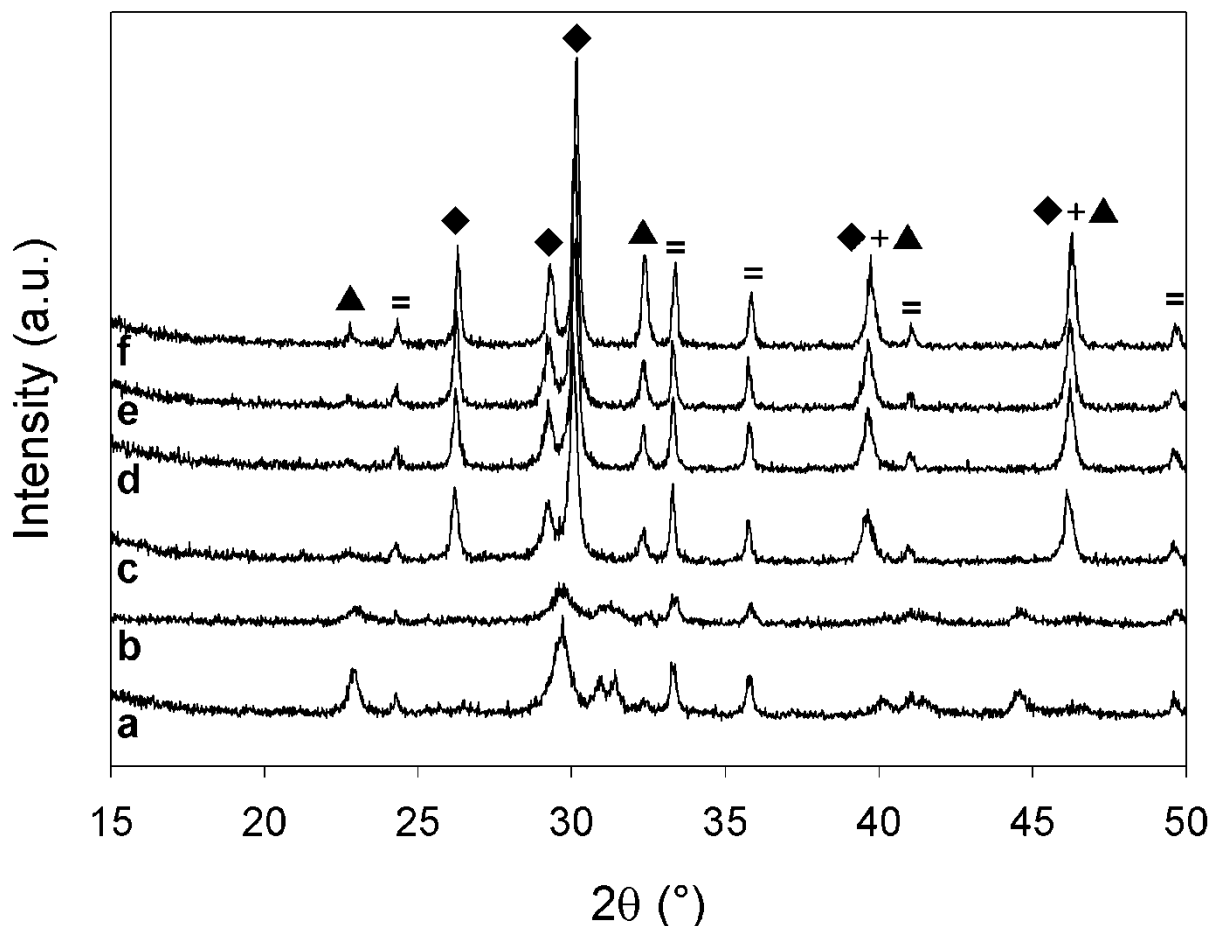


Figure 6 – XRPD patterns recorded on samples of the physical mixture annealed 3h at (a) 550°C; (b) 600°C; (c) 650°C; (d) 700°C; (e) 750°C; (f) 800°C. ▲: LaFeO₃; = : Fe₂O₃; ◆ : La₂O₃

It can be seen that, although the peaks of LaFeO₃ 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 (La₂O₃ and Fe₂O₃).

The obtained results suggest that, starting from the activated mixture, LaFeO₃ forms directly from the oxides mixture formed by thermal decomposition of the precursors. The situation is different when the synthesis is attempted starting from a physical mixture: the oxide mixture formed by

thermal decomposition of the precursors in the same temperature range of the milled mixtures reacts only very slowly leading to a mixture $\text{La}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-LaFeO}_3$.

3. Characterization of LaFeO_3 synthesized from mechanical activated mixtures

It is reported in the literature [18] that the samples of LaFeO_3 prepared by different routes can be contaminated by carbonate that presumably forms from the interaction of unreacted La oxide with atmospheric carbon dioxide or to the presence of still not decomposed La oxycarbonate formed during the combustion process of the acetate.

To assess if 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 to 650°C are shown in Figure 7.

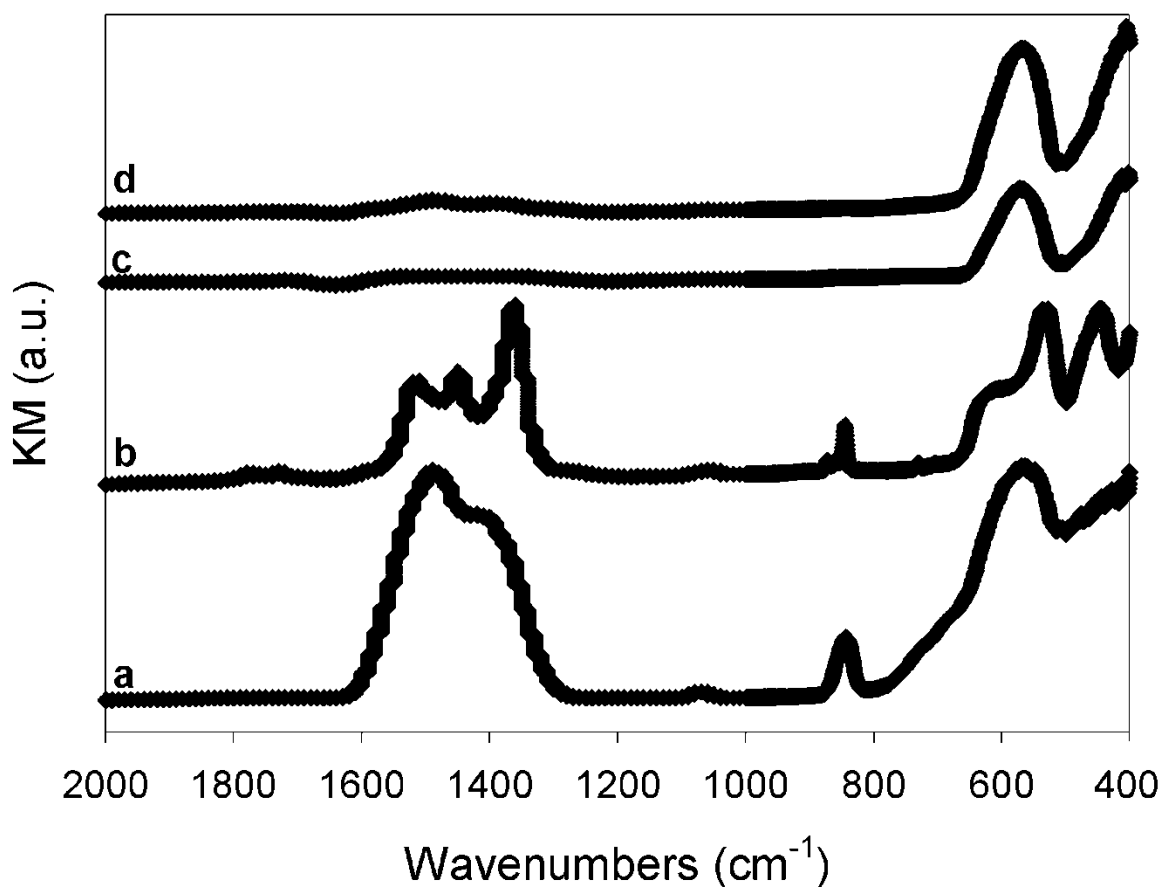


Figure 7 – FT-IR spectra recorded on samples of the activated mixture annealed 3h at (a)500°C; (b) 550°C;(c) 600°C;(d) 650°C.

It can be observed that bands at 1500-1450 cm^{-1} , 1059 cm^{-1} and 844 cm^{-1} , suggesting the presence of $\text{La}_2\text{O}(\text{CO}_3)_2$ [18], are present only in the IR spectra of the activated mixture annealed 3h at 500 and 550°C. The spectra of the sample annealed at $T \geq 600^\circ\text{C}$ do not longer show these peak but only the doublet at 570 and 430 cm^{-1} [18] that is due to the stretching of Fe-O bonds in LaFeO_3 . Therefore, according to the IR evidence, a thermal treatment of 3h 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 also by TG measurements performed on the samples of milled mixture annealed for different times at different temperatures. The samples have been heated up to 900°C and the residual mass attained at the end of the runs are reported in Table 1

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

$T_{\text{anneal}}(^{\circ}\text{C})/\text{time (h)}$	$M_{\text{residual},900^{\circ}\text{C}} (\%)$	$T_{\text{anneal}}(^{\circ}\text{C})/\text{time (h)}$	$M_{\text{residual},900^{\circ}\text{C}} (\%)$
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

From the obtained results it can be concluded that the reaction hasn't been completed yet after the 3h-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 ($T \geq 600^\circ\text{C}$): the relevant samples show a negligible mass loss in the TG runs.

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 for longer times. Indeed 83h (at 500°C) and 24h (at 550°C) are needed to obtain residual mass that are near to those obtained at $T \geq 600^\circ\text{C}$. The XRD patterns of these mixtures confirm that LaFeO_3 is the only phase present in the mixtures annealed for 3h at $T \geq 600^\circ\text{C}$ and for 83h (500°C) and 24h (550°C).

The specific surface area has been determined on samples of LaFeO_3 obtained from 83h-annealing of milled mixture at 500, 24h at 550 and 3h at 600, 700 and 800°C. The results are reported in Table 2, showing that the specific surface area decreases by increasing the annealing temperature.

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

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

CONCLUSIONS

- 1) The mechanism of the solid state reactions in the $\text{La}(\text{CH}_3\text{COO})_3 \cdot 1.5\text{H}_2\text{O} - \text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ mixtures has been studied by TG-DSC and XRPD. From the XRPD it has been shown that LaFeO_3 is the product formed when starting from milled mixtures while a mixture of LaFeO_3 and of the forming oxides (La_2O_3 - Fe_2O_3) is the product obtained when starting from a physically prepared mixture. The different path of the solid state reaction is also revealed by the DSC results ;
- 2) 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 3h-annealing at temperatures as low as 600°C;

- 3) The LaFeO_3 is free from carbonaceous impurities when synthesized at $T \geq 600^\circ\text{C}$. 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;
- 4) The heat capacity of LaFeO_3 synthesized at $T \geq 600^\circ\text{C}$ has been determined as a function of temperature

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