JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 6, June 2007, p. 1793 - 1796

Synthesis of lanthanum ferrite nanopowder by combustion method

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We report the synthesis of lanthanum ferrite by solution combustion method using metal nitrates and some natural and cheap compounds as raw materials. The combustion reactions of metal nitrates, as oxidants with sorbitol, glucose, saccharose, or starch as fuels were investigated by thermal analysis. $LaFeO_3$ nanopowders were characterised by X-ray diffraction, scanning electron microscopy and specific surface area measurement (B.E.T. method).

(Received November 14, 2006; accepted April 26, 2007)

Keywords: Solution combustion method, Perovskite, Lanthanum ferrite, Nanopowders

1. Introduction

Pure and doped lanthanum ferrites are widely studied as materials for solid oxide fuel cells (SOFC) [1], catalysts for hydrocarbons [2] or ammonia oxidation [3] and gas sensors [4]. Recently, $La_{1-x}Sr_xFe_{1-y}Co_yO_3$, become more important due to their electrochemical properties. The high ionic and electronic conductivity in these materials make them very promising cathode materials for SOFC operated below 1073 K [5,6].

Preparations conditions are in many cases responsible for structural differences and thus for the different catalytic, electrocatalytic and electrochemical properties of oxides. $LaFeO_3$ nanopowders has been prepared by a variety of wet-chemical methods including hydrothermal [7], co-precipitation [8], polymerizable complex route [9], mechanochemical synthesis [10] or colloidal crystal templating method [11]. The combustion method has large advantages in synthesis of nanopowders: simple equipment, formation of high purity products, stabilisation of metastable phases and it is characterised by short reaction time, fast heating rates, high synthesis temperatures [12,13].

We present in this paper the synthesis and characterisation of lanthanum ferrite nanopowders obtained by solution combustion method using as starting materials the metal nitrates and different organic substances.

2. Experimental

Lanthanum ferrite samples were prepared by solution combustion method from different precursors. Oxidiser (metal nitrates) - fuel (organic compound) compositions were calculated using oxidising valence of metal nitrates and reducing valence of carbohydrate compounds. The four precursors were obtained in the following systems:
$La(NO_3)_3$: $Fe(NO_3)_3$: glucose, $C_6H_{12}O_6$; molar ratio, 1:1:1.25
$La(NO_3)_3$: $Fe(NO_3)_3$: saccharose, $C_{12}H_{22}O_{11}$; molar ratio, 1:1:0.625
$La(NO_3)_3$: $Fe(NO_3)_3$: starch, $(C_6H_{10}O_5)_n$; molar ratio, 1:1:1.25
$La(NO_3)_3$: $Fe(NO_3)_3$: sorbitol, $C_6H_{14}O_6$; molar ratio, 1:1:1.15.

The reaction mixtures were obtained from 0.2 M aqueous solution of metal nitrates (Merck, >99%) added in stoichiometric ratio to a corresponding quantity of organic compound. The reaction mixture was heated at ~100°C on a hot plate with stirring, to evaporate the water. By increasing the temperature, the precursors have ignited forming brown powders named as-synthesized powders. For establishing the thermal treatment conditions, the isolated precursors, obtained after water evaporation and drying in vacuum, were analysed by thermal analysis (DTA-TG). The combustion products were investigated by X-ray diffraction and were found to be amorphous.

DTA-TG was performed in air, in the temperature range 25° - 600 °C, at a heating rate of 10°C/min using SHIMADZU TG-60 equipment. X-ray diffraction data were collected using a Shimadzu XRD 6000 diffractometer with Cu$K\alpha$ radiation at a step of 2°/min in the range $2\theta = 10 - 70°$.

Lanthanum ferrite samples were prepared by annealing the as-synthesized powders in air at 700°C, 3h. The annealed samples were characterised by X-ray diffraction (XRD), scanning electron microscopy (SEM) and specific surface area measurements. Particles sizes (*D)* were calculated by means of the Scherrer equation $D = K\lambda/\beta \cos\theta$, where K is a constant equal to 0.89, λ, the wavelength of the X-ray used, and β, the full width at half-maximum (FWHM) of the X-ray reflection. SEM micrographs were obtained using a HITACHI S2600N scanning electron microscope. The specific surface areas were measured using nitrogen adsorption-desorption isotherms at liquid nitrogen temperature.

3. Results and discussion

$LaFeO_3$ precursors were analysed by thermal analysis. Figs. 1-4 present the thermal decomposition of the four precursors prepared in water.

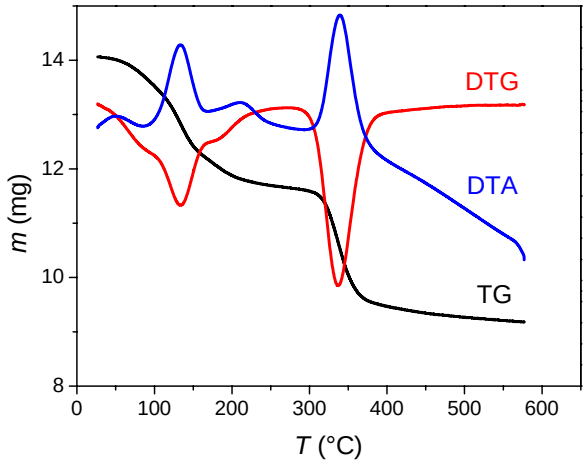

Fig.1. DTA-TG curves of glucose-based precursor.

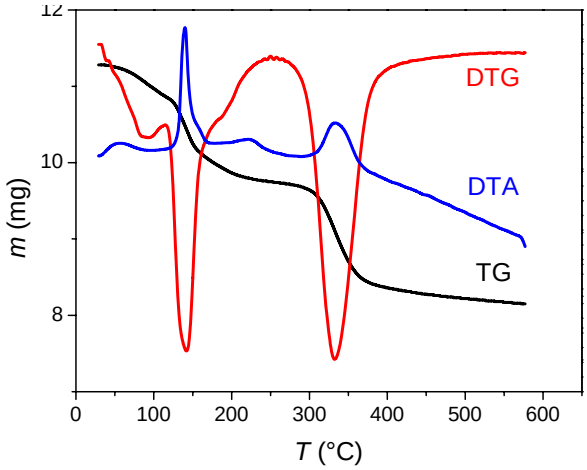

Fig. 2. DTA-TG curves of saccharose-based precursor.

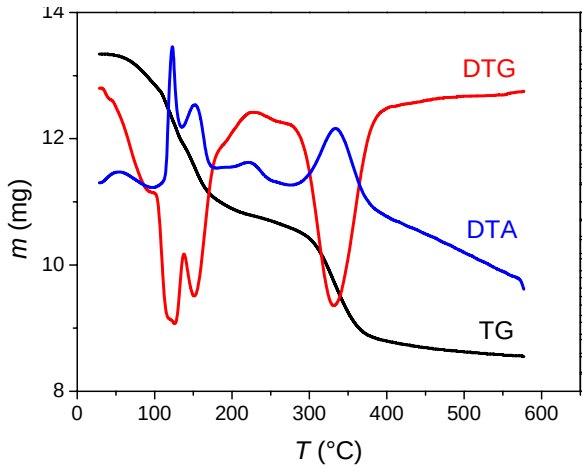

Fig. 3. DTA-TG curves of starch based-precursor.

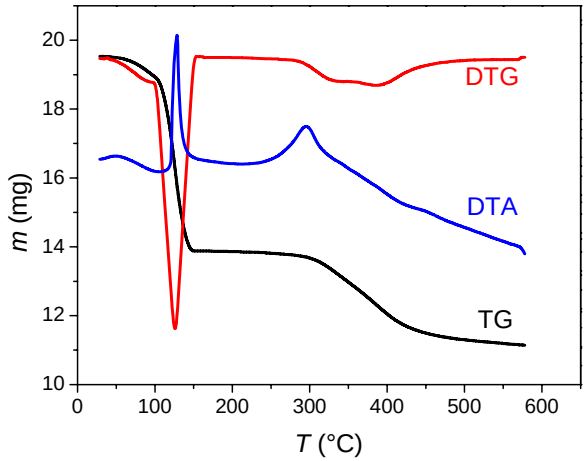

Fig. 4. DTA-TG curves of sorbitol based-precursor.

Thermal analyses of glucose, saccharose and starch based precursors show almost similar decomposition steps. In the range 90-180 °C, a higher rate of decomposition could be observed in the case of saccharose and a split of the DTA maximum in the case of starch. The last two steps are almost identical for all three precursors. The decomposition of sorbitol precursor is different and starts with a strong exothermic effect in the range 100-150 °C with a maximum at 124 °C and ends with a very weak exothermic decomposition. For all precursors it could be assumed that the decomposition is total at around 600 °C.

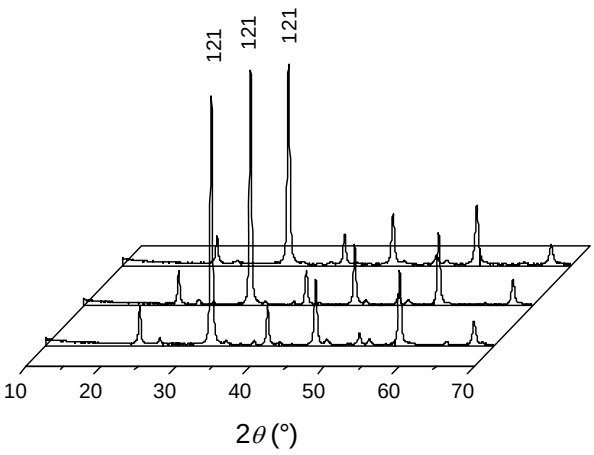

Fig. 5. XRD patterns of $LaFeO_3$ samples prepared from different precursor.

The *XRD data* for $LaFeO_3$ samples obtained by calcining the as-synthesised powders at 700°C, 3h show that all the samples are single phase with orthorhombic perovskite structure. No secondary phase was observed for all annealed samples. The refined lattice parameters and unit cell volume values are presented in Table 1. Unit cell parameters are in good agreement with JCPDS 37-1493 in the case of all samples, except of the sample from sorbitol-based precursor. In this case, the XRD pattern was indexed according to JCPDS 74-2203.

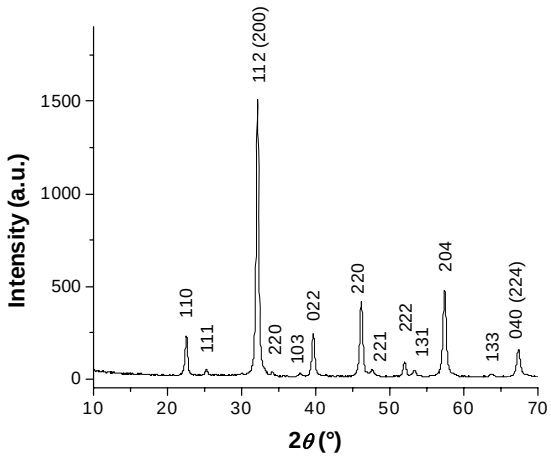

Fig. 6. XRD pattern of $LaFeO_3$ prepared from sorbitol-based precursor.

Table 1. Lattice parameters and unit cell volume values of lanthanum ferrite samples.

Used fuel	*a [Å]*	*b [Å]*	*c [Å]*	*V [Å^3]*
Glucose	5.554	7.847	5.547	241.75
Saccharose	5.552	7.840	5.540	241.14
Starch	5.557	7.849	5.548	241.98
Sorbitol	5.546	5.556	7.859	242.16

Table 2 lists the crystallite sizes, *D*, determined from FWHM of the (121) or (112) diffraction peak (the most intense peak) using Scherrer's equation and the specific surface area values of $LaFeO_3$ samples determined by BET method.

Table 2. Crystallite size and specific surface area values for $LaFeO_3$ samples.

Used fuel	*D [nm]*	*S [m^2/g]*
Glucose	24	13.4
Saccharose	27	17.2
Starch	26	7.3
Sorbitol	26	24

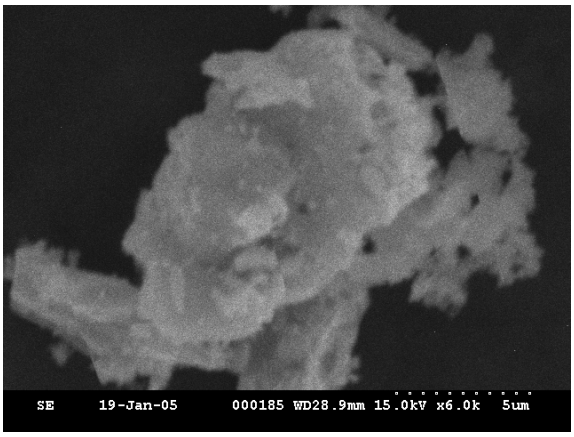

Fig. 7. SEM picture of $LaFeO_3$ obtained from glucose based-precursor.

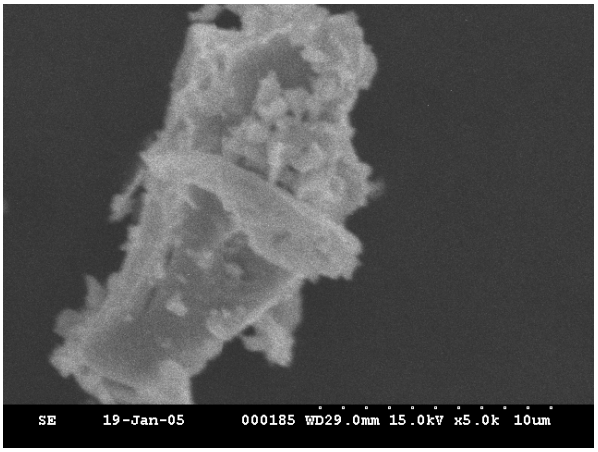

Fig. 8. SEM picture of $LaFeO_3$ obtained from saccharose based-precursor.

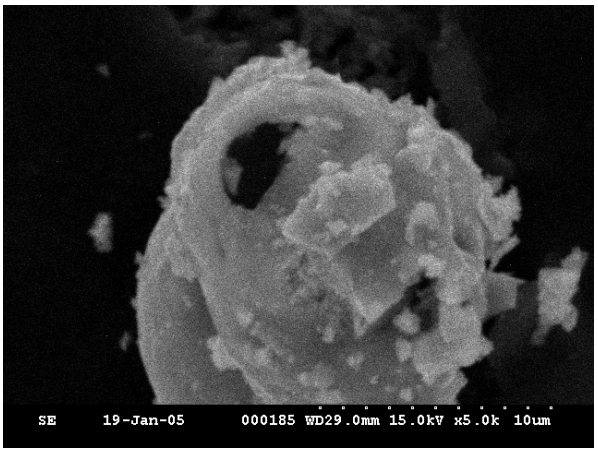

Fig. 9. SEM picture of $LaFeO_3$ obtained from starch based-precursor.

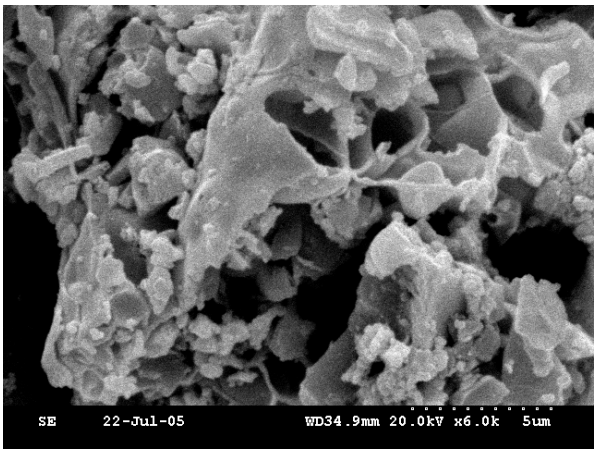

Fig. 10. SEM picture of $LaFeO_3$ obtained from sorbitol based-precursor.

From Table 2 it can notice that $LaFeO_3$ obtained from combustion of sorbitol based-precursor has the largest surface area value. SEM examination of the $LaFeO_3$ powders show that the samples have fine primary particles with tendency of agglomerates formation with irregular

shape (Figs. 6 - 9). The degree of agglomeration is lower in the case of the sample prepared from sorbitol-based precursor. The SEM investigation could be correlated with the higher specific surface area values obtained for the samples prepared from sorbitol-based precursor.

4. Conclusions

$LaFeO_3$ has been successfully obtained by solution combustion method using cheap and nontoxic raw compounds. All $LaFeO_3$ samples obtained at 700°C are single phase with orthorhombic perovskite like structure. The unit cell parameters are in good agreement with literature data. Lanthanum ferrite powders have the crystallite sizes in 24-27 nm range. $LaFeO_3$ sample obtained from sorbitol-type precursor presents the highest specific surface area value.

Acknowledgements

The present research has been partial financed by the grant CNCSIS 1477.

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