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Pure and doped lanthanum manganites obtained by combustion method

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Abstract

Pure and strontium-doped lanthanum manganite nanopowders were obtained by solution combustion method using metal nitrates as oxidants and different organic compounds as fuel (α-alanine, glycine, urea and semioxamazide). Different molar ratios, fuel/oxidant, were chosen to study the effect of the fuel content on the phase formation and powder properties. The complex precursors isolated before ignition of the system, were characterized by FT-IR spectroscopy and thermal analysis. After ignition, the as-synthesized powders were calcined at different temperatures for obtaining single phases. Lanthanum manganite powders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), specific surface area and magnetic measurements.

Keywords: Nanomaterials; Perovskites; Powders-chemical preparation; Manganites

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1. Introduction

Pure and doped lanthanum-based perovskites show besides interesting magnetic and electric properties, a high catalytic activity for light hydrocarbons combustion and CO oxidation.[1,2] The morphology of the perovskite oxides depends on the synthesis procedure, which makes necessary to perform systematic studies on the synthesis parameters.[1,3]

The solution combustion method has the advantage of the exothermic, fast and self-sustaining chemical reaction between the metal nitrates and a suitable organic fuel. This method is a simple method for oxides synthesis and has been used to produce homogeneous, crystalline nanopowders,[4–7] but its success depends on the correct understanding of the influence of the synthesis parameters.

This paper is devoted to the synthesis and characterization of pure and Sr-doped lanthanum manganites with large surface area by combustion synthesis. Another aim of this research is to obtain more information about the chemistry of the solution combustion for lanthanum manganite synthesis using different reaction conditions.

2. Experimental

$La(NO_3)_3{\cdot}9H_2O$, $Mn(NO_3)_2{\cdot}4H_2O$, $Sr(NO_3)_2$ (Merck, > 99%) and α-alanine (Fluka, > 99%), glycine, urea, semioxamazide (Acros, > 99%) were used as received. The combustion ratio (O/F) was calculated using the reducing valence of the fuel (organic compound) and the total valence of oxidisers (nitrates) according to the propellants rule. All the syntheses in this work were performed in fuel-rich conditions with 10% ($\varphi = 1.1$) and 40% ($\varphi = 1.4$) excess of fuel. In the case of α-alanine we found $\varphi = 1.25$ as optimal to obtain the highest surface area and all the data in this paper are presented for this value. For example, the overall reaction between metal nitrates and α-alanine for $LaMnO_3$ synthesis is presented in equation (1):

$$La(NO_3)_3 + Mn(NO_3)_2 + 1.6\,\varphi C_3H_7NO_2 + 6(\varphi - 1)O_2 \rightarrow LaMnO_3 + 4.8\,\varphi CO_2 + 5.6\,\varphi H_2O + (2.5 + 0.8\,\varphi)N_2 \tag{1}$$

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Note that the combustion ratio ($\varphi = 1$) signifies that no oxygen is needed for the combustion.

The 0.2 M aqueous solutions of metal nitrates in stoichiometric amounts was mixed with the fuel and the reaction mixtures were heated on a hot plate to evaporate water. By increasing the temperature, the precursors have ignited forming as-synthesized powders. These products were annealed in air at 700 °C, 6 h, to eliminate the residual carbon and to obtain single-phase compounds. When α-alanine was used the as-synthesized powders were annealed at 600 °C, 3 h to obtain $LaMnO_3$ (LM) and 800 °C, 4 h for $La_{0.9}Sr_{0.1}MnO_{3+\delta}$ (LSM). Samples of precursors were isolated before the ignition of the systems, dried under vacuum and analysed by FT-IR spectroscopy (Nicolet Magna 550), thermogravimetry (Setaram B70) and differential scanning calorimetry (Mettler Toledo DSC 823). XRD data were collected using a Shimadzu 6000 diffractometer with Cu Kα radiation at 0.02°/s step. SEM micrographs were obtained using a Hitachi S2600N microscope. The specific surface areas were determined by BET method and the magnetic measurements were carried out at room temperature with a Faraday-type magnetometer. XPS data were acquired on a VG Scientific ESCA-3 Mk-II spectrometer with Al Kα radiation (1486.7 eV) at 10^{-7} Pa.

3. Results and discussions

Generally, the fuels used in the solution combustion method are chelating agents, which contain carboxyl, carbonyl or amine groups. The energy released during the combustion should be enough to form oxide powders, but not excessive to avoid the agglomeration of the particles. Two aminoacids, glycine (Gly) and α-alanine (Ala), urea (U) and semioxamazide (Soh) have been chosen. Two combustion regimes have been tested, volume combustion ($\varphi = 1.1$) and self-sustained combustion ($\varphi = 1.4$).[7] Table 1 lists theoretical parameters for the combustion systems.

We have noticed in the FT-IR spectrum of α-alanine-based precursor (La–Mn–Ala), comparing with of α-alanine (Fig. 1(a and b)) shifts of the intense bands from 1597 and 1412 cm^{-1} (ν_{asCO} and ν_{sCO}) to 1632 cm^{-1} (characteristic to heavy cations as La^{3+}) and 1395 cm^{-1}, respectively that indicate the coordination of α-alanine by oxygen atoms. The coordination of alanine by nitrogen is sustained by the shift of ρ_{rNH_2} band from 1237 to 1202 cm^{-1}. The La–Mn–Ala spectrum presents the characteristic bands for NO_3^- anion (1041, 825, 741 cm^{-1}) and those of coordinated water (668 and 3430 cm^{-1}).[9]

In the FT-IR spectrum of semioxamazide-based precursor (La–Mn–Soh), it is noticed that the shift of both CO groups vibration modes to lower frequencies from 1688 cm^{-1} (ν_{CO} amide) and 1655 cm^{-1} (ν_{CO} hydrazide) to 1674 and 1643 cm^{-1}, respectively which sustain the coordination of both CO groups to metallic cations (Fig. 1(c and d)). The FT-IR spectrum of La–Mn–Soh shows the presence of nitrate ions (1385, 825 cm^{-1}) and the shifted frequencies of amino groups from 3380 cm^{-1} (ν_{sNH} amide), 3293 cm^{-1} (ν_{sNH} hydrazide) and 777 cm^{-1} (ω_{NH2}) to 3358, 3233 and 729 cm^{-1}, respectively.[10] It is well known that lanthanum ions are oxophilic, so, we could assume that semioxamazide and alanine are coordinated to lanthanum ions by oxygen atoms and to manganese cations by nitrogen atoms, a similar coordination as in urea-based precursor.[6]

Table 1
Theoretical parameters of combustion systems

Parameters of combustion	Fuel			
	α-Ala	Gly	Soh	U
$\Delta_C H^0_{(s)}$ (kJ / mol)	1598.3	973.1	NF[a]	631.6
O/F	8/5	8/3	8/3	8/2
$\Delta_C H^0_{(s)} \cdot$O/F (kJ / mol)	2557.3	2595	–	2526
Moles of gases for 1 mol $LaMnO_3$	13.7	15.83	18.5	18.5

[a] NF: not found; $\Delta_C H^0_{(s)}$: energy of combustion for solid state.[8]

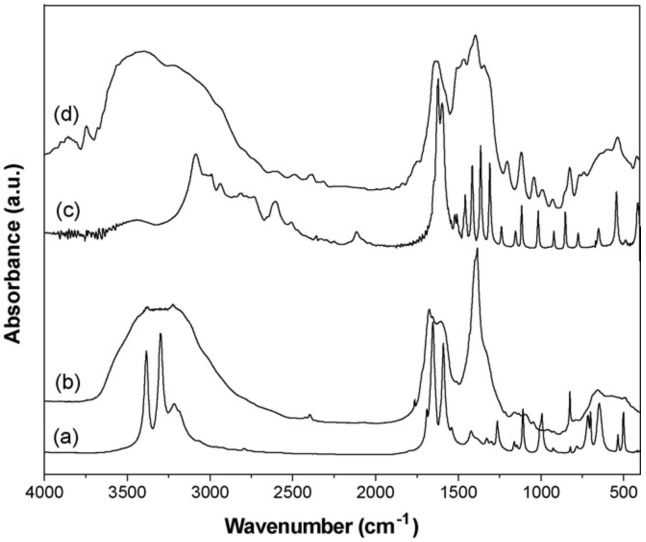

Fig. 1. FT-IR spectra of Ala (a), La–Mn–Ala, $\varphi = 1.25$ (b), Soh (c) and La–Mn–Soh, $\varphi = 1.4$ (d).

Thermal decomposition of glycine-based precursors (La–Mn–Gly) undergoes in several steps (Fig. 2(a_1, a_2)). The first endothermic effect (up to 142 °C) could be assigned to water loss. The two exothermic effects (in the temperature range 144–185 °C) correspond to the reaction between glycine

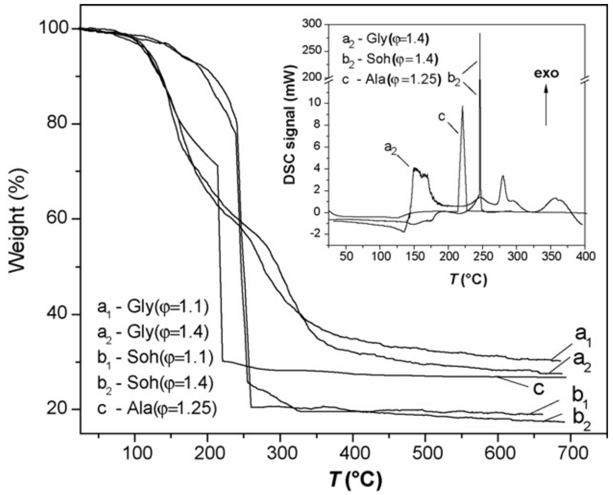

Fig. 2. TG (inset, DSC) curves of complex precursors at heating rate 5°/min, in air: La–Mn–Gly (a_1, a_2), La–Mn–Soh (b_1, b_2) and La–Mn–Ala (c).

Table 2
Properties of investigated systems

Fuel used (φ value)	As- synthesized powders		Calcined powder (700 °C, 6 h)	
	Obtained phase	S (m^2/g)	Obtained phase	S (m^2/g)
Gly (1.1)	~Amorphous	ND[a]	$LaMnO_{3.26}$	13.0
U (1.1)	~Amorphous	ND	$LaMnO_{3.15}$	8.0
Soh (1.1)	$LaMnO_{3.00}$	1.5	$LaMnO_{3.15}$	6.0
Gly (1.4)	Amorphous	30.1	$La_{1-x}Mn_{1-z}O_3$	19.5
U (1.4)	Amorphous	ND	$La_{1-x}Mn_{1-z}O_3$	5.0
Soh (1.4)	$La_{1-x}Mn_{1-z}O_3$	2.2	$La_{1-x}Mn_{1-z}O_3$	7.6

[a] ND: not determined.

molecules detached from complex precursor and nitrates anions with formation of aqua-hydroxo species.[7,11] The next four exothermic effects up to 382 °C are rather difficult to be assigned. The thermal behaviour of La–Mn–Soh precursors shows a fast and total decomposition around 250 °C, releasing all the reaction energy at this temperature (Fig. 2(b_1, b_2)). Prakash et al.[12] consider that the water molecules in the precursor could decrease the system temperature, due to utilization of the combustion heat for water evaporation and so, hindering the formation of crystalline as-synthesized powders. La–Mn–Soh precursors have no coordinated water and that could explain the formation of crystalline as-synthesized powders. In the case of α-alanine, DSC curve (Fig. 2c) shows a slight endothermic process before the ignition, corresponding to humidity and coordinated water loss followed by combustion around 220 °C.

The as-synthesized powders were calcined for obtaining single-phase compounds. After the annealing treatment, for all samples corresponding to $\varphi = 1.1$ (excepting La–Mn–Gly) orthorhombic $LaMnO_{3.15}$ was obtained, whereas for $\varphi = 1.4$, nonstoichiometric lanthanum manganites with higher surface area values were formed (Table 2).

XRD patterns have proved that single-phases with orthorhombic perovskite structure were obtained for LM and LSM (Fig. 3) in agreement with other literature data.[13] Table 3 lists the parameters and volume of unit cell, crystallite size calculated with Scherrer's equation, surface area and magnetic susceptibility, χ, for LM and LSM samples.

The specific surface areas of LM and LSM are much higher than of the other samples presented in this paper. La^{3+} substitution by Sr^{2+} determines an increasing of specific surface area and magnetic susceptibility values. Presence of Sr^{2+} could determine an increase of Mn^{4+} content as a result of charge compensation. SEM investigation of LM sample shows that the powder has spongy aspect, fine primary particles forming agglomerates with different shapes, large number of pores and voids (Fig. 4).

The superficial elemental composition of the LM and LSM samples was determined by XPS from the intensities of La3d, Sr3d and Mn2p doublets. Oxygen concentration was not taken into account, due to the superposed contributions to O1s line from the oxygen atoms in manganite structure and in the adventitious layer on the sample surface. The XPS results lead to the following approximate formula of the samples surface: $La_{0.78}MnO_x$ (LM) and $La_{0.69}Sr_{0.28}MnO_x$ (LSM). For both samples, the main component of $La3d_{5/2}$ lies at about 834.5 eV and the satellite at 838.4 eV characteristic for lanthanum manganite.[14] It is difficult to establish the Mn valence by XPS, due to the slight changes of Mn2p peaks with the oxidation state. The LM and LSM samples manifest the $Mn2p_{3/2}$ and $Mn2p_{1/2}$ components at 641.8–641.9 eV and 653.5–653.7 eV, respectively (Fig. 5). By comparing these results with those

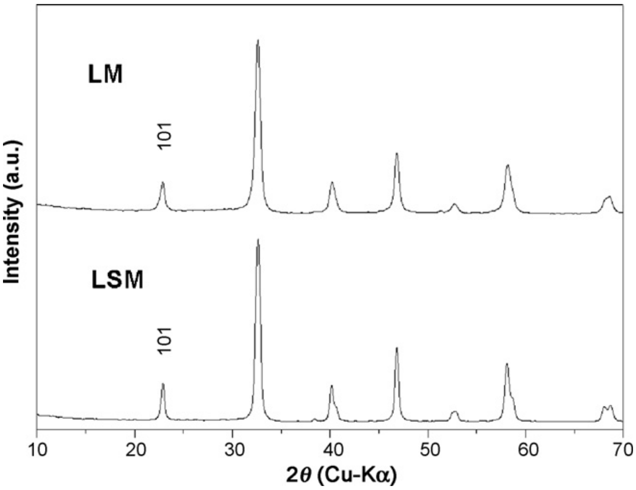

Fig. 3. XRD patterns of LM and LSM annealed samples.

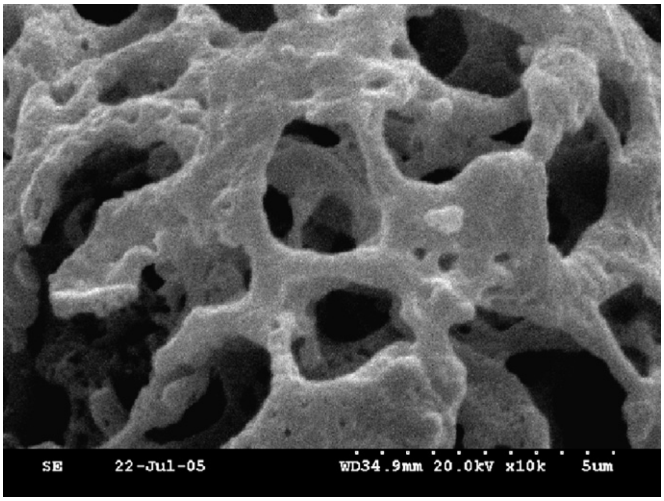

Fig. 4. SEM micrograph of LM annealed sample.

Table 3
Properties of lanthanum manganites prepared from alanine-based precursors

Sample	a (Å)	b (Å)	c (Å)	V ($Å^3$)	S (m^2/g)/D_{101} (nm)	χ (× 10^4 cm^3/g)
LM	5.470	7.756	5.514	233.93	40/16	0.97
LSM	5.464	7.757	5.507	233.40	43/19	1.65

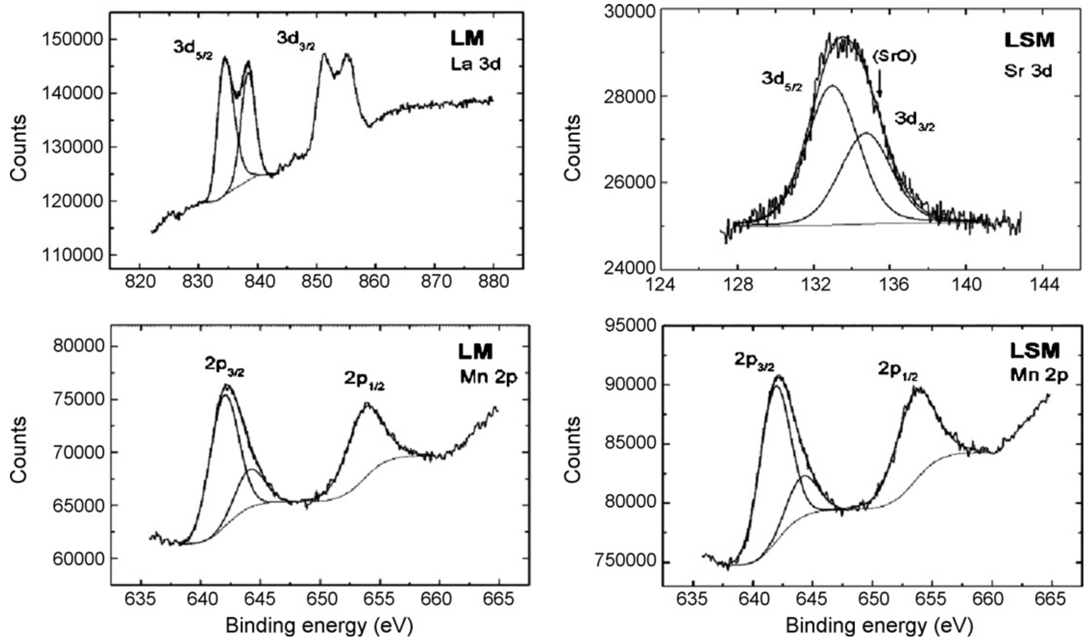

Fig. 5. La3d, Mn2p and Sr3d core-level spectra of LM and LSM annealed samples.

reported in literature,[14] one can estimate an intermediate valence of manganese between 3+ and 4+, however, with most of Mn atoms in the 3+ state.

Sr3d spectrum of LSM was fitted by the two components $3d_{5/2}$ and $3d_{3/2}$. Their BE's of 133.0 and 134.7 eV are nearly identical with the values reported for Sr–O bond in $La_{0.5}Sr_{0.5}MnO_3$.[15] The broad Sr3d spectrum could suggest the presence of an additional SrO phase in LSM superficial composition. The broadening of Sr3d spectrum could be attributed to a chemical inhomogeneity of Sr atoms, possibly placed on different crystallographic sites in the manganite structure.[16]

4. Conclusions

Pure and strontium-doped lanthanum manganites obtained by solution combustion method have perovskite structure rich in oxygen. The fuel used has a significant influence on the temperature of perovskite-phase formation and the powder morphology. The samples prepared from α-alanine based-precursors show high surface area and primary nanoparticles, structured to form pores.

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