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Short communication

A simple way to prepare nanosized $LaFeO_3$ powders at room temperature

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Abstract

Nanosized $LaFeO_3$ powders of 30 nm particle size were directly prepared by sol-gel auto-combustion at room temperature. The overall process involves three steps: formation of homogeneous sol; formation of dried gel; and combustion of the dried gel. Experiments revealed that $LaFeO_3$ dried gel derived from citrate and nitrate sol exhibits self-propagating combustion at room temperature once it is ignited in air. After auto-combustion, the gel directly transforms into nanosized $LaFeO_3$ particles. The auto-combustion was considered as a heat-induced exothermic oxidation–reduction reaction between nitrate ions and carboxyl group. Differential thermal analysis–thermogravimetry (DTA–TG) was used to study the decomposition of the precursor. The structure of the nanosized $LaFeO_3$ powders was characterized by X-ray diffraction (XRD).

Keywords: A. Sol–gel processes; A. Powders: chemical preparation; Self-propagating combustion

Perovskite $LaFeO_3$ and related compounds have attracted considerable attention due to their wide uses in fuel cells [1], catalysts [2] and environmental monitoring applications [3]. Preparation of $LaFeO_3$ and related compounds have been achieved by many methods, including sol-gel [4,5], combustion synthesis [6–8], and hydrothermal synthesis [9]. However, all of these wet chemical methods, to some extent, still need calcining at relative high temperature and long soaking to produce powders with good crystal structure. Since raising the calcining temperature and prolonging the soak time make the crystalline grains grow larger in size and weaken the reactivity, obtaining nanosized particles has been difficult. Here we report a novel means to prepare monophasic nanosized $LaFeO_3$ powders by sol-gel auto-combustion. This process perfectly combines the sol-gel process and low temperature combustion processes; it uses inexpensive raw materials; can be performed at room temperature, and does not need further calcination.

Analytical grade Fe $(NO_3)_3{\cdot}9H_2O$, La $(NO_3)_3{\cdot}6H_2O$, $C_6H_8O_7{\cdot}H_2O$ and $NH_3{\cdot}H_2O$ were used as raw materials to prepare of $LaFeO_3$. According to the stoichiometric composition reactants, specified amounts of Fe $(NO_3)_3{\cdot}9H_2O$ and La $(NO_3)_3{\cdot}6H_2O$ were first dissolved in citric acid solution. The molar amount of citric acid was equal to total molar amount of metal nitrates in solution. Ammonia water was slowly added to adjust the pH to 7 and stabilize the nitrate–citrate sol. During this procedure, the solution was continuously stirred and kept at a temperature of 60 °C. Then, the stabilized nitrate–citrate sol was poured into a tray and heated slowly to 130 °C. Viscosity and color changed as the sol turned into a brown, puffy, porous dry gel. If ignited at room temperature, the dried gel burned completely to loose powder, known as as-synthesized powder.

Fig. 1 is the X-ray diffraction (XRD) spectra of $LaFeO_3$ dried gel, as-synthesized powder and powders obtained from $LaFeO_3$ dried gel directly heated at 700 and 1200 °C for 2 h, respectively. It could be observed that the dried gel was amorphous while the as-synthesized powder exhibited well-defined crystalline structure consisting of monophasic $LaFeO_3$, similar to that of $LaFeO_3$ dried gel annealed at 700 and 1200 °C for 2 h. From the formula $d = 6\ /\rho{\cdot}s$ (where ρ is the theoretical

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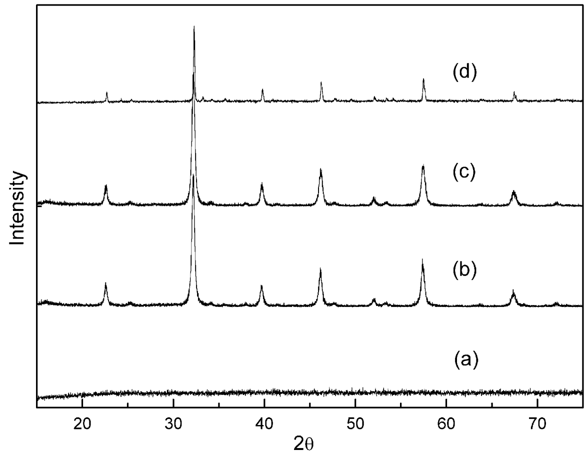

Fig. 1. X-ray diffraction (XRD) patterns of $LaFeO_3$ dried gel (a), as-synthesized powder (b) and powders obtained from $LaFeO_3$ dried gel calcined at different temperature for 2 h, (c) 700 °C and (d) 1200 °C.

density and *s* is the specific area), the average particle size of as-synthesized powder was calculated to be 30 nm. This indicates that 30 nm $LaFeO_3$ powder can be directly prepared by this sol-gel auto-combustion process without further calcination.

To understand the reaction mechanism, we studied the decomposition of the precursor. Fig. 2 shows the TG and DTA curves of $LaFeO_3$ dried gel. It can be seen that in the temperature region 150–200 °C, a small endothermic peak with a weight loss of 2.0% appeared which was attributed to vaporization of inner water. The maximum exothermic peak, at appropriate 230 °C, is a nearly vertical step in the DTA curve, accompanied by drastic weight loss at the same temperature; this indicates that auto-combustion occurs during the decomposition of the nitrate–citrate dried gel. The weight loss associated with this sharp exothermic reaction is about 76%, in good agreement with the value calculated from Eq. (1):

$$\mathrm{La\ (NO_3)_3 \cdot 6H_2O + Fe\ (NO_3)_3 \cdot 9H_2O + C_6H_8O_7 \cdot H_2O + 4NH_3 \cdot H_2O = LaFeO_3 + 6CO_2 + 5N_2 + 30H_2O} \tag{1}$$

corresponding to a wide temperature region from 430 to 500 °C, there is a slight weight loss and a broad exothermic region, which is ascribed to the burning of the residual organic components. From Eq. (1), it can be seen that the reaction is an oxidation–reduction reaction, in which nitrate ions act as oxidizers and the carboxyl is the reducing agent.

Nanosized $LaFeO_3$ powders of 30 nm particle sizes were directly prepared by the sol-gel auto-combustion at room temperature. The overall process of synthesizing pure nanosized $LaFeO_3$ powders involves three steps: the formation of sols; formation of the dried gel; and combustion of the dried gel in air at room temperature to obtain pure nanosized $LaFeO_3$ powders. The auto-combustion can be considered as a heat-induced exothermic oxidation–reduction reaction between nitrate ions and carboxyl group. This new process is easy, simple, and low cost because of using cheap inorganic reagents and without further annealing. Further study is being carried on.

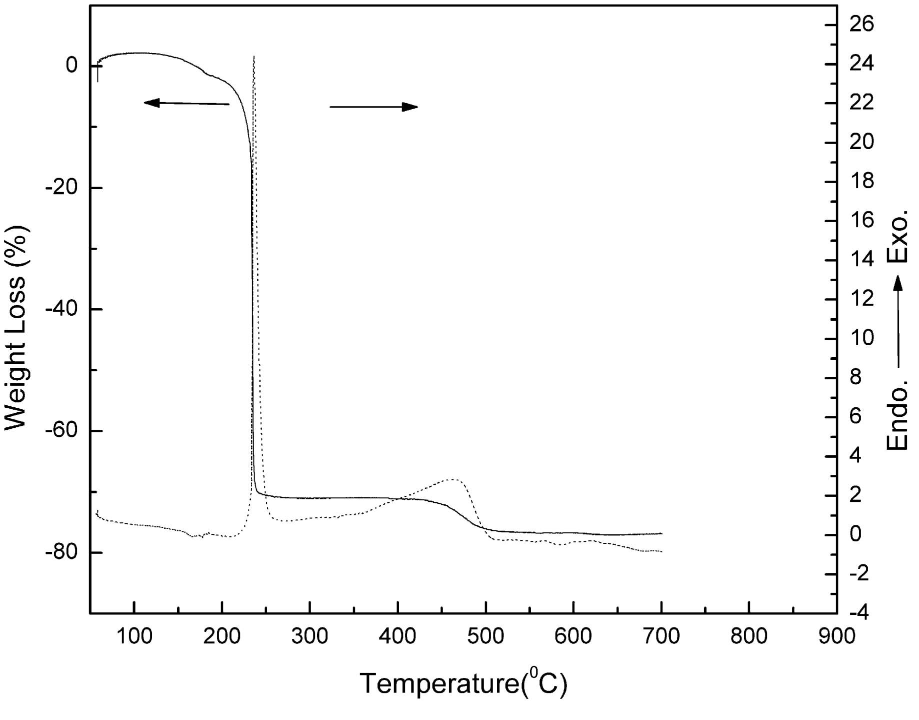

Fig. 2. DTA and TG curves of $LaFeO_3$ dried gel.

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