

Effects of PVA content on the synthesis of LaFeO₃ via sol–gel route

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Abstract

LaFeO₃ were synthesized via a sol–gel route based on polyvinyl alcohol (PVA). Differential scanning calorimetry (DSC), Thermogravimetric (TG), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), Raman spectroscopy and field emission scanning electron microscopy (FESEM) techniques were used to characterize precursors and derived oxide powders. The effect of the ratios of positively charged valences to hydroxyl groups of PVA (M^{n+}/OH) on the formation of LaFeO₃ was investigated. XRD analysis showed that single-phase and well-crystallized LaFeO₃ was obtained from the $M^{n+}/\text{OH} = 4:1$ molar ratio precursor at 700 °C. For the precursor with $M^{n+}/\text{OH} = 2:1$, nanocrystalline LaFeO₃ with average particle size of ~50 nm was formed directly in the charring procedure. With increase of PVA content to $M^{n+}/\text{OH} = 1:1$, phase pure LaFeO₃ was obtained at 500 °C.

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1. Introduction

Perovskite-type LaFeO₃ has attracted considerable attention due to its wide uses as solid oxide fuel cells [1], catalysts [2], gas sensors [3] and environmental monitoring applications [4]. LaFeO₃ are commonly prepared by solid-state reactions at high temperatures. This technique, which uses metal oxides as starting precursors and requires several annealing processes at high temperatures during long periods of time with frequent intermediate grindings, has several problems, e.g., poor homogeneity and high porosity of the samples, no control on the particle size, etc. The development of innovative processing methods through chemistry permits one to lower the preparation temperature and to improve homogeneity and reproducibility of the ceramic products, with the synthesis of ultrafine and chemically pure powders of mixed-metal oxides at low temperatures. For the preparation of LaFeO₃, several wet chemical methods have been proposed, including hydrothermal synthesis [5], solution combustion synthesis [6–9], sol–gel [8–13], coprecipitation [8,9], thermal decomposition of bimetallic compound [14–17], sonochemical method [18], microemulsion method [19], polymerisable

complex [20] and poly(vinyl alcohol) (PVA) route [21]. Most of these wet chemical methods, however, need calcining at relatively high temperature in order to obtain the desired final powders with good crystal structure. A new route to obtain LaFeO₃ is worth exploring.

PVA solution polymerization method has been used successfully to synthesize various monophases, fine, and pure mixed-oxide powders [22–24]. Although Wang et al. [21] synthesized LaFeO₃ via a PVA-based sol–gel route at a fixed PVA content, no literature currently reports the effects of PVA content on the formation of LaFeO₃. In the present paper, sol–gel method based on PVA is used to prepare LaFeO₃ powders and the effect of PVA content on the formation of LaFeO₃ was investigated. Single phase LaFeO₃ has been successfully prepared at lower temperature.

2. Experimental procedure

La₂O₃ (Ultrafunction Enterprise Co. Ltd., purity of >99.999%), Fe(NO₃)₃·9H₂O (Sinopharm Chemical Regent Co. Ltd., purity of >98.5%) and PVA (MW = 79,000, Chengdu Union Chemical Engineering Regent Institute, chemical purity) were used as raw materials. A 5 wt% PVA solution was made by adding PVA to deionized water. The polymer was dissolved by stirring at a temperature of about 80 °C. La₂O₃ was dissolved in nitric acid and mixed with PVA solution with

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stirring. Then stoichiometric $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added. During the process, the molar ratios of positively charged valences to hydroxyl groups (M^{n+}/OH) of PVA were 4:1, 2:1 and 1:1, respectively. The solution was continuously stirred and kept at a temperature of 80°C . The obtained La–Fe–nitrate–PVA solution was evaporated by stirring and heating until a brown sticky gel was formed. Subsequently, the gel was placed in a drying cabinet with a preparatory temperature of 250°C to get a brown, puffy and porous dry mass. It was lightly ground to powder, to which we refer to as the powder precursor. Finally, the powder precursor was calcined at different temperatures in air for 2 h to obtain LaFeO_3 powders.

Simultaneous differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis (NETZSCH STA 449C) was used to monitor the decomposition and pyrolysis of the precursor at a heating rate of $10^\circ\text{C}/\text{min}$ in static air. Phase identification was checked by powder X-ray diffraction (X'Pert PRO, Panalytical B.V.) using $\text{Cu K}\alpha$ radiation and nickel as the filter. Fourier Transform Infrared (FTIR) spectra were recorded in the $400\text{--}4000\text{ cm}^{-1}$ range with a Bruker Vertex 70 FT-IR, using the KBr pellet technique. Raman spectra were measured at room temperature using a Renishaw in via Raman Microscope. The green line ($\lambda = 514.5\text{ nm}$) of Ar ion laser was used as the excitation source. Raman measurements covered the range between 100 and 1700 cm^{-1} . Field emission scanning electron microscopy (FESEM, Sirion 200, FEI) was used to observe the grain size and the morphology of LaFeO_3 powders.

3. Results and discussion

The simultaneous DSC and TG curves of the as-prepared LaFeO_3 precursor up to 1000°C are shown in Fig. 1. The TG curve shows a weight loss of 5.6% below 600°C , which may correspond to the release of adsorbed moisture in the samples. Then, the weight of the samples remains almost constant until the temperature reaches 1000°C . In the DSC curve, the most important aspect evident from the thermal study is the absence of enthalpy changes at high temperatures, which implies that the reaction is complete and no organic species are present in

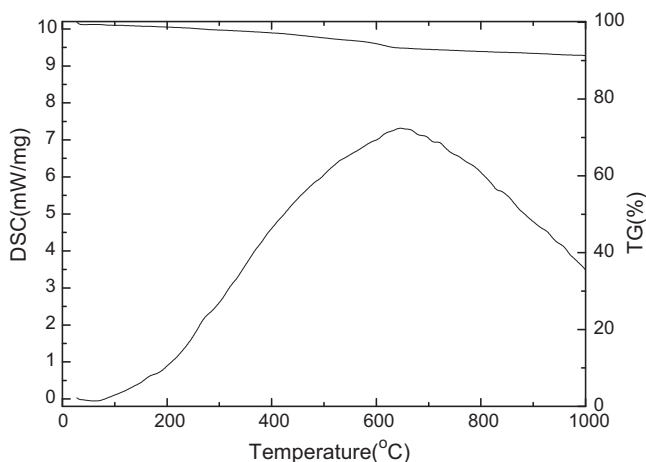


Fig. 1. DSC/TG curves of LaFeO_3 precursor with $\text{M}^{n+}/\text{OH} = 2:1$.

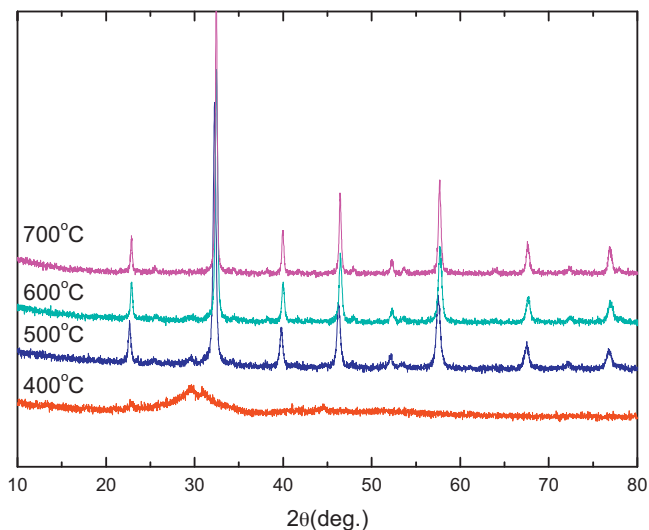


Fig. 2. XRD patterns of the LaFeO_3 precursor ($\text{M}^{n+}/\text{OH} = 4:1$) calcined at various temperatures for 2 h.

the sample. There is no evidence of a phase transition taking place in the samples up to a temperature of 1000°C .

Fig. 2 shows the XRD patterns of the LaFeO_3 precursor ($\text{M}^{n+}/\text{OH} = 4:1$) calcined at various temperatures for 2 h. When the precursor was calcined at 400°C , the powder is predominantly amorphous with some weak XRD-peaks showed up in addition to the continuum corresponding to reflections from $\text{La}_2\text{O}_2\text{CO}_3$ (ICCD file 48-1113). Heating the precursor at 500°C for 2 h, orthorhombic LaFeO_3 phase formed and a small peak centered at about $2\theta = 29.5^\circ$ attributed to $\text{La}_2\text{O}_2\text{CO}_3$ can still be found. The situation did not change for calcination temperatures of 600°C although the small impurity peak decreased further. Increasing the temperature to 700°C , the impurity phase $\text{La}_2\text{O}_2\text{CO}_3$ disappeared completely and single phase LaFeO_3 was obtained.

Fig. 3 shows the XRD patterns of the LaFeO_3 precursor ($\text{M}^{n+}/\text{OH} = 2:1$) calcined at various temperatures for 2 h. The

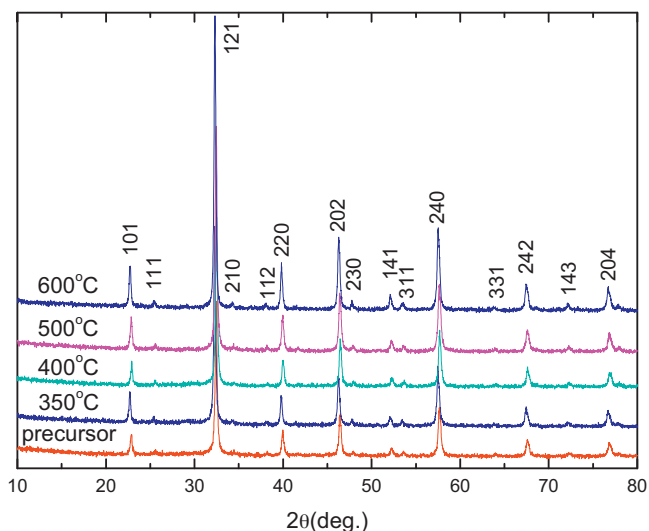


Fig. 3. XRD patterns of the LaFeO_3 precursor ($\text{M}^{n+}/\text{OH} = 2:1$) calcined at various temperatures for 2 h.

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