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Synthesis of $La_{1-x}Sr_xMO_3$ (M = Mn, Fe, Co, Ni) nanopowders by alanine-combustion technique

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Abstract

$La_{1-x}Sr_xMO_3$ (M = Mn, Fe, Co, Ni, x = 0–0.3) powders were obtained by solution combustion technique using metal nitrates and α-alanine. The as-prepared powders, resulted by the combustion reaction, were annealed at different temperatures to investigate the evolution of crystalline phases. For the strontium-doped lanthanum-based perovskites, higher annealing temperatures than for the corresponding pure lanthanum-based perovskites are needed to obtain single-phase compounds depending on M-site metal and strontium content. The oxide powders were investigated by FT-IR spectra, X-ray diffraction (XRD), scanning electron microscopy (SEM) and specific area measurements. Based on our results we propose different mechanisms for $La_{1-x}Sr_xMO_3$ (M = Mn, Fe, Ni, x = 0–0.3) obtaining, depending on the intermediary compounds formed in the combustion reaction or during the thermal treatment of the as-prepared powders.

Keywords: A. Powders-chemical preparation; D. Perovskites; Combustion method

1. Introduction

Perovskite-type oxides, $LaMO_3$, where M is a transition metal, are interesting materials for catalytic applications, solid oxide fuel cells, electrochemistry, sensors, etc.[1–4] One of the soft chemistry route applied to synthesise a large variety of oxide powders is the solution combustion method, which has some advantages as relatively cheap raw compounds (metals nitrates and easily available organic molecules) and set-ups, fast reactions, preservation of the metallic cations stoichiometry in the obtained oxides, and low energy consumption.[5,6] The success of the solution combustion technique in the oxide powders synthesis at low temperature is due to the formation of a chelating compound between metallic cations and a suitable fuel (e.g., urea, glycine, and citric acid) that helps in preventing metal cations selective precipitation and maintains compositional homogeneity. The oxide powder morphology, like particles size, surface area and degree of agglomeration depend on the enthalpy and flame temperature generated during combustion, which itself is influenced by the nature of the fuel and oxidiser/fuel ratio.[5,6]

Previously, we have reported studies on the synthesis of some perovskite oxide powders by solution combustion method using different fuels like urea, oxamic hydrazide, α-alanine, etc. at different oxidizer/fuel ratio values.[7–10] Though, the combustion method is a simple and fast route to prepare pure lanthanum-based perovskite, $LaMO_3$ (M = Mn, Fe, Co, Ni), at low temperatures, we have noticed that higher temperatures are necessary to obtain strontium-doped lanthanum-based perovskites, and depending on the transition metal, M, only a limited amount of Sr^{2+} ions can replace La^{3+} cations in the perovskite crystalline structure by this method. These important aspects of the solution combustion synthesis are scarcely presented and/or explained in the literature.[11]

The aim of our work was to give a deep insight into the mechanism of pure and Sr-doped lanthanum-based perovskite synthesis by combustion method and the paper presents the effect of transition metal, M, on the evolution of crystalline phase pure and of Sr-doped $LaMO_3$ (M = Mn, Fe, Co, Ni) using alanine–nitrate synthesis at Sr:La molar ratio values, $x:1-x$ (x = 0–0.3).

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2. Experimental

Lanthanum-based perovskites, $La_{1-x}Sr_xMO_3$ (M = Mn, Fe, Co, Ni, x = 0–0.3), were obtained by solution combustion technique from metal nitrates (oxidizing agents) and α-alanine (fuel), in fuel-rich conditions with 25% excess of alanine. More details about the experimental procedure are presented elsewhere.[7,8]

Briefly, the reaction mixture was heated on a hot plate with magnetic stirring, to evaporate the water, followed by the ignition and combustion of the precursor producing a fine ash (named as-prepared powder), which was annealed at different temperatures and durations to investigate the mechanism of $La_{1-x}Sr_xMO_3$ (M = Mn, Fe, Co, Ni; x = 0–0.3) formation.

The isolated precursors (before the ignition of the reaction mixture), as-prepared powder and annealed compounds were analysed by infrared spectroscopy performed on a Bruker Tensor 27 Spectrometer (KBr-pellet technique). XRD data were collected using a Rigaku Miniflex II diffractometer with CuK_α radiation at a step of 0.01° in the range $2\theta = 10–70^o$. The average crystallite size values (D) were calculated by means of the Rigaku PDXL software and specific surface areas were measured by using Quantachrome Autosorb 1. Scanning electron micrographs of pure and doped lanthanum-based perovskites were obtained by using a Hitachi S 2600N scanning electron microscope.

3. Results and discussions

The FT-IR analyses have been performed in order to check the coordination of the organic compound (α-alanine) to the metallic cations in the precursors and the presence of carbonate-type species or residual organic compounds in the as-prepared powders, respectively. The FT-IR spectra of $La_{1-x}Sr_xMO_3$ alanine-based precursors are very similar and the metallic cations form complex compounds with α-alanine.[7,8,10] The coordination of the aminoacid molecules by oxygen atom of carboxilate group is proved by the shift of ν_{as}(CO) of α-alanine at higher frequencies, from 1597 cm^{-1} to 1620 cm^{-1}, and by nitrogen of amine group, by the shift of $\rho_r(NH_2)$ at lower frequencies, from 1237 cm^{-1} to 1200–1205 cm^{-1}, depending on the transition metal (Fig. 1a and b).[12] The FT-IR spectrum of $La_{0.8}Sr_{0.2}MnO_3$ as-prepared powder (Fig. 1c) shows the intense band of the perovskite oxide (at 600 cm^{-1} assigned to the vibration of Mn–O bond in the octahedral coordination).

The oxide powders were characterised by XRD, SEM and specific surface area measurements. The as-prepared powders were annealed at different temperatures and durations to study the evolution of crystalline phases.

3.1. Pure lanthanum-based perovskites

The perovskite single-phase compound with orthorhombic symmetry is obtained directly from combustion reaction, only in the case of $LaFeO_3$ as it can be noticed in Fig. 2. XRD patterns of $LaFeO_3$ as-prepared powder have been indexed by ICDD 88-0641 and no phase modification has been observed in the annealed sample at 400 °C, 3 h (Fig. 2). XRD patterns of lanthanum manganite (Fig. 3) show that the as-prepared powder presents some amorphous phases and the perovskite one. At 400 °C, 3 h, single-phase lanthanum manganite rich in oxygen, $LaMnO_{3.15}$, with distorted perovskite structure is obtained. If the annealing treatment is performed at 600 °C, 3 h, the amorphous residual carbon is removed completely (checked by thermogravimetric analysed performed in air) and the crystallinity of $LaMnO_{3.15}$ single-phase compound with orthorhombic symmetry increases.[8]

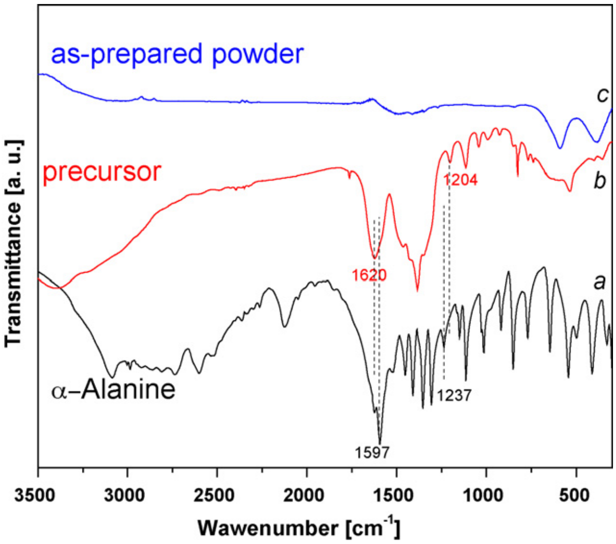

Fig. 1. FT-IR spectra of: (a) α-alanine, (b) alanine-based precursor of $La_{0.8}Sr_{0.2}MnO_3$ and (c) $La_{0.8}Sr_{0.2}MnO_3$ as-prepared powder.

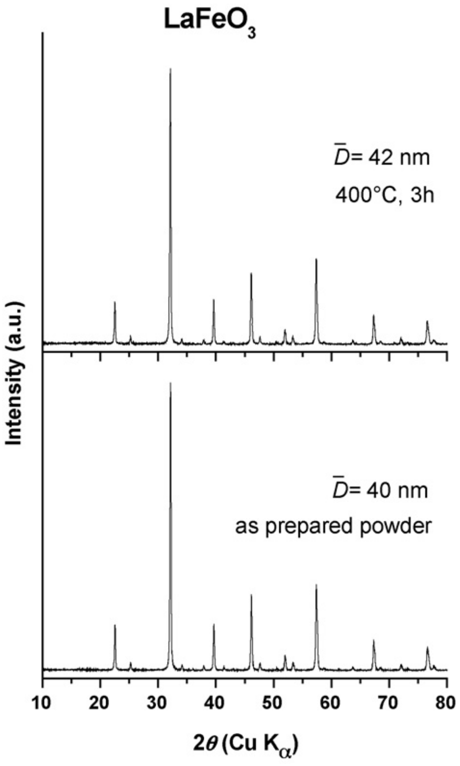

Fig. 2. XRD patterns of $LaFeO_3$ samples.

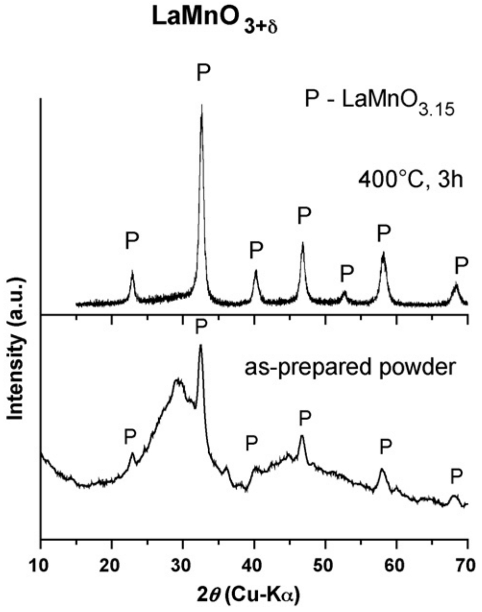

Fig. 3. XRD patterns of $LaMnO_{3+\delta}$ powders.

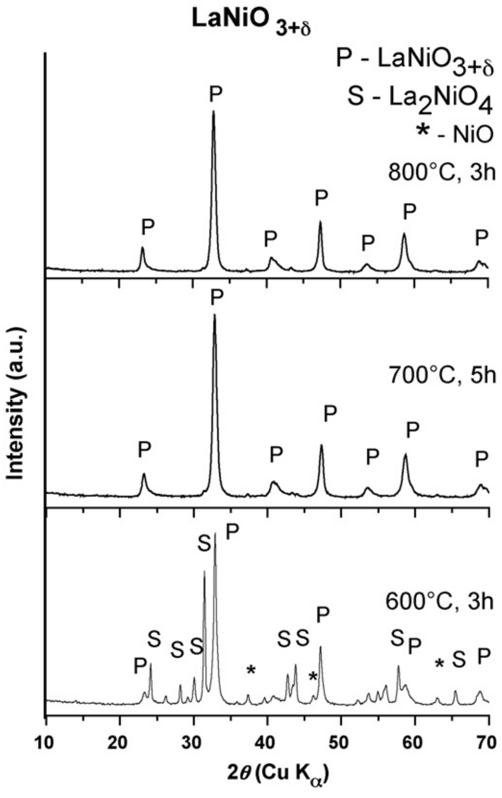

Fig. 4. XRD patterns of $LaNiO_{3+\delta}$ samples prepared by calcining as-prepared powder at different temperatures and durations.

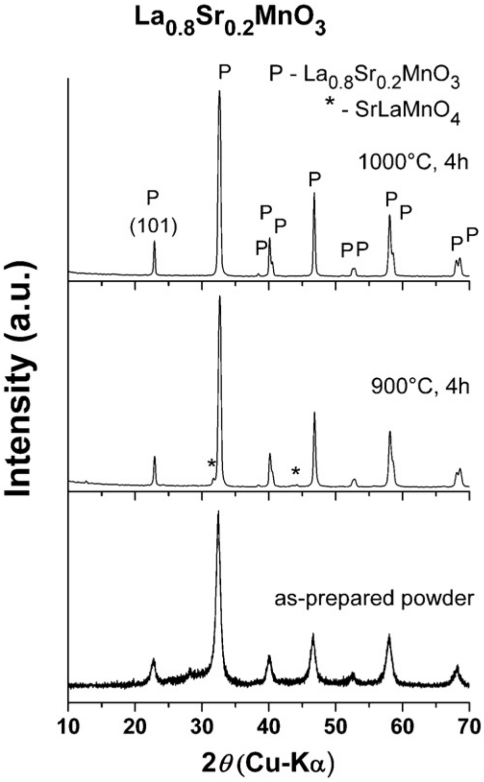

Fig. 5. XRD patterns of $La_{0.8}Sr_{0.2}MnO_3$ obtained at different temperatures.

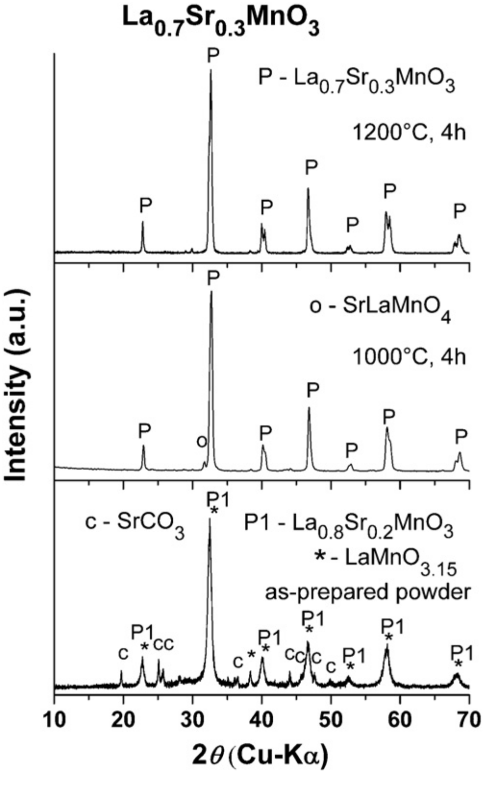

Fig. 6. XRD data for $La_{0.7}Sr_{0.3}MnO_3$ prepared by annealing as-prepared powders at different temperatures.

Previously, we have reported that pure lanthanum cobaltite with rhombohedral distorted perovskite-like structure was obtained by annealing the as-prepared powder at 600 °C, 3 h and the as-prepared powder was mainly amorphous.[7] $LaNiO_{3+\delta}$ with perovskite structure and rhombohedral symmetry is formed by annealing as-prepared powder at 700 °C, 5 h or 800 °C, 3 h,

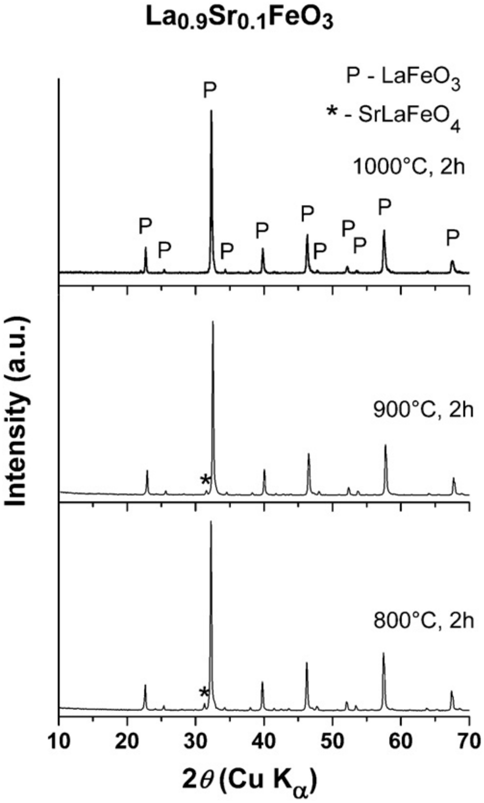

Fig. 7. XRD data for $La_{0.9}Sr_{0.1}FeO_3$ samples obtained by nitrate–alanine synthesis at different temperatures.

respectively (Fig. 4). At 600 °C a mixture of spinel La_2NiO_4, NiO and perovskite $LaNiO_3$ phases have been formed (Fig. 4).

3.2. Strontium-doped lanthanum-based perovskites

For Sr-doped lanthanum-based perovskites, higher annealing temperatures than for the corresponding pure $LaMO_3$ are needed for obtaining single-phase compounds depending on M-site metal.

In the case of strontium-doped lanthanum manganites, $La_{0.9}Sr_{0.1}MnO_3$ single-phase is formed by annealing as-prepared powder at 800 °C, 4 h,[8] and by rising the strontium content of $La_{1-x}Sr_xMnO_3$ ($x = 0.2, 0.3$), $SrLaMnO_4$ (tetragonal K_2NiF_4-type structure) is formed as secondary phase and its concentration increases with strontium content. This secondary phase disappears at high temperature, 1000 °C for $x = 0.2$ and 1200 °C for $x = 0.3$, respectively (Figs. 5 and 6). The mechanism of $La_{0.7}Sr_{0.3}MnO_3$ obtaining is different than the one of $La_{1-x}Sr_xMnO_3$ ($x = 0.1, 0.2$) because of the formation of strontium carbonate during the combustion reaction. The XRD data of $La_{0.7}Sr_{0.3}MnO_3$ as-prepared powder (Fig. 6) have shown the formation of a multiphase compound that contains two perovskite phases, rhombohedral $La_{0.8}Sr_{0.2}MnO_3$ (ICDD 40-1100) and orthorhombic $LaMnO_{3.15}$ (ICDD 50-0298), as well as $SrCO_3$ phase (ICDD 84-1778). The annealing treatment of the as-prepared powder at 900 °C, 4 h or 1000 °C, 4 h leads to the formation of $La_{0.7}Sr_{0.3}MnO_3$ and $SrLaMnO_4$ phases. The last phase concentration diminishes with the increasing of the annealing temperature and disappears completely after the thermal treatment at 1200 °C, 4 h (Fig. 6).

Table 1
Some data for lanthanum-based perovskite oxide samples.

Sample (symmetry)	Annealing conditions	D (nm)	S (m^2/g)
$LaMnO_3$ (O)	600 °C, 3 h	16	25.6
$La_{0.9}Sr_{0.1}MnO_3$ (O)	800 °C, 4 h	19	8.8
$La_{0.8}Sr_{0.2}MnO_3$ (R)	1000 °C, 4 h	31	5.9
$LaFeO_3$ (O)	As-prepared powder	40	4.0
$LaFeO_3$ (O)	400 °C, 3 h	42	3.9
$La_{0.9}Sr_{0.1}FeO_3$ (O)	1000 °C, 2 h	49	3.1
$La_{0.8}Sr_{0.2}FeO_3$ (O)	1000 °C, 2 h	49	3.0
$LaCoO_3$ (R)[7]	600 °C, 3 h	19	39.6
$LaNiO_{3+\delta}$ (R)	800 °C, 3 h	34	5.2

O: orthorhombic symmetry; R: rhombohedral symmetry.

Although, $LaFeO_3$ is easily formed by nitrate–alanine synthesis, strontium-doped lanthanum ferrites, $La_{1-x}Sr_xFeO_3$ ($x = 0.1$–0.3) are obtained by annealing as-prepared powders at high temperatures (1000 °C, 2 h for $x = 0.1$; 0.2). The high stability of $SrLaFeO_4$ secondary phase (tetragonal K_2NiF_4-type structure), produced directly as crystalline phase in the combustion reaction, is responsible for the difficulty of $La_{1-x}Sr_xFeO_3$ obtaining. The concentration of the secondary phase varies with strontium content and temperature in a similar manner as for $La_{1-x}Sr_xMnO_3$, but no strontium carbonate phase has been detected by XRD or FT-IR investigation in the as-prepared powders. By annealing $La_{0.7}Sr_{0.3}FeO_3$ as-prepared powder at

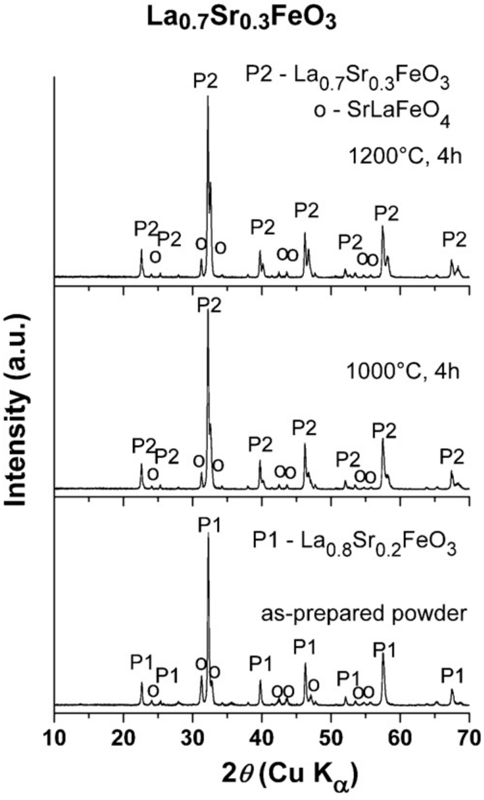

Fig. 8. XRD patterns of $La_{0.7}Sr_{0.3}FeO_3$ samples obtained by different annealing treatments.

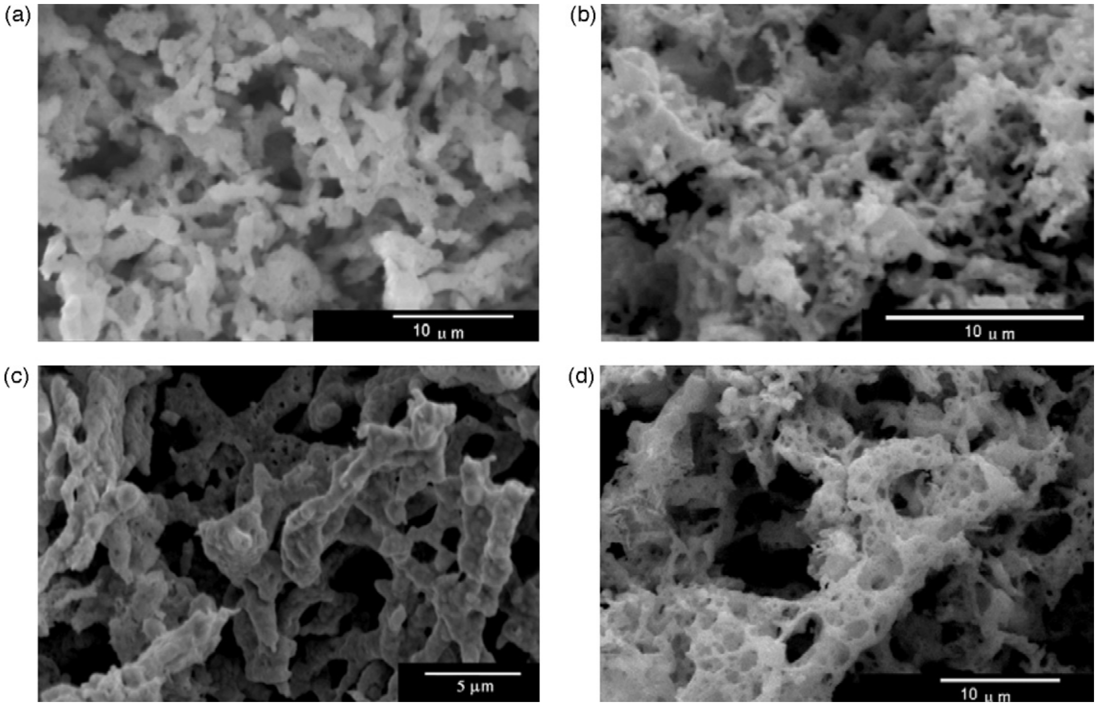

Fig. 9. SEM micrographs of: (a) $LaFeO_3$ (as-prepared powder); (b) $LaNiO_3$ (800 °C, 3 h); (c) $La_{0.9}Sr_{0.1}FeO_3$ (1000 °C, 2 h); (d) $La_{0.8}Sr_{0.2}MnO_3$ (1000 °C, 4 h).

1000–1200 °C, 2–4 h, it has been obtained $La_{0.7}Sr_{0.3}FeO_3$ with orthorhombic symmetry (ICDD 89-1269) besides $SrLaFeO_4$ secondary phase (ICDD 29-1305) (Figs. 7 and 8).

Strontium-doped lanthanum cobaltite powders, $La_{1-x}Sr_xCoO_3$, were prepared as single-phase compounds by calcining as-prepared powder at 1000 °C up to $x = 0.3$ as we have previously reported.[7]

The crystallite size and specific surface area values of some pure and strontium-doped lanthanum-based perovskite samples are listed in Table 1.

The SEM micrographs reveal that the lanthanum-based perovskite samples present relatively similar morphology with fine primary particles with tendency of agglomerates formation with irregular shape, high porosity and spongy aspect (Fig. 9). Lanthanum-based perovskites have different specific surface area values depending on the transition metal; pure and Sr-doped lanthanum cobaltite samples have the highest values[7] and have showed good catalytic activities.[13] Generally, the Sr-doped samples have lower specific surface area values because they are obtained at higher temperature. Among pure $LaMO_3$ perovskites, lanthanum ferrite has the lowest specific surface area ($4\,m^2/g$), lower value than $LaNiO_3$ ($5.2\,m^2/g$), though the last sample was obtained at higher temperature (Table 1).

4. Conclusions

$La_{1-x}Sr_xMO_3$ powders (M = Mn, Fe, Co, Ni; $x = 0$–0.3) were synthesised by a simple technique, nitrate–alanine synthesis. Only $LaFeO_3$ is obtained directly in the combustion reaction. Though $LaMO_3$ perovskites are relatively easy synthesized at low temperature by combustion method, strontium-doped lanthanum-based perovskites are obtained at high temperatures depending on the transition metal and strontium content. $La_{0.7}Sr_{0.3}FeO_3$ single-phase compound has not been obtained even at 1200 °C, 4 h by nitrate–alanine synthesis.

We have noticed the formation of different intermediary compounds function of the transition metal and strontium content. Based on the XRD data, we propose different reaction mechanism for $La_{1-x}Sr_xMO_3$ powders formation. For example, in the case of $La_{0.7}Sr_{0.3}MnO_3$, in the combustion reaction results $LaMnO_{3.15}$, $La_{0.8}Sr_{0.2}MnO_3$ and $SrCO_3$ compounds, which react in solid-state at 900–1000 °C with $La_{0.7}Sr_{0.3}MnO_3$ and $SrLaMnO_4$ formation, that produce at 1200 °C $La_{0.7}Sr_{0.3}MnO_3$ single-phase compound. In the case of strontium-doped lanthanum ferrite samples, only crystalline compounds and no carbonate-type species are formed directly in the combustion reactions. The mechanism of Sr-doped lanthanum ferrites, $La_{1-x}Sr_xFeO_3$ ($x = 0$–0.3) similar with $La_{0.8}Sr_{0.2}MnO_3$ formation, consists in a solid-state reaction between the perovskite and $SrLaMO_4$ (M = Fe or Mn) phases. The secondary phase obtained directly in the combustion reaction makes difficult to produce $La_{1-x}Sr_xMO_3$ single-phase compounds, especially at high dopant content.

The morphology of the lanthanum-based perovskites is relatively similar, but the specific surface values are very different depending on the transition metal and strontium content, the highest specific surface area values are measured for lanthanum cobaltite samples.[7]

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References

1. Tanaka, H. and Misono, M., Advances in designing perovskite catalysts. *Curr. Opin. Solid State Mater. Sci.*, 2001, **5**, 381–387.
2. Holtappels, P., Vogt, U. and Graule, T., Ceramic materials for advanced solid oxide fuel cells. *Adv. Eng. Mater.*, 2005, **7**, 292–302.
3. Weidenkaff, A., Preparation and application of nanostructured perovskite phases. *Adv. Eng. Mater.*, 2004, **6**, 709–714.
4. Campagnoli, E., Tavares, A., Fabbrini, L., Rossetti, I., Dubitsky, Yu., Zaopo, A. *et al.*, Effect of preparation method on the activity and stability of $LaMnO_3$ and $LaCoO_3$ catalysts for the flameless combustion of methane. *Appl. Catal. B: Environ.*, 2005, **55**, 133–139.
5. Patil, C. K., Aruna, S. T. and Mimani, T., Combustion synthesis: an update. *Curr. Opin. Solid State Mater. Sci.*, 2002, **6**, 507–512.
6. Mukasyan, A. S., Costello, C., Sherlock, K. P., Lafarga, D. and Varma, A., Perovskite membranes by aqueous combustion synthesis: synthesis and properties. *Sep. Purif. Technol.*, 2001, **25**, 25117–25126.
7. Berger, D., Matei, C., Papa, F., Voicu, G. and Fruth, V., Pure and doped lanthanum cobaltites obtained by combustion method. *Prog. Solid State Chem.*, 2007, **35**, 183–191.
8. Berger, D., Matei, C., Papa, F., Macovei, D., Fruth, V. and Deloume, J. P., Pure and doped lanthanum manganites obtained by combustion method. *J. Eur. Ceram. Soc.*, 2007, **27**, 4395–4398.
9. Matei, C., Berger, D., Stoleriu, S., Papa, F. and Fruth, V., Synthesis of lanthanum ferrite nanopowders by combustion method. *J. Optoelec. Adv. Mater.*, 2007, **9**, 1793–1796.
10. Berger, D., Ionica, C., van Landschoot, N., Papa, F. and Fruth, V., Synthesis of pure and doped lanthanum cobaltite by combustion method. *J. Optoelec. Adv. Mater.*, 2003, **5**, 719–724.
11. Striker, T., Ruud, J. A., Gao, Y., Heward, W. J. and Steinbruchel, C., A-site deficiency, phase purity and crystal structure in lanthanum strontium ferrite powders. *Solid State Ionics*, 2007, **178**, 1326–1336.
12. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part B*. John Wiley and Sons, New York, 1997, pp. 63.
13. Bosomoiu, M., Bozga, G., Berger, D. and Matei, C., Studies on combustion catalytic activity of some pure and doped lanthanum cobaltites. *Appl. Catal. B: Environ.*, 2008, **84**, 758–765.