Journal of Thermal Analysis and Calorimetry, Vol. 87 (2007) 3, 801–804

LANTHANUM CHROMITES PARTIALLY SUBSTITUTED BY CALCIUM, STRONTIUM AND BARIUM SYNTHESIZED BY UREA COMBUSTION
Thermogravimetric study

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Because of their electrical, magnetic and catalytic properties rare earth and transition metal mixed oxides are important compounds. Lanthanum chromites have been extensively used as solid oxide fuel cell (SOFC) interconnect materials. In this work, lanthanum chromites partially substituted by alkaline earth metals were synthesized by the urea combustion process. TG and DSC techniques were used to evaluate the presence of the organic material in the powder after reaction on the hot plate. The powders were calcinated at 900°C and characterized by XRD and SEM. The results show that the particles have nanometric dimensions and the perovskite structure was formed.

Keywords: *doped lanthanum chromite, DSC, SEM, TG*

Introduction

Besides their catalytic properties [1] Perovskite-type solid solutions of $La_{1-x}M_xCrO_{3-\delta}$ oxide (M=Ca or Sr) was found as the most suitable materials for solid oxide fuel cell (SOFC) interconnects [2, 3]. This is due to the high electrical conductivity of $La_{1-x}M_xCrO_{3-\delta}$, good compatibility with other materials in SOFCs and excellent stability against reducing and oxidizing atmospheres. Extensive studies on $La_{1-x}M_xCrO_{3-\delta}$ have been reported, especially on its crystal structure, electrical properties, and defect chemistry [3]. Pure $LaCrO_3$ is a *p*-type conductor with low electrical conductivity, approximately 0.6 S cm^{-1}. Doping using alkaline earth ions (such as Ca, Sr and Mg) enhances the electrical conductivity by two orders of magnitude [4]. Doping with different species (Ca or Sr) and amounts (0–30 mol%) modifies the thermal expansion coefficient and phase transition characteristics, and therefore may cause thermal expansion mismatch with neighboring components [5, 6].

The SOFC interconnect serves as an electrical contact between individual cells and, additionally, separates the gas compartments in a planar system. A number of requirements should be fulfilled with a good interconnect material: high purity, high electrical conductivity, good thermal stability with respect to adjacent components (anode and cathode) and thermal expansion matched with the other components. Alkaline earth doped lanthanum chromite perovskite have been almost the only choice for decades because they meet most of these criteria.

In general, a perovskite-type oxide has an ABO_3 type crystal structure wherein cations with a large ionic radius have twelve coordination and occupy A-sites, and cations with a smaller ionic radius have six coordination and occupy B-sites. A perovskite that has both A and B cations adopts the formal +3 valence states needed to impose divalent cation substitution and to increase the population of mobile oxygen vacancies. Incorporation of a divalent cation into a trivalent cation lattice site results in a charge imbalance that requires charge compensation by another lattice defect [7–12]. There are three potential compensation mechanisms: either by a host lattice oxygen vacancy by a dopant (2+) interstitial ion or by a lattice self-interstitial cation. The oxygen vacancy and host interstitial mechanisms are related through the Schottky and Frenkel cation equilibria. Although the dopant and interstitial mechanisms are stated their energies are significantly higher than those of the processes that form oxygen vacancies [13]. Oxygen nonstoichiometry in Ca- and Sr-doped $LaCrO_3$ is a function of the doping amount, oxygen partial pressure and annealing temperature [14]. Depending on the oxygen partial pressure two things can happen: oxidation of the transition metal (chromium) in the structure, or creation of oxygen vacancies in the oxygen sublattice. The variation in the defect chemistry, i.e., the interplay between the redox of Cr and the creation-disappearance of the oxygen vacancies, has pro-

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1388–6150/$20.00

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found effects on the performance of SOFCs [7–12]. $LaCrO_3$ polycrystalline powder can be prepared by the Pechini method using $La(NO_3)_3$ and $Cr(NO_3)_3\cdot 9H_2O$ as raw materials [15]. This work aims to synthesize alkaline earth (Ca, Sr and Ba) doped lanthanum chromite using the urea combustion technique [16]. A key feature of this technique is that the heat required to drive the synthesis is provided mainly by an exothermal reaction occurring among the reactants, thus greatly reducing the amount of heat that has to be supplied by an external source. Actually, metal nitrates can also be decomposed by simple calcination to metal oxides upon heating upto or above their decomposition temperature; afterwards these oxides can further react, giving new substances. However, in this case a constant external heat source is necessary to maintain the system at the required high temperature to accomplish the appropriate reaction. On the contrary, the combination of nitrates with a sacrificial fuel causes the ignition of this mixture of precursors at a rather low temperature as well as the progress of an exothermal reaction that provides itself the necessary heat for the synthesis. In this way the system is not forced to stay at high temperature for a long time thus preventing the particles from sintering. In addition, since the reactants are mixed in an aqueous solution, this method enables a good chemical homogeneity of the system, which leads to a nearly instantaneous reaction [16, 17]. Thus, combustion synthesis provides an interesting alternative to other elaborate techniques because it offers several attractive advantages such as simplicity of experimental set-up, surprisingly short time between the preparation of reactants and the availability of the final product and low cost due to energy savings.

Experimental

Synthesis

The compounds were prepared by a combustion process [16]. A flow chart of the steps involved is shown in Fig. 1. The aqueous solution of metal nitrates were mixed with the fuel (urea) and heated to 80°C in a hot plate until the water evaporated resulting a viscous material. Then, the temperature was increased approximately to 300°C. A few minutes later the mixture ignited and brown gases were emitted indicating nitrate decomposition.

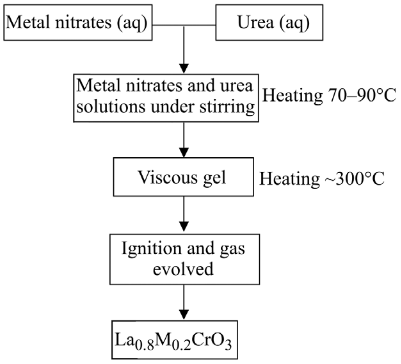

Fig. 1 Schematic illustration of the urea combustion

The selected proportion between urea and nitrates were based on the chemical propellant. According to propellant chemistry, the usual products of the combustion reaction are CO_2, H_2O and N_2 [16]. The stoichiometric composition of the redox mixture for the combustion synthesis is calculated based on the total oxidizing and reducing valences of the oxidizer and fuel in order to release the maximum energy for the reaction [16]. The total valences in bivalent metal nitrates add up to –10, the total valences in trivalent metal nitrates add up to –15 and the total valences in urea add up to +6. Adopting that the products of the combustion reaction are usual [16], we have:

In the synthesis of lanthanum chromite:

$$1\cdot(-15)+1\cdot(-15)+6n=0 \therefore n=5 \text{ (moles of urea)}$$

$$La(NO_3)_3(aq)+Cr(NO_3)_3+5CO(NH_2)_2\rightarrow$$

$$LaCrO_3+5CO_2\uparrow+8N_2\uparrow+10H_2O\uparrow$$

In the synthesis of *M* (calcium, strontium or barium) doped lanthanum chromite:

$$0.8\cdot(-15)+0.2\cdot(-10)+1\cdot(-15)+6n=0 \therefore n=4.83 \text{ (moles of urea)}$$

$$0.8La(NO_3)_3(aq)+0.2M(NO_3)_2(aq)+$$

$$Cr(NO_3)_3(aq)+4.83CO(NH_2)_2\rightarrow$$

$$La_{0.8}M_{0.2}CrO_3+4.83CO_2\uparrow+7.73N_2\uparrow+9.66H_2O\uparrow$$

In this work, the evolved products of the reactions have not been analyzed. However, formation of gaseous product with brown color was observed suggesting the emission of nitrogen oxide, although the decomposition products suggested by propellant chemistry are CO_2, H_2O and N_2. However, it does not change the proportion between the reactants used here to synthesize the oxides.

Instrumentation

TG curves were recorded using a Shimadzu 50H thermobalance at a heating rate of 10°C min^{-1}. The DSC measurement was carried out at 10°C min^{-1} heating rate under air atmosphere, using Shimadzu DSC. The FTIR spectra of the samples were collected using a Bomen 100 spectrophotometer in the range of 4000 to 500 cm^{-1} using KBr discs. Phase analysis was performed by X-ray powder diffraction using a

Shimadzu XRD 6000 powder diffractometer with monochromatic CuK_α radiation. Spectra were recorded in the 2θ range from 20 to 60°. The specific surface area (SSA) of the catalysts was measured by the BET method using nitrogen as adsorbate. The adsorption isotherms were obtained at 77 K on samples previously heated to 250°C using a NOVA 2000 instrument. SEM analyses were carried out with a Shimadzu SSX-550 Super Scan scanning electron microscope.

Results and discussion

The DSC curve of the fuel used in the synthesis of the lanthanum chromites shows that urea presents a fusion peak at 136°C. After melting the urea begins to decompose between 150 and 260°C. Above 400°C, ammelide sublimation occurs. The generated products have already been described in the literature [17].

The TG curve shows that the powder obtained by the urea combustion process has approx. 16% of organic materials due to incomplete decomposition. It happens because the process is very fast, so there is not enough time to ensure that all nitrates and urea molecules participate in the reaction. TG curves of the sample after treatment at 900°C are shown in Fig. 2. The calcined samples loose approximately 3% of their mass due to the release of organic residues.

Table 1 shows the results of specific area measurements by BET method. According to the results, the samples have low specific surface areas as expected for perovskite structures however they are higher than the same perovskite obtained from a solid state reaction [18]. It is possible to notice that the presence of dopant decreases the specific surface area of the lanthanum chromites.

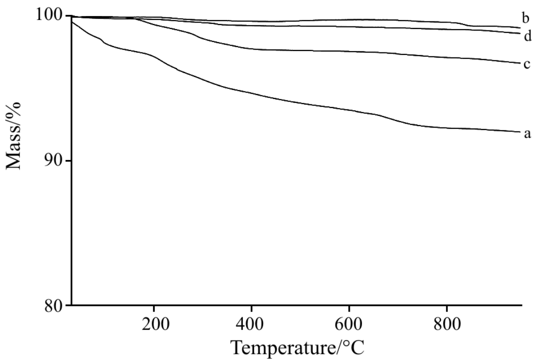

Fig. 2 TG curves of a – $LaCrO_3$, b – $La_{0.8}Ca_{0.2}CrO_3$, c – $La_{0.8}Sr_{0.2}CrO_3$ and d – $La_{0.8}Ba_{0.2}CrO_3$ powders

Table 1 Specific area measured by BET analysis for lanthanum chromites using combustion method

Sample	S_{BET}/m^2 g^{-1}
$LaCrO_3$	4.58
$La_{0.8}Ca_{0.2}CrO_3$	2.27
$La_{0.8}Sr_{0.2}CrO_3$	3.17
$La_{0.8}Ba_{0.2}CrO_3$	2.93

The X-ray diffraction patterns of the samples are shown in Fig. 3. The observed peaks reveal the formation of the perovskite type structure besides the presence of the chromate phase in the doped lanthanum chromite. Secondary phases, such as $CaCrO_4$, $SrCrO_4$ and $BaCrO_4$ appeared after calcination around 900°C. It is seen that stoichiometric compositions do have better stability [2]. The presence of the chromate phase can affect the catalytic activity in oxidation reactions due to chromium(VI) oxide species [19]. According to the literature the main factor, which is responsible for the catalytic activity seems to be related to the formation of an actual mixed oxide upon substitution of lanthanum by strontium in the perovskite structure of the chromite likely inducing the generation of Cr^{4+} species [18].

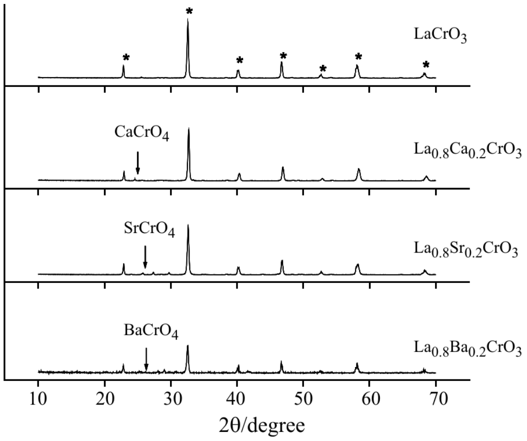

Fig. 3 X-ray diffraction patterns of the powders calcined at 900°C, * – perovskite

Figure 4 shows the FTIR spectra of the samples. The band at approximately 600 cm^{-1} is attributed to the stretching vibration of the Cr–O bonds in the lanthanum chromites [20]. This band is present in all samples. The bands at 834, 848 and 908 cm^{-1} are attributed to chromate and in agreemnt with the XRD results [19, 21].

Undoped lanthanum chromite and doped lanthanum chromite powders were characterized by scanning electronic microscopy. Figure 5 shows the micrograph of the undoped sample. According to the micrograph, the powders obtained by urea combustion method are nanosized with a dimension of 80–180 nm. The undoped lanthanum chromite has smaller particles (~80 nm). Their shape is spherical and all samples have a tendency to form aggregates.

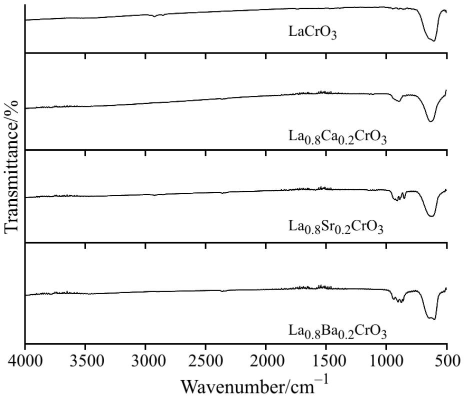

Fig. 4 FTIR of lanthanum chromite and calcium, strontium and barium doped-lanthanum chromites obtained by urea combustion process

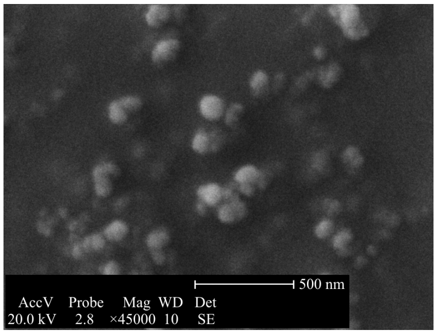

Fig. 5 SEM image of $LaCrO_3$ obtained by urea combustion and calcined at 900°C

Conclusions

According to the results, the urea combustion is a successful method to synthesize undoped and Ca, Sr- or Ba-doped lanthanum chromite. It is possible to synthesize a perovskite structure and the powders obtained have good microscopic characteristics for use as SOFC and catalyst.

Acknowledgements

The authors are grateful to CNPq and FAPESQ-PB for the financial support.

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DOI: 10.1007/s10973-006-7877-7