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Effects of PVA content on the synthesis of $LaFeO_3$ via sol–gel route

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Abstract

$LaFeO_3$ 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 $LaFeO_3$ was investigated. XRD analysis showed that single-phase and well-crystallized $LaFeO_3$ was obtained from the M^{n+}/–OH = 4:1 molar ratio precursor at 700 °C. For the precursor with M^{n+}/–OH = 2:1, nanocrystalline $LaFeO_3$ with average particle size of ~50 nm was formed directly in the charring procedure. With increase of PVA content to M^{n+}/–OH = 1:1, phase pure $LaFeO_3$ was obtained at 500 °C.

Keywords: A. Powders: chemical preparation; A. Sol–gel process; D. Perovskites; $LaFeO_3$

1. Introduction

Perovskite-type $LaFeO_3$ 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]. $LaFeO_3$ 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 $LaFeO_3$, 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 $LaFeO_3$ 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 $LaFeO_3$ 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 $LaFeO_3$. In the present paper, sol–gel method based on PVA is used to prepare $LaFeO_3$ powders and the effect of PVA content on the formation of $LaFeO_3$ was investigated. Single phase $LaFeO_3$ has been successfully prepared at lower temperature.

2. Experimental procedure

La_2O_3 (Ultrafunction Enterprise Co. Ltd., purity of >99.999%), $Fe(NO_3)_3 \cdot 9H_2O$ (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. La_2O_3 was dissolved in nitric acid and mixed with PVA solution with

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stirring. Then stoichiometric $Fe(NO_3)_3{\cdot}9H_2O$ 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 °C/min in static air. Phase identification was checked by powder X-ray diffraction (X'Pert PRO, Panalytical B.V.) using Cu Kα radiation and nickel as the filter. Fourier Transform Infrared (FTIR) spectra were recorded in the 400–4000 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 ($\lambda = 514.5$ 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 the sample. There is no evidence of a phase transition taking place in the samples up to a temperature of 1000 °C.

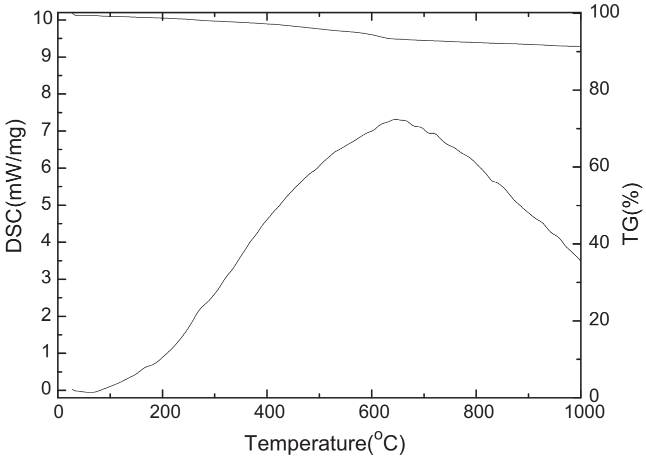

Fig. 1. DSC/TG curves of $LaFeO_3$ precursor with M^{n+}/–OH = 2:1.

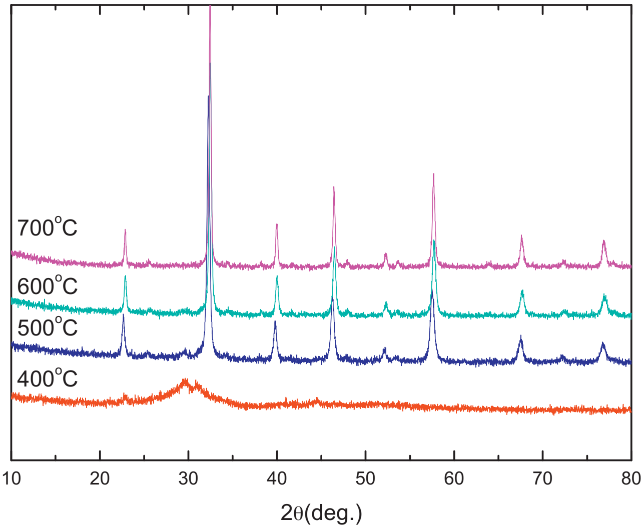

Fig. 2. XRD patterns of the $LaFeO_3$ precursor (M^{n+}/–OH = 4:1) calcined at various temperatures for 2 h.

Fig. 2 shows the XRD patterns of the $LaFeO_3$ precursor (M^{n+}/–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 $La_2O_2CO_3$ (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 $La_2O_2CO_3$ 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 $La_2O_2CO_3$ disappeared completely and single phase $LaFeO_3$ was obtained.

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

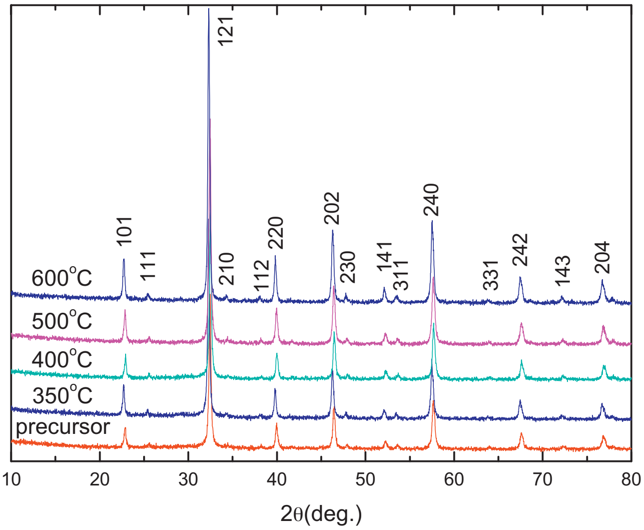

Fig. 3. XRD patterns of the $LaFeO_3$ precursor (M^{n+}/–OH = 2:1) calcined at various temperatures for 2 h.

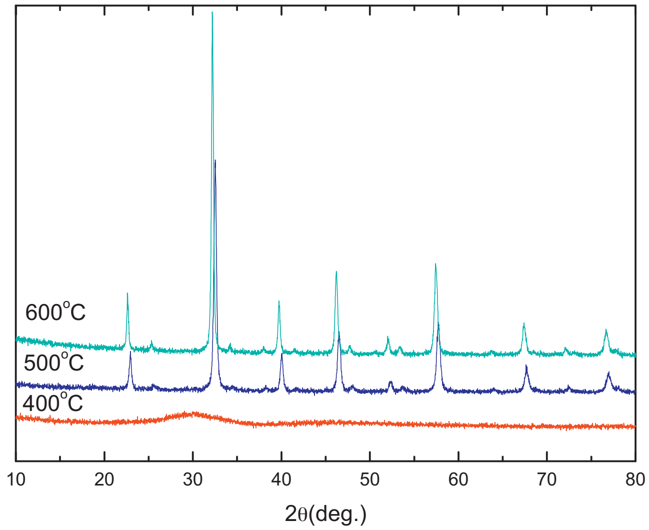

Fig. 4. XRD patterns of the $LaFeO_3$ precursor (M^{n+}/–OH = 1:1) calcined at various temperatures for 2 h.

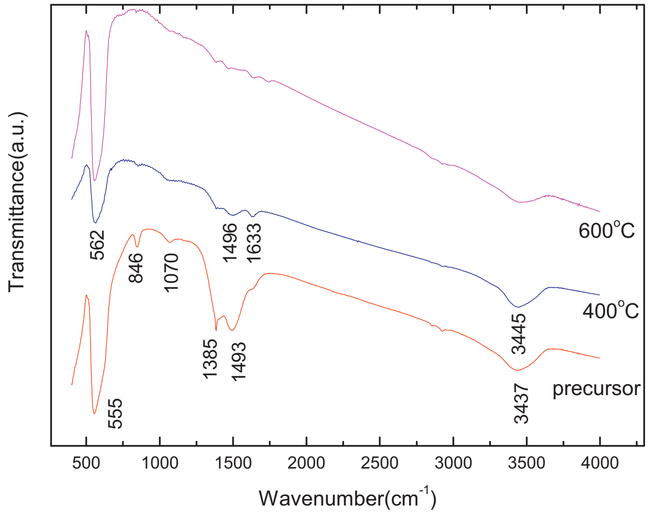

Fig. 5. FT-IR spectra of $LaFeO_3$ precursor (M^{n+}/–OH = 2:1) and powders calcined at 400 °C and 600 °C.

precursor shows crystalline $LaFeO_3$ structure instead of an amorphous structure, which suggests that the $LaFeO_3$ phase with an orthorhombic structure has been formed directly, without the crystallization of any undesired intermediate phase. With increasing heating to 350, 400, 500 and 600 °C, the diffraction peaks become stronger and sharper, reflecting greater crystallization. No other significant changes are observed and all diffraction lines could be indexed to the orthorhombic system. The XRD patterns are in excellent accord with ICCD file 88-641.

Fig. 4 shows XRD patterns of the $LaFeO_3$ precursor (M^{n+}/–OH = 1:1) calcined at various temperatures for 2 h. The product after the calcination at 400 °C for 2 h was primarily amorphous in structure, as is characterized by the broad continuum. The XRD patterns of the precursor heated at a temperature of 500 °C showed only the patterns of the orthorhombic $LaFeO_3$. No peaks attributed to $La_2O_2CO_3$, La_2O_3 and/or Fe_2O_3 were observed. As the calcination temperature increased to 600 °C, the XRD patterns show no obvious changes. Therefore, phase pure $LaFeO_3$ was obtained from the precursor with M^{n+}/–OH = 1:1 at a temperature of 500 °C. As we can see, the molar ratios of positively charged valences to hydroxyl groups of PVA (M^{n+}/–OH) have significant influence on the crystallization behavior of $LaFeO_3$.

Fig. 5 shows the FTIR spectra obtained from the precursor and $LaFeO_3$ powders calcined at different temperatures in the wavenumber range from 400 to 4000 cm^{-1}. For the precursor, this spectrum shows well-established strong absorption bands at 555 cm^{-1} indicating the formation of lanthanum ferrite. The 555 cm^{-1} band is attributed to the Fe–O stretching vibration, being characteristics of the octahedral FeO_6 groups in the perovskite compounds [25]. This is in accordance with the XRD data. The absorption band at about 1493 and 1385 cm^{-1} can be assigned to the splitting of the ν_3 asymmetric stretching of metal carbonates [26] while the other bands at about 1070 and 846 cm^{-1} have been assigned to the ν_1 and ν_2 modes of the carbonate ions, respectively [18,27]. The broad absorption band in the range of 3437 cm^{-1} is assigned to O–H stretching. For powder calcined at 400 °C for 2 h, a $\delta(H_2O)$ band at about 1633 cm^{-1} was observed [14,15]. With the increase of calcination temperature, the intensities of bands related to carbonate and adsorbed water decrease obviously. The carbonates were not detected by XRD. The carbonates detected by FTIR are formed mainly on the surface due to exposure to ambient air. The surface of the $LaFeO_3$ particles is active to chemisorption of gases such as CO_2 in ambient, leading to the formation of carbonate ions [15,16]. Formation of carbonate species on the surface of perovskite-type oxide is usually observed [7,9,10,14–16,28].

Raman spectroscopy is a powerful method for phase structural analysis. It is more surface-sensitive than X-ray diffraction because its excitation energy is less penetrating than X-ray. Fig. 6 shows Raman spectra of $LaFeO_3$ precursor (M^{n+}/–OH = 2:1) and powder calcined at 600 °C for 2 h. There are no

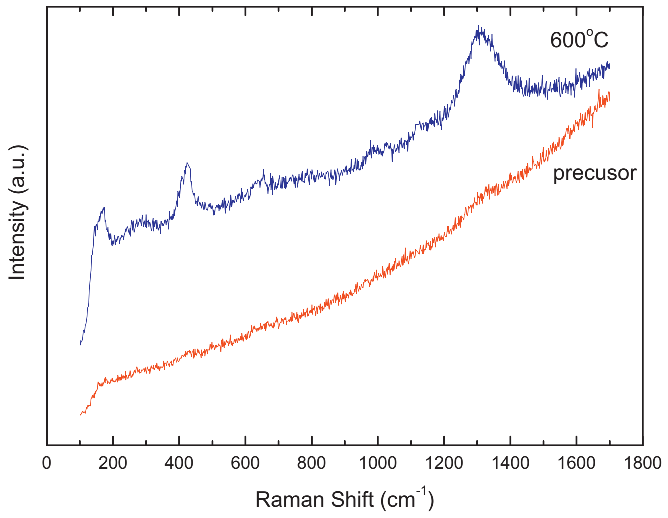

Fig. 6. Raman spectra of $LaFeO_3$ precursor (M^{n+}/–OH = 2:1) and powders calcined at 600 °C.

clear Raman bands in the Raman spectra of $LaFeO_3$ precursor although the XRD patterns show $LaFeO_3$ crystalline. One possible reason may be the small penetration depth of the excitation radiation. This is consistent with the FT-IR spectra: the carbonates are formed mainly on the surface of the $LaFeO_3$ particles due to exposure to ambient air. For the powders calcined at 600 °C for 2 h, the carbonates at the surface of the $LaFeO_3$ particles disappear and the Raman bands are observed. The bands at around 174, 289, 424, 637, 978, 1126 and 1304 cm^{-1} are more similar to that reported in Refs. [20]. Fewer studies of lattice dynamical calculations and assignment of the Raman modes are reported for $LaFeO_3$ materials. Moreover, there are some controversy points in the assignment of the mode [20].

Fig. 7 shows the field emission scanning electron microscopy micrographs of $LaFeO_3$ precursor with M^{n+}/–OH = 2:1 and powders calcined at 600 °C for 2 h. The $LaFeO_3$ powders are composed of porous networks, which is due to the evaluation of a large amount of gases during charring. The individual particles of $LaFeO_3$ precursor appear to be near round grains with an average particle size of ~50 nm. Calcination at 600 °C resulted in an increase of the particle size from ~50 nm to around 70–90 nm.

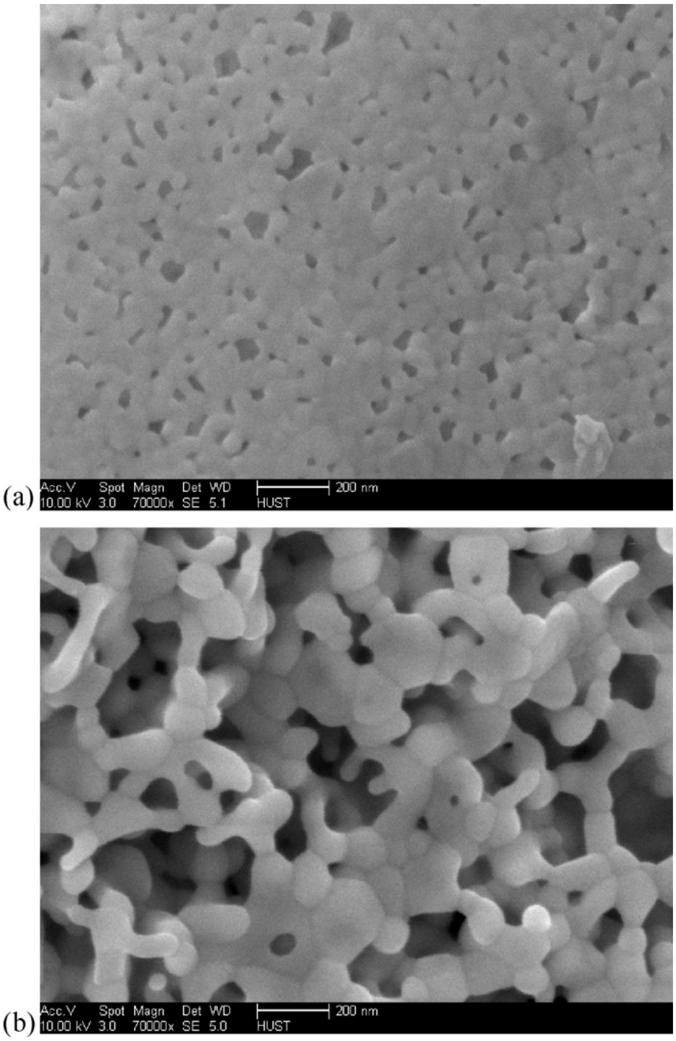

Fig. 7. FESEM micrographs of (a) $LaFeO_3$ precursor with M^{n+}/–OH = 2:1 and (b) powders calcined at 600 °C for 2 h.

Many researchers have reported on the wet chemical synthesis of $LaFeO_3$. The thermal decomposition of a heteronuclear complex $La[Fe(CN)_6]\cdot 5H_2O$ leads to the preparation of nanosized single-phase perovskite-type $LaFeO_3$ powders at 600 °C [14,15,17]. Using microwave irradiation instead of conventional furnace, Farhadi et al. [16] synthesized single-phase $LaFeO_3$ via the decomposition of $La[Fe(CN)6]\cdot 5H_2O$ at 400 °C. This temperature is the lowest reported in literatures. Chung et al. [12] have prepared $LaFeO_3$ powders using nitrates as metal precursors and tartaric acid as complexing agent and phase-pure $LaFeO_3$ was obtained at 500 °C for 2 h. Aono et al. [13] synthesized $LaFeO_3$ nanopowders using ethylene glycol as complexing agent and single phase $LaFeO_3$ was prepared at 600 °C for 1 h, with $La_2O_2CO_3$ as an intermediate phase. Ethylene glycol content affects the formation temperature of pure $LaFeO_3$ with $LaFeO_3$ starting to crystallize at a temperature of as low as 350 °C. As reported by Kumar et al. [8] during synthesis of $LaFeO_3$ by the co-precipitation method, $La(OH)_3$ phase was observed in XRD patterns of samples calcined at 900, 1100 and 1300 °C. Only at higher temperature of 1500 °C was the pure phase of perovskite obtained. In contrast, using the Pechini method required a calcinations temperature of 900 °C to obtain pure phase $LaFeO_3$ [8]. In the present work, the formation temperature of phase pure $LaFeO_3$ depended on M^{n+}/–OH. Single-phase and well-crystallized $LaFeO_3$ was obtained from the M^{n+}/–OH = 4:1 precursor at a temperature of 700 °C. Within the temperature range of 500–600 °C, trace $La_2O_2CO_3$ exists as an impure phase. It is similar to Refs. [13–15]. For the precursor with M^{n+}/–OH = 2:1, $LaFeO_3$ formed directly during the charring procedure. This is similar to solution combustion synthesis [6–9] but fewer organics were used in the present work. With increase of PVA content to M^{n+}/–OH = 1:1, phase pure $LaFeO_3$ was obtained at 500 °C. Wang et al. [21] obtained $LaFeO_3$ at 500 °C via PVA route, but they have not provided detailed PVA content. It is possible that their PVA content was around M^{n+}/–OH = 1:1. As we can see, single phase $LaFeO_3$ can be synthesized via PVA base sol–gel method at lower temperature.

The main function of PVA is to provide a polymeric network to hinder cation mobility allowing local stoichiometry to be maintained and minimizing precipitation of unwanted phases. In aqueous PVA solutions, many metals can be stabilized at the polymer via interactions with OH groups [23]. For precursors with M^{n+}/–OH = 4:1, there were more cations in the precursor solutions than there were functional groups (OH groups) in the polymer, yet, no precipitation during precursor processing was observed. Formation of these stable precursors with very high amounts of metal ions indicated that the cations had to be stabilized in the structure of the polymer by means other than mere chemical linking [23]. For a precursor with M^{n+}/–OH = 2:1 and 1:1, there were more OH groups than cations in the precursor solutions. Therefore, the formation temperature of pure $LaFeO_3$ from the two precursors with M^{n+}/–OH = 2:1

and 1:1 decreased. In the present work, the optimized M^{n+}/–OH ratio is 2:1 for the preparation of $LaFeO_3$ at a lower temperature. Pure $LaFeO_3$ being obtained at lower temperature is attributed to the molecular level mixing of the cations in the solution and precursors.

4. Conclusion

PVA base sol–gel method has been used to synthesize $LaFeO_3$. The effects of the molar ratios of positively charged valences to hydroxyl groups of PVA (M^{n+}/–OH) on the formation of $LaFeO_3$ were studied. Single-phase and well-crystallized $LaFeO_3$ was obtained from the M^{n+}/–OH = 4:1 precursor at 700 °C and the $La_2O_2CO_3$ phase was observed as reaction intermediates. For the precursor with M^{n+}/–OH = 2:1, nanocrystalline $LaFeO_3$ with an average particle size of ~50 nm can be directly obtained from the charring procedure, without any other undesired phases. With increase of PVA content to M^{n+}/–OH = 1:1, phase pure $LaFeO_3$ was achieved at 500 °C.

Acknowledgments

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