

A microwave-induced solution-polymerization synthesis of doped LaGaO₃ powders

Yuling Zhai, Chang Ye, Jianzhong Xiao*, Lei Dai

Institute of Fuel Cell, Department of Material Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China

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Abstract

A new method, called the microwave-induced solution-polymerization synthesis (denoted as MW), and the conventional Pechini (denoted as PH) method have been used to prepare powders of La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{2.815} (denoted as LS_{0.2}GM_{0.17}) and La_{0.8}Sr_{0.2}(Ga_{0.9}Co_{0.1})_{0.83}Mg_{0.17}O_{2.815} (denoted as LS_{0.2}GCM_{0.17}). A higher heating rate and a more homogenous heating manner without thermal gradients in the microwave oven resulted in a pure LSGCM powder after calcination at 1400 °C for 9 hours (h) and purer LSGM (6.2% secondary phases). The grain size of the pellets of the above two powders was 2–3 μm without segregation. The densities of LS_{0.2}GM_{0.17}/MW and LS_{0.2}GCM_{0.17}/MW pellets, sintered at 1400 °C for 9 h, were 6.45 and 6.30 g cm⁻³, respectively.

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1. Introduction

The solid oxide fuel cell (SOFC) has recently captured great interest because of its characteristics such as environment-friendliness, high efficiency, good fuel adaptability and low noise. Sr- and Mg-doped LaGaO₃ (LSGM) as electrolytes in SOFCs exhibit a higher oxygen ionic conductivity, especially at intermediate temperature. Huang and Goodenough [1] reported that La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{2.815} (denoted as LS_{0.2}GM_{0.17}) showed oxygen-ion conductivity of 0.17, 0.08 and 0.03 S cm⁻¹ at 800, 700 and 600 °C, respectively, over a wide range of oxygen partial pressures, exceeding that of YSZ at the same temperatures. Thus, LSGM is a potential candidate electrolyte for use in reduced-temperature SOFCs [1–3].

Furthermore, it was found that the oxide ion conductivity was also improved by doping with Co in Ga sites in the LSGM [4]. The highest ionic conductivity, which at 600 °C was twice as high as LSGM, was found for A-substoichiometric La_{0.85}Sr_{0.15}(Ga_{0.9}Co_{0.1})_{0.8}Mg_{0.2}O_{3-xδ} [5,6].

LSGM materials are usually prepared by a conventional ceramic method, namely by solid state reaction [7–9], which cannot provide controlled crystalline growth, composition homogeneity and grain size uniformity. So, many researchers use a wet chemical synthesis such as sol-gel [10] or coprecipitation [11], hydrothermal synthesis [10], glycine-nitrate combustion method [12,13] and the amorphous citrate process [14] to synthesize the LSGM powders. Tas and co-workers [15,16] have studied the preparation of LSGM powders by the Pechini method. The Pechini method, also called the polymeric precursor process, is based on forming a chelate between mixed cations (dissolved as salts, such as nitrates) and a hydroxycarboxylic acid (citric acid is preferred), then mixing the chelate with a polyhydroxyl alcohol (either ethylene or diethylene glycol) at moderate temperature, finally resulting (resulted) in a solid polymeric cross-linked or uncross-linked resin, which was then further processed. The process is quite complicated and the most important factor is the homogeneous mixing manner that affects the final product, because nonhomogeneity may result in undesirable phases, abnormal grain growth and poor reproducibility.

Due to the narrow composition range for the stability of the perovskite phase, small deviations from the ideal composition would result in secondary phases [1]. So, both phase purity and

* Corresponding author. Tel.: +86 2787542800; fax: +86 2787544307.
E-mail addresses: zhaiyuling@gmail.com (Y. Zhai),
helloyc2002@gmail.com (C. Ye), jzxiao@public.wh.hb.cn (J. Xiao).

the microstructure of LSGM materials depend on the synthetic procedure and processing and, as a matter of fact, the synthesis of a pure single phase ($\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.815}$) material is rather difficult [17]. Even the Pechini method can give rise to only a small amount of undesired phases such as SrLaGaO_4 , $\text{SrLaGa}_3\text{O}_7$ and MgO at the end of the preparation process of LSGM material [15].

On the other hand, microwave-induced processing has recently been applied to many systems to improve the final products [18,19]. Some researchers have used activated microwave sintering to obtain denser and purer LSGM pellets with finer particles [20,21]. However, the microwave furnace used in that method is too costly. Different from the traditional heating mechanism by heat radiation from exterior to interior, the microwave, which provides volumetric heat conduction, can provide a higher heating rate and a more homogenous heating manner without thermal gradients. It can also produce fine powders with a small particle size due to the reaction between the molecules and the large amount of gas produced during the reaction. So far, no reports on the microwave-induced wet chemical synthesis of $\text{LS}_{0.2}\text{GM}_{0.17}$ and $\text{La}_{0.8}\text{Sr}_{0.2}(\text{Ga}_{0.9}\text{Co}_{0.1})_{0.83}\text{Mg}_{0.17}\text{O}_{2.815}$ ($\text{LS}_{0.2}\text{GCM}_{0.17}$) powders have been published.

In this paper, a microwave-induced solution-polymerization synthesis was first used and has obtained ultrafine and homogeneous particles of $\text{LS}_{0.2}\text{GM}_{0.17}$ and pure $\text{LS}_{0.2}\text{GCM}_{0.17}$ powders. This method is compared with the conventional Pechini method. Since the purpose of this work is to confirm the advantages of microwave heating, we only picked a single recipe (in terms of citric acid and ethylene glycol contents) to evaluate, as used by Tas et al. [15]. The calcination behavior at different temperatures was also studied. The products were characterized by X-ray diffraction (XRD), thermal analysis, Fourier transform infrared (FTIR) spectroscopy, Brunauer–Emmitt–Teller (BET) and scanning electron microscopy (SEM).

2. Experimental section

2.1. Materials and preparation

For each precursor, Ga_2O_3 (99.99%), La_2O_3 (99.99%), MgO (98%), SrCO_3 (99%) and Co_2O_3 (99%) were used as the starting materials. Before weighing, MgO and La_2O_3 were fired at 1000°C for 7 hours (h) to decompose carbonate and hydroxide impurities. The absence of impurities in reagents was checked by XRD.

By the conventional Pechini method, stoichiometric amounts of Ga_2O_3 , La_2O_3 , MgO and SrCO_3 that corresponded to 2.5 g of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.815}$ (denoted as $\text{LS}_{0.2}\text{GM}_{0.17}$) were dissolved in $\text{HNO}_3\cdot\text{H}_2\text{O} = 1:1$ to get nitrate solutions. Then, pure citric acid monohydrate citric acid (99.8%) (1.88:1 the molar ratio of acid to total cations) was dissolved in distilled water. After that, ethylene glycol (98%) with 40 wt.% that of the total amount of citric acid and ethylene glycol was dissolved in hot distilled water. These nitrate solutions were then mixed together in a glass beaker and then the citric acid solution and ethylene glycol solution were separately added in the beaker. The clear resulting solution (volume of 150 ml) was stirred for 1 h at room

temperature and then evaporated on a hot plate for 2 h until brown resins formed. The obtained resins (after overnight drying in an oven at 110°C) were isothermally calcined over a temperature range of $250\text{--}1400^\circ\text{C}$ to study the evolution from the resins to the perovskite phases.

The same starting materials as used for the Pechini method were used for the microwave-induced solution-polymerization synthesis of LSGM and $\text{La}_{0.8}\text{Sr}_{0.2}(\text{Ga}_{0.9}\text{Co}_{0.1})_{0.83}\text{Mg}_{0.17}\text{O}_{2.815}$ (denoted as $\text{LS}_{0.2}\text{GCM}_{0.17}$). The main difference with respect to the Pechini process was that the as-prepared clear resulting solution was subsequently heated to polymerization in a modified household microwave (MW) oven (2.45 GHz, 700 W) for 15 min ($T < 220^\circ\text{C}$ measured by thermometer). The picture of the modified household microwave oven is shown in Fig. 1. The MW oven was operated at its maximum power setting. The solutions were heated to evaporate till the puff brown powder formed, which were then milled using an agate mortar and pestle, and finally calcined in air furnace over a temperature range of $250\text{--}1400^\circ\text{C}$ and characterized.

2.2. Sample characterization

The phases present in the calcined powders were analyzed by X-ray diffraction (Model x' Pert Pro, Phillips). Scans were taken with a 2θ step of 0.017° (over the range of $20^\circ\text{--}80^\circ 2\theta$) by $\text{Cu K}\alpha$ radiation (40 kV, 40 mA). The analysis work was done using the Philips X'pert Highscore software (V1.0b). Environmental scanning electron microscopy (ESEM) (Model Quanta 200, FEI), field scanning electron microscopy (FSEM) (Model Sirion 200, FEI) and energy dispersive analysis (EDAX) (Model GENESIS, America EDAX Inc.) were used to study the morphology and microstructure. The surface area of the powders calcined at 900°C for 6 h was measured by the Brunauer–Emmitt–Teller (BET) surface area measurement (Model JW-04). Resin thermal evolutions were studied by thermogravimetric analysis (TGA) (Model TGA 7, America Perkin-Elmer) and differential thermal analysis (DTA) (Model DTA 7, America Perkin-Elmer) with air flow and a $10^\circ\text{C min}^{-1}$ rising temperature rate. Fourier transform infrared (FTIR) analysis was performed (Model VERTEX

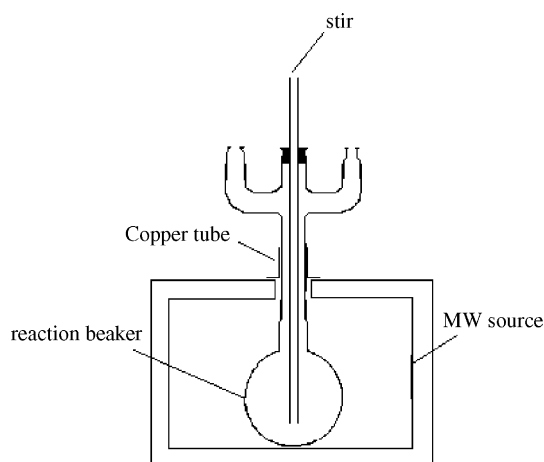


Fig. 1. Modified household microwave oven.

70, Germany Bruker) in the range of 400–4000 cm^{-1} using dry KBr to form the pellets.

Pellets (6 mm diameter) of $\text{LS}_{0.2}\text{GM}_{0.17}$ and $\text{LS}_{0.2}\text{GCM}_{0.17}$ powders precalcined at 900 °C for 6 h synthesized by microwave-induced solution-polymerization method were made by uniaxially pressing using compaction pressure of 200 MPa and sintered in air at 1400 °C for 9 h. The densities of the sintered pellets were measured via the Archimedes method.

3. Results and discussion

3.1. X-ray diffraction

X-ray diffraction patterns of the as-received powders annealed at different temperatures (500 °C, 700 °C, 900 °C, 1100 °C, 1300 °C for 6 h and 1400 °C for 9 h) are shown in Figs. 2–4. It was found that all the products remained amorphous

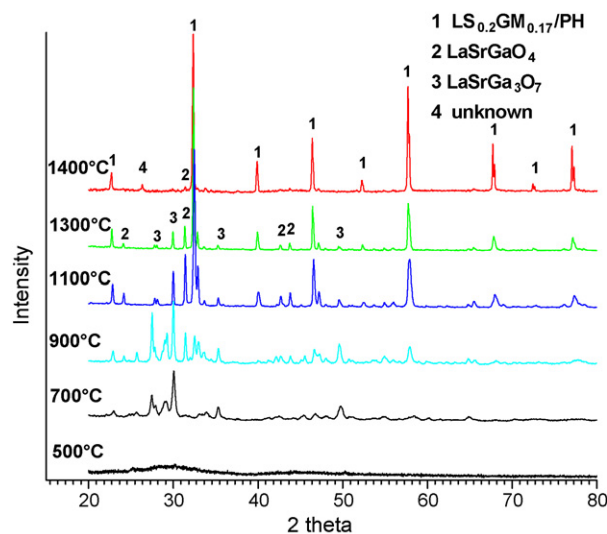


Fig. 2. XRD patterns of $\text{LS}_{0.2}\text{GM}_{0.17}$ precursors prepared by the PH method calcined at different temperatures.

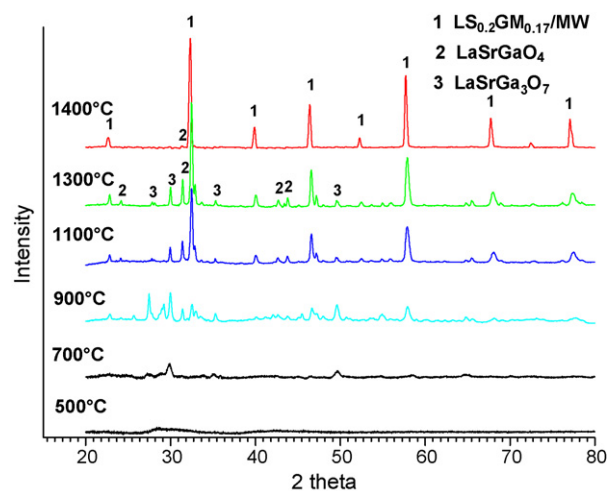


Fig. 3. XRD patterns of $\text{LS}_{0.2}\text{GM}_{0.17}$ precursors prepared by the MW method calcined at different temperatures.

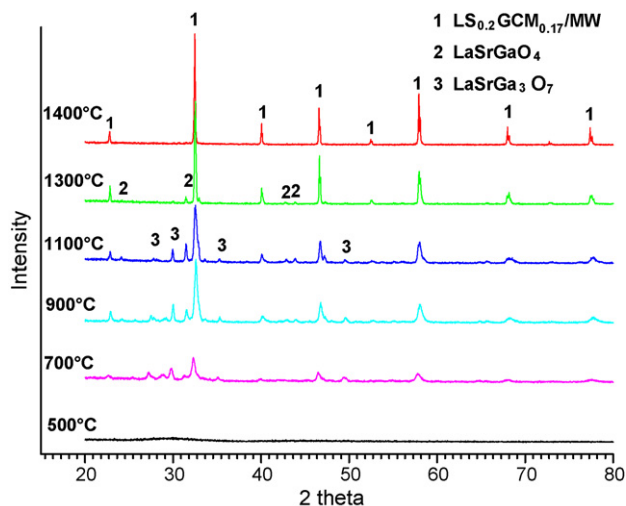


Fig. 4. XRD patterns of $\text{LS}_{0.2}\text{GCM}_{0.17}$ precursors prepared by the MW method calcined at different temperatures.

up to 500 °C. After calcination at 700 °C, only low intensity crystalline peaks could be detected in the XRD curves and the powders consisted of several intermediate phases. These results were in accordance with the DTA and TGA analysis. For the $\text{LS}_{0.2}\text{GM}_{0.17}$ shown in Figs. 2 and 3, the most intense diffraction peaks were perovskite phase and the main secondary phases were SrLaGaO_4 and $\text{SrLaGa}_3\text{O}_7$ up to 1100 °C. However, the formation temperature of the perovskite phase for $\text{LS}_{0.2}\text{GCM}_{0.17}$ was 900 °C, lower than that of $\text{LS}_{0.2}\text{GM}_{0.17}$, shown in Fig. 4. Table 1 lists the comparative amounts of these two secondary phases of the powders prepared by different methods.

Table 1
Estimation of the secondary phases in calcined powders

Powders (1400 °C, 9 h)	As/Asp
$\text{LS}_{0.2}\text{GM}_{0.17}/\text{PH}$	9.8
$\text{LS}_{0.2}\text{GM}_{0.17}/\text{MW}$	6.2
$\text{LS}_{0.2}\text{GCM}_{0.17}/\text{MW}$	0

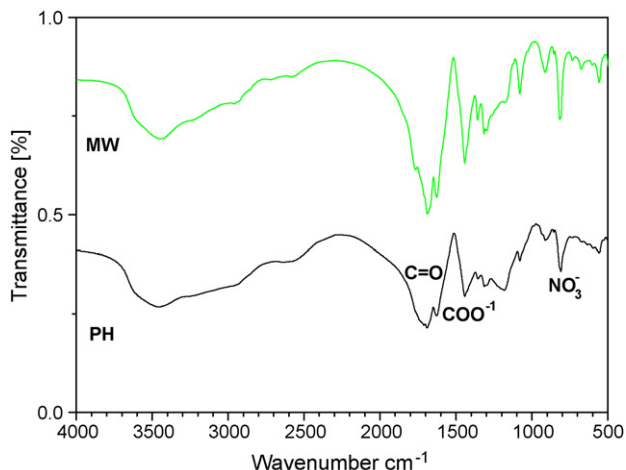


Fig. 5. IR spectra of $\text{LS}_{0.2}\text{GM}_{0.17}$ uncalcined precursors prepared by two methods.

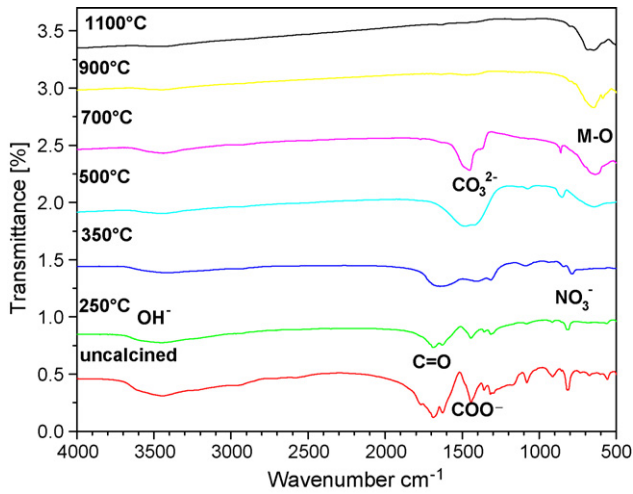


Fig. 6. IR spectra of $LS_{0.2}GM_{0.17}$ precursors prepared by the MW method calcined at different temperatures.

The As/Ap values represent the ratio of the total integrated intensity of the most intense XRD peaks of secondary phases to the integrated intensity of the (1 2 1) peak of the perovskite phase.

The data showed that:

- (1) All the samples needed to be calcined at $1400\text{ }^{\circ}\text{C}$ to obtain the highest purity. The samples of $LS_{0.2}GCM_{0.17}/MW$ had no secondary phases at $1400\text{ }^{\circ}\text{C}$, which was not reported before.
- (2) Due to the narrow composition range for the stability of the perovskite phase, small deviations from the ideal composition would result in secondary phases [1]. It is generally hard to get pure powder of $LS_{0.2}GM_{0.17}$ by wet chemical synthesis [10,12,15]. In this work, the powder of $LS_{0.2}GM_{0.17}$ prepared by the MW method had a higher purity (6.2% secondary phases) than that by the Pechini method (9.8% secondary phases) at $1400\text{ }^{\circ}\text{C}$. This might be attributed to

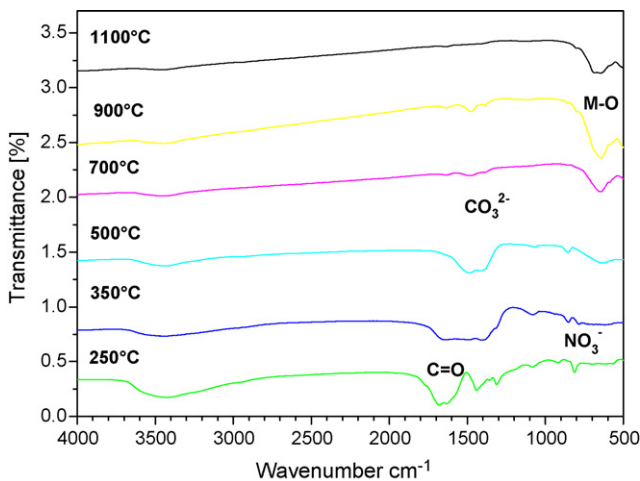


Fig. 7. IR spectra of $LS_{0.2}GCM_{0.17}$ precursors prepared by the MW method calcined at different temperatures.

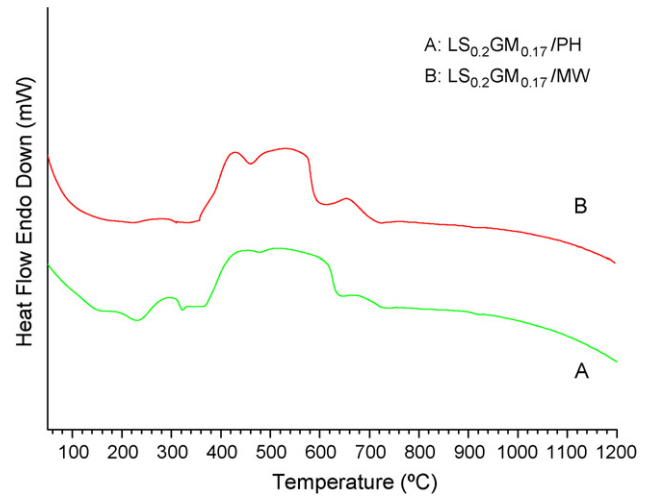


Fig. 8. DTA curves of $LS_{0.2}GM_{0.17}$ precursors prepared by two different methods.

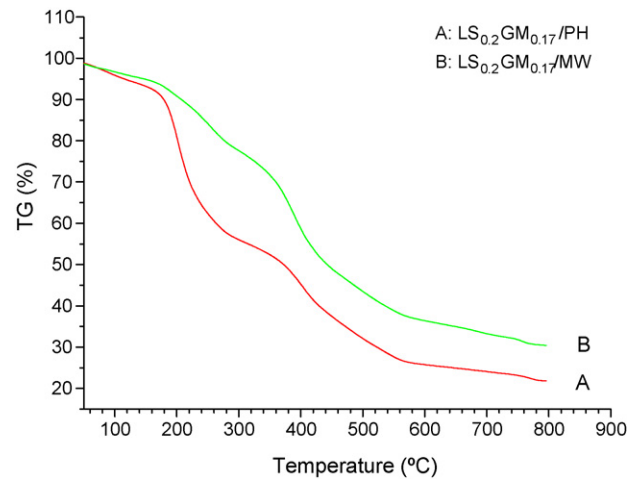


Fig. 9. TGA curves of $LS_{0.2}GM_{0.17}$ precursors prepared by two different methods.

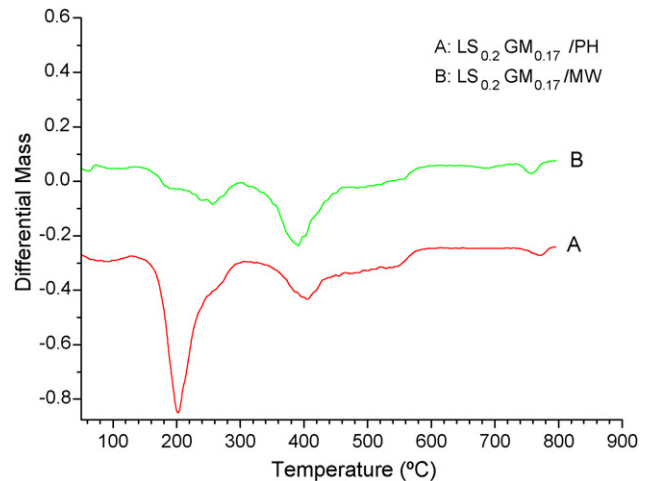


Fig. 10. DTG curves of $LS_{0.2}GM_{0.17}$ precursors prepared by two different methods.

the homogeneous mixing manner of the precursor made by the heating mechanism without thermal gradients in the microwave oven.

- (3) For $LS_{0.2}GM_{0.17}$, precursors prepared by the MW method calcined at $1100\text{ }^{\circ}\text{C}$ had fewer secondary phases than those at $1300\text{ }^{\circ}\text{C}$. This result was opposite to that of the powder prepared by the Pechini method. It was possibly attributed to the metastable or thermodynamically stable conditions of the secondary phases and LSGM. However, we did not find this phenomenon in the sample of $LS_{0.2}GCM_{0.17}/MW$.

3.2. IR spectra

IR plots of the uncalcined precursors prepared by two methods are given in Fig. 5. It can be seen that they were very similar. The broad band located at about 3500 cm^{-1} was due to O–H stretching. Vibrations at 1743 cm^{-1} ($V_{C=O}$) and $1050\text{--}1300\text{ cm}^{-1}$ (V_{C-O}) were related to the stretching modes of the ester (R–COO–R). Two strong bands at 1625 cm^{-1} ($V_{as\text{ COO}^-}$) and 1436 cm^{-1} ($V_{s\text{ COO}^-}$) were the characteristics of COO^- stretching modes. 1312 cm^{-1} (V_{as}) and 823 cm^{-1} (V_s)

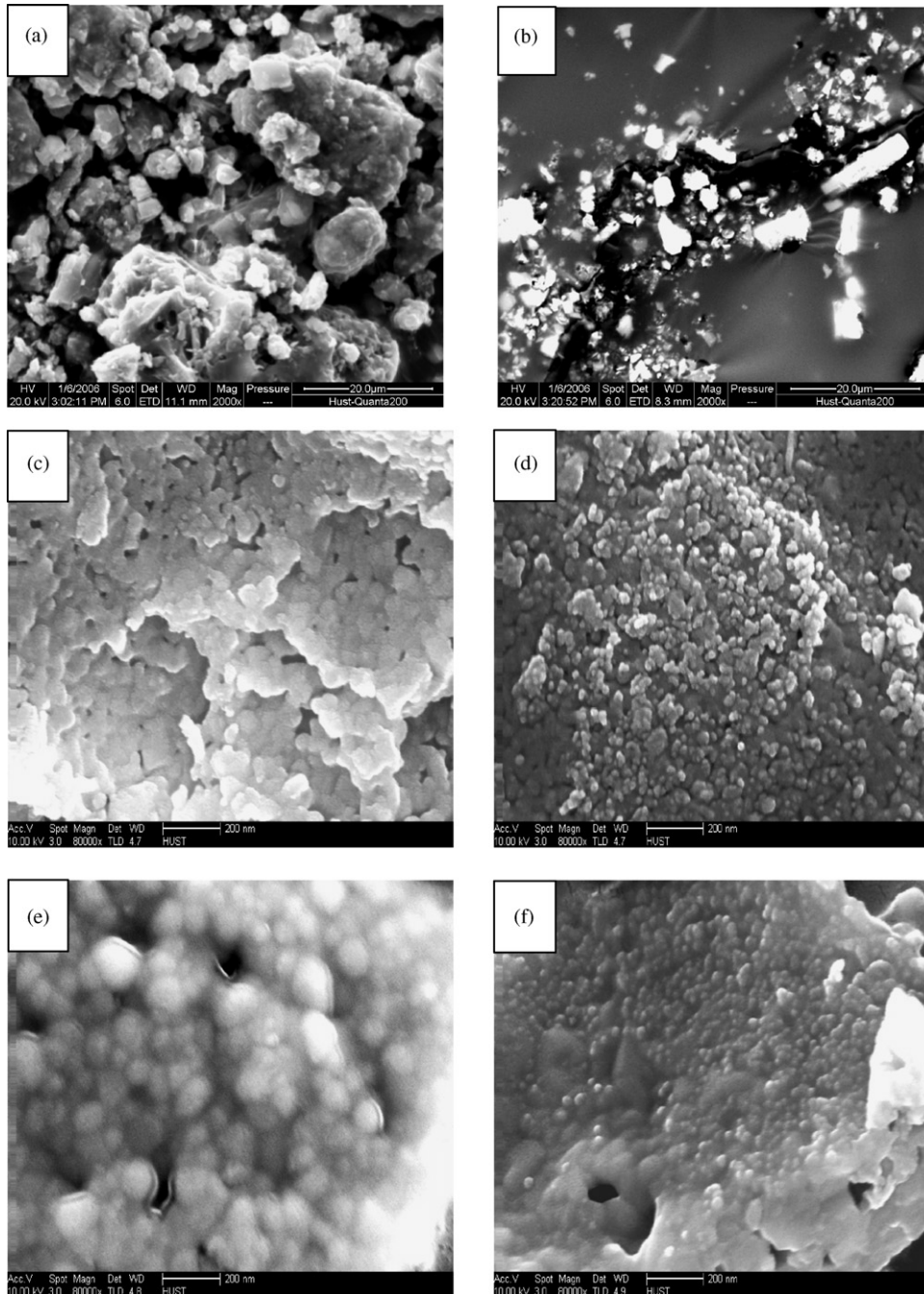


Fig. 11. SEM micrographs of $LS_{0.2}GM_{0.17}$ precursors prepared by two different methods: (a) uncalcined/PH; (b) uncalcined/MW; (c) $500\text{ }^{\circ}\text{C}$, 6 h/PH; (d) $700\text{ }^{\circ}\text{C}$, 6 h/MW; (e) $900\text{ }^{\circ}\text{C}$, 6 h/PH; (f) $900\text{ }^{\circ}\text{C}$, 6 h/MW.

were assigned to nitrate ions. 1690 cm^{-1} belonged to $\text{V}_{\text{C=O}}$ of bicarboxylic acid. Due to the presence of these bands, we can conclude that hydroxycarboxylic acid esterified with ethylene glycol in both methods.

Considering that the discussed XRD curves and the IR spectra for the precursors prepared by two methods are very similar, the thermal evolution by means of the IR spectra has been only checked for the $\text{LS}_{0.2}\text{GM}_{0.17}/\text{MW}$ and $\text{LS}_{0.2}\text{GCM}_{0.17}/\text{MW}$ samples. The IR plots of the precursors prepared by the MW method calcined at different temperatures are given in Figs. 6 and 7. We can see that the IR vibrations of $\text{LS}_{0.2}\text{GM}_{0.17}/\text{MW}$ and $\text{LS}_{0.2}\text{GCM}_{0.17}/\text{MW}$ samples are similar. The plot at 250°C presented similar bands with the uncalcined precursor powders except the lower intensity, which might be attributed to the gradual loss of water and carbocylate groups. At 700°C , samples generally showed the presence of CO_3^{2-} (1453 and 861 cm^{-1}), while the hydrocarbon skeleton and the carboxylate anions have disappeared. The broad band about 640 cm^{-1} was for the vibration of M–O. After calcination at 1100°C , there are no anion vibrations, which indicated that all organics have disappeared.

3.3. Thermal analysis

For the similar behavior of $\text{LS}_{0.2}\text{GM}_{0.17}/\text{MW}$ and $\text{LS}_{0.2}\text{GCM}_{0.17}/\text{MW}$ samples analyzed by XRD and IR curves, we only studied the thermal behavior of $\text{LS}_{0.2}\text{GM}_{0.17}$. The DTA curves of the $\text{LS}_{0.2}\text{GM}_{0.17}$ precursors prepared by the two different methods are given in Fig. 8. In sample B, it showed exothermic peaks at 300 , 380 – 600 and 650°C . However, sample A showed a clear endothermic peak at 220°C , which corresponded to the evaporation of excessive EG (around 200°C in accordance with the boiling temperature of EG in the literature [22]). This indicated that there were more EG in the precursor prepared by the PH method than by MW method. The broad weak exothermic peak at 300°C was thought to be the polyester decomposition [23]. The exothermic peaks in the temperature range from 380 to 600°C corresponded to the combustion of organic matter and decomposition of the combustion products, consistent with the sharp weight loss peaks at about 400°C in the DTG curves (Fig. 10). The exothermic peak at 650°C indi-

cated that a large portion of amorphous LSGM transformed to perovskite phase, agreed well with the XRD and IR results.

In the TGA curves (Fig. 9) and the differential thermogravimetric (DTG) curves (Fig. 10), sample A exhibited nearly two times higher rate of mass loss at 200°C than sample B and the final weight loss was also higher. For a complete reaction between ethylene glycol and citric acid, equal amounts of mass are needed. We define the equal mass equation as below:

$$\text{EM} = \frac{m}{f}$$

where m is the molecular weight and f is the functionality (number of reactive sites). So $\text{EM}_{\text{citric acid}}$ (EM_{CA}) is 49 and $\text{EM}_{\text{ethylene glycol}}$ (EM_{EG}) is 31. According to 100 g of ethylene glycol (G_{EG}), we get the G_{CA} by: $\text{EM}_{\text{CA}} \times G_{\text{EG}} = \text{EM}_{\text{EG}} \times G_{\text{CA}}$. So G_{CA} is equal to 158.9 g. It shows that about 61.4% to 38.6% in mass is needed in the reaction. Approximately, we prepared the precursors using 60/40 according to the traditional Pechini method. However, with complexation of metal cations in citric acid, the functionality of citric acid decreases so that EM_{CA} value increases. This implies that the amount of ethylene glycol is excessive with the invariable 60/40 ratio.

The uniform volumetric heating by microwave caused a larger quantity of heat absorption and vaporized more ethylene glycol than in conventional heating. So DTG curves had a sharp peak in the A curve and the total weight losses were different for the two samples in the TG curves (Fig. 9), consistent with the results of DTA curves.

3.4. Microstructure and particle size

Fig. 11(a) and (b) shows the uncalcined $\text{LS}_{0.2}\text{GM}_{0.17}$ precursors prepared by two methods. Irregular shape particles with agglomerations were found in the powders prepared by the conventional Pechini method. However, the homogenous mixing manner of the precursor can prepare precursor powders with fine particles, which will in turn, will result in the small grain size of the final products. So the powders prepared by the microwave method exhibited more homogeneous and fine particles due to higher heating rate and more homogenous heating manner

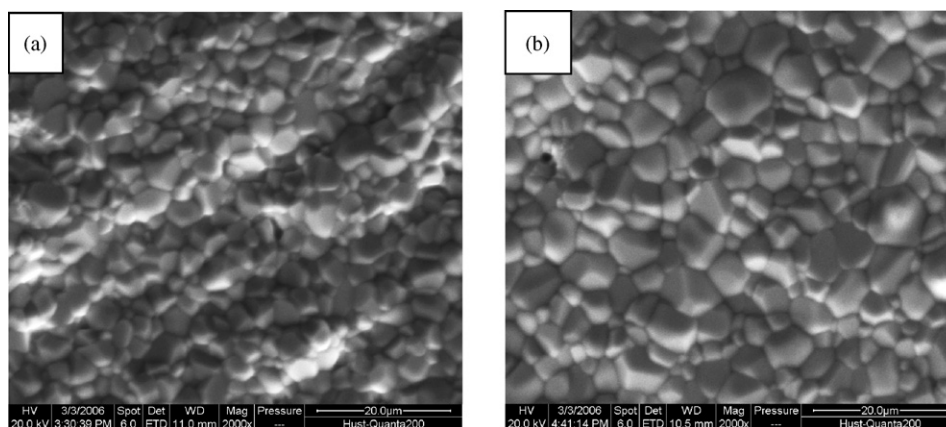


Fig. 12. SEM micrographs of the surface area of the pellets of sample powders prepared by the MW method sintered at 1400°C , 9 h: (a) $\text{LS}_{0.2}\text{GM}_{0.17}$ and (b) $\text{LS}_{0.2}\text{GCM}_{0.17}$.

without thermal gradients. The particle size of the calcined powders prepared by MW was smaller than those prepared by PH (Fig. 10(c)–(f)). The BET surface area of the $\text{LS}_{0.2}\text{GM}_{0.17}$ powder calcined at $900\text{ }^\circ\text{C}$ for 6 h is $3.21\text{ m}^2\text{ g}^{-1}$ (MW) higher than $2.64\text{ m}^2\text{ g}^{-1}$ (PH). The surface area of the pellets of the two powders indicated that the final grain size was about $2\text{--}3\text{ }\mu\text{m}$ homogeneously (Fig. 12), smaller than that of the pellet prepared by traditional sol–gel method ($8\text{--}15\text{ }\mu\text{m}$) [14,24,25]. The densities of $\text{LS}_{0.2}\text{GM}_{0.17}/\text{MW}$ and $\text{LS}_{0.2}\text{GCM}_{0.17}/\text{MW}$ pellets, sintered at $1400\text{ }^\circ\text{C}$ for 9 h, were 6.45 and 6.30 g cm^{-3} , respectively, higher than those of samples prepared by other methods [14,24,25].

4. Conclusions

The microwave-induced solution-polymerization synthesis method (MW) has been employed to prepare a polymeric precursor of doped LaGaO_3 by citric acid and ethylene glycol in a modified microwave oven. Fine, homogeneous and high density pellets of pure $\text{LS}_{0.2}\text{GM}_{0.17}$ and $\text{LS}_{0.2}\text{GCM}_{0.17}$ was obtained after calcination at $1400\text{ }^\circ\text{C}$ for 9 h. Due to the more homogeneous mixing manner of the microwave oven, we got pure $\text{LS}_{0.2}\text{GCM}_{0.17}$ powder after calcination at $1400\text{ }^\circ\text{C}$ for 9 h, which was not reported before. In addition, $\text{LS}_{0.2}\text{GM}_{0.17}$ (6.2% secondary phases) powder prepared by the MW method has a lower secondary phase rate than that (9.8% secondary phases) by the PH method. When using the MW method, the time needed to remove the excess solvents to complete the polyesterification reaction was significantly reduced from hours to a few minutes. A higher heating rate and a more homogenous heating manner without thermal gradients in the microwave oven also produced a smaller grain size ($2\text{--}3\text{ }\mu\text{m}$) and without segregation.

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