

# Synthesis of and densification of oxygen-conducting $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.8}$ nano powder prepared from a low temperature hydrothermal urea precipitation process

Te-Yuan Chen, Kuan-Zong Fung\*

*Center for Micro/Nano Science and Technology, Department of Materials Science and Engineering,  
National Cheng Kung University, 1 Ta-Hsueh Road, Tainan 701, Taiwan, ROC*

Received 25 November 2006; received in revised form 27 July 2007; accepted 5 August 2007

Available online 19 November 2007

## Abstract

In this work, the solid electrolyte powder having a composition of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$  (LSGM) was prepared by the hydrolysis of a urea-containing ( $\text{CO}(\text{NH}_2)_2$ ) solution under hydrothermal conditions and followed by calcination at a temperature range between 350 and 900 °C in air. The particles precipitated after reaction between ammonia, decomposed from urea, and a stock solution containing metal nitrates. Samples characterizations were performed using X-ray diffractometry (XRD), thermogravimetry analysis (TGA), differential thermal analysis (DTA), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Thermal analysis was used to verify the decomposition of the precursor. The results show that crystalline phase of  $\text{GaO}(\text{OH})$  was formed in the dried precursors. After heating up to ~350 °C, the crystalline  $\text{La}(\text{OH})_3$  was gradually formed. Subsequently, the  $\text{La}(\text{OH})_3$  decomposed to  $\text{La}_2\text{O}_3$  at temperatures ranging from 500 to 800 °C. Several reflections based on LSGM perovskite were observed at 800 °C. After the precursors were further calcined at 900 °C for 12 h, single-phase perovskite, LSGM, was formed without any traceable impurities based on XRD diffraction analysis. TEM observations show LSGM powders with an average particle size of ~150 nm after calcination at 900 °C for 12 h. The LSGM powders agglomerated together due to the necking behavior at 1100 °C. This result also indicates that LSGM powders started to densify at relatively low temperature when the powder is synthesized using a hydrothermal urea precipitation process. The hydrothermally processed LSGM samples were finally sintered at 1400 °C for 3 h. The relative density of sintered LSGM bulk sample was as high as 98%. The electrical conductivity of hydrothermally processed LSGM was measured to be 0.056 S/cm at 800 °C. © 2007 Published by Elsevier Ltd.

**Keywords:** SOFC; Hydrothermal;  $\text{LaGaO}_3$ ; Electrolyte; Urea hydrolysis

## 1. Introduction

Solid oxide fuel cells (SOFCs) is able to convert the chemical energy of fuel directly into electrical energy with high current density and high efficiency (more than 60%). A typical SOFC operates near 1000 °C and yttria-stabilized zirconia (YSZ) is the most widely used electrolyte, which exhibits an oxide ion conductivity of about 0.1 S/cm.<sup>1</sup> However, the operation of SOFC at an intermediate-temperature (600–800 °C) has been recently focused. Doped lanthanum gallate oxide,  $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-\delta}$ , was proposed as an appropriate electrolyte. Moreover, lowering the operating tem-

perature of SOFC to 600–800 °C gives the advantages of enhanced reliability, longer cycle life and lower material cost.  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.8}$  (LSGM) is well known due to its high oxide ion conductivity, 0.17 S/cm at 800 °C, which is about 8.5 times as high as that of conventional YSZ electrolyte at the same temperature, over a wide range of oxygen partial pressure. Therefore, LSGM is a promising solid electrolyte for using at intermediate temperatures.

The LSGM is commonly prepared by the conventional solid-state reaction method (SSR),<sup>2–4</sup> nevertheless, requiring much time and energy for calcination and sintering. Thus, several alternative approaches have been reported for the preparation of LSGM electrolyte. For example, the LSGM fine powders were obtained by coprecipitation,<sup>5</sup> sol–gel process,<sup>6</sup> Pechini method<sup>6,7</sup> and glycine–nitrate combustion method.<sup>8,9</sup> Huang and Goodenough also adopted the technique of coprecipita-

\* Corresponding author. Tel.: +886 6 2757575x62969; fax: +886 6 2380208.  
E-mail address: [kzfung@mail.ncku.edu.tw](mailto:kzfung@mail.ncku.edu.tw) (K.-Z. Fung).

tion to successfully synthesize the LSGM powders. The route of sol–gel (with  $\text{NH}_4\text{OH}$  addition), starting with an aqueous mixture of the acetates of La, Sr, and Mg, and of Ga nitrate, were further studied by Huang and Goodenough.<sup>8</sup> As for other wet chemical synthesis methods, Pechini route and combustion method also have been employed by Tas et al. and Cong et al., respectively.<sup>10,11</sup> However, both phase purity and microstructure of LSGM materials highly depend on synthesis procedure. In fact, the synthesis of a single-phase perovskite is rather difficult.<sup>12</sup> Even for sol–gel methods, LSGM materials also contain, at the end of the preparation process, small amounts of undesired phases such as  $\text{LaSrGa}_3\text{O}_7$ ,  $\text{LaSrGaO}_4$  and  $\text{MgO}$ . Some researchers reported that it is very difficult to synthesize pure LSGM phase due to the thermodynamic, and kinetics limitations as well as Ga vaporization above  $1400^\circ\text{C}$ .<sup>13</sup> To obtain single-phase powders and dense LSGM bulk from solid-state oxide mixture using higher-temperature calcination ( $\sim 1400^\circ\text{C}$ ) and sintering ( $\sim 1500^\circ\text{C}$ ), respectively, is usually needed. Therefore, a low-temperature synthesis process and lowering sintering temperature is desired to obtain homogeneous LSGM powders and to avoid the formation of non-stoichiometric powder. Using fine particles is regarded as promising way to improve the homogeneity and sinterability of the green body and finally to achieve the desirable properties for the applications.

In order to obtain nano-crystalline lanthanum gallium oxide powders the hydrothermal methods have shown great potential for the low temperature fabrication of nano oxide powders.<sup>8</sup> It is an aqueous ceramic process that uses hot and pressurized water for precipitation of anhydrous, well-crystallized ceramics powders. Because the hydrothermal reaction replaces the high-temperature calcination required by sol–gel and coprecipitation processes, this technique is able to produce agglomerate-free ceramic powders. The other advantage of this route results from the homogeneous nucleation processes.

For commonly hydrothermal treatment, a gel similar to sol–gel process was used as the precursors. Huang and Goodenough<sup>8</sup> reported that the gel properties may be affected by the complex hydroxo and acetate ligands with the cations precipitates, then single-phase LSGM cannot be prepared by the further hydrothermal treatment due to the nonsimultaneous precipitation during the hydrothermal reaction.  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Zn}_{0.2}\text{O}_{2.8}$  (LSGZ) powders were prepared via precipitation of hydrolysis urea in aqueous solutions, then the single-phase LSGZ was formed after calcination at about  $1300^\circ\text{C}$  for 6 h.<sup>14</sup>

The hydrolysis of urea in aqueous solutions is accompanied by the slow and controlled supply of ammonia and carbon dioxide into the solution.<sup>9</sup> The gradually increasing pH obtained by the decomposition of urea ( $\text{CO}(\text{NH}_2)_2$ ) in unison with the steady supply of  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  ions, typically lead to the precipitation of metal hydroxycarbonates ( $\text{MHCO}_3^-$ ) with controlled particle morphology.<sup>15,16</sup> Homogeneous precipitation from aqueous solutions, in the presence of urea, has been used to produce mono-sized and spherical particles of yttrium oxide,<sup>17</sup> cerium oxide,<sup>18</sup> and yttrium aluminum garnet.<sup>19</sup>

More recently, Yan et al. developed a soft chemical approach towards the synthesis of weakly agglomerated nano-crystalline rare earth stabilized zirconia powders, via a two-step hydrother-

mal urea homogeneous precipitation,<sup>11,12,20</sup> in which a stock solution of metal nitrates and urea was heated at  $80^\circ\text{C}$  for 48 h and then at  $180^\circ\text{C}$  for 72 h. Consequently, weakly agglomerated  $(\text{ZrO}_2)_{1-x}(\text{Yb}_2\text{O}_3)_x$  ( $x = 0.02\text{--}0.2$ ) nanosized powders with high surface area were obtained at low temperature. Even after calcination at  $800^\circ\text{C}$ , the average crystallite size of the products was still in the range of 7.9–13 nm.

Therefore, a stock solution containing homogeneously distributed urea and metal nitrates followed by two-step hydrothermal hydrolysis may give a desired nanosized oxide powders. This process can be quickly stopped at a desired pH by cooling the reaction solution to room temperature. During urea hydrolysis, the precipitates formed via homogeneous nucleation. The nucleation and crystallite growth are thus readily controlled by adjusting the hydrolysis rate and the resultant pH (urea amount), which depend on the process parameters (including the concentrations of urea and metal ions, and reaction time and reaction temperature, etc.).

The aims of this work were to utilize a facile urea hydrolysis based on hydrothermal urea precipitation method to synthesize nanosized doped lanthanum gallium solid solutions with good structural homogeneity and reduced sintering temperature, and to investigate the microstructure and electrical properties of this system. Finally, the doped lanthanum gallium nanosized powders synthesized by the facile urea based hydrothermal method were characterized by thermogravimetry/differential thermal analysis (TG/DTA), Fourier transform infrared spectra (FTIR), X-ray diffractometry (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

## 2. Experimental procedure

Nanosized LSGM powders were prepared by the hydrothermal urea precipitation method.<sup>11,12,20</sup> The powders were synthesized by using appropriate separate stock solutions of the following chemicals:  $\text{La}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (99%, Merck),  $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  (99.9%, Alfa),  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Showa, 99.0%),  $\text{Sr}(\text{NO}_3)_2$  (Showa, 98.0%) and urea (Aldrich, 99.5%). An accurate determination of the  $x$  value (assigned by the manufacturer) of the gallium nitrate hydrate is important for the stock solution. The value of  $x$  given in the formula of gallium nitrate hydrate was experimentally found to be 4.06 (by TG analyses conducted on the raw material). The stock solutions were prepared by separately dissolving the chemicals in water and then mixing with urea ( $\text{CO}(\text{NH}_2)_2$ ) at cation/anion ratio being 10. The solution was sealed into Teflon-lined steel autoclaves and hydrothermally treated at  $200^\circ\text{C}$  for 6 h under autogenous pressure in an oven, then cooled to room temperature. Then, the gel-like precipitates were removed from the autoclave. The precipitated powders were washed with deionized water and ethanol, and separated by centrifugation and followed by freeze-drying for 3 days. The dried powder was calcined at 1173 K for 12 h in air. The powder was then pressed into several circular disks of 25 mm diameter and 4 mm thickness using a uniaxial die pressing at 30 MPa, followed by cold isostatic pressing under a pressure of 200 MPa. The samples

were then sintered at 1673 K for 3 h in air with a heating rate of 2 K/min. X-ray diffraction (XRD) studies were carried out using a Rigaku D/Max-III X-ray powder diffractometer with Cu K $\alpha$  ( $\lambda = 1.5408 \text{ \AA}$ ) radiation. Transmission electron microscopy images were taken using a Hitachi HF-2000 FE TEM under a working voltage of 200 kV. An inductively coupled plasma atomic emission spectroscopy (ICP-AES, Plasma-Spec, Leeman Labs. Inc.) was used to analyze the chemical composition of final products. TG–DTA traces were obtained by a Setaram Thermal Analyzer (Setsys Evolution) and measurements were carried out from room temperature to 1000 °C, with a heating rate of 10 °C min<sup>-1</sup>. Fourier transform infrared (FTIR) spectra were recorded at RT using a Perkin-Elmer spectrometer (Model 2000). The FTIR spectrometer was coupled with a personal computer loaded with the IRDM (IR Data Manager) program to process the recorded spectra. The specimens were pressed into small discs using a spectroscopically pure KBr matrix as a standard. The ionic conductivity of LSGM samples was measured using the two-probe ac impedance method. Platinum paste was applied on both surfaces of the sintered disks to be used as the electrodes. The platinum paste was fired at 700 °C for 2 h to remove the organic binders. Silver wires were used as the lead wires connected to both electrodes. The impedance of samples was measured over a frequency range between 20 Hz and 1 MHz using an HP-4284A LCR meter. The electrical conductivity of sintered samples was then measured as a function of temperature from 773 to 1173 K in air.

### 3. Results and discussion

#### 3.1. DTA/TG and structure analysis of LSGM precipitate

Thermogravimetry analysis and DTA traces of the precipitate powders obtained from the hydrothermal urea hydrolysis precipitation method after freeze-drying for 3 days are shown in Figs. 1 and 2. These curves show the complete thermal reaction of the precipitate powders from room temperature to 1000 °C at a constant heating rate of 10 K/min. Several endothermic peaks appeared during heating of the precipitated powders. The TGA curve shows a continuous weight loss up to 14.5% until 400 °C, with a transition at 470 °C, followed an additional 7.4% weight loss up to ~680 °C, and another obvious transition at about 780 °C. Above 780 °C, there is no further weight loss up to 1000 °C. The sharp weight loss was observed just below 470 °C. This weight loss can be ascribed to (1) the decomposition and burn out of most ammonium nitrate in the precipitated powders and (2) the removal of the chemically adsorbed water (430 °C) from the surface of the precipitate powders, even though the samples were freeze-dried below -55 °C. The DTA curve also shows the endothermic peaks at about 430, 470 and 780 °C. The decomposition of hydrothermally formed precursors and the conversion of the perovskite phase may be divided into three stages based on the analyses of TGA and DTA curves. The traces taken from the precipitated powders showed these endothermal reactions accompanied by a certain extent of weight loss at 430, 470 and 780 °C, respectively. Finally, the precipitated powders exhibit a total weight loss of about 22%, on heating to 1000 °C.

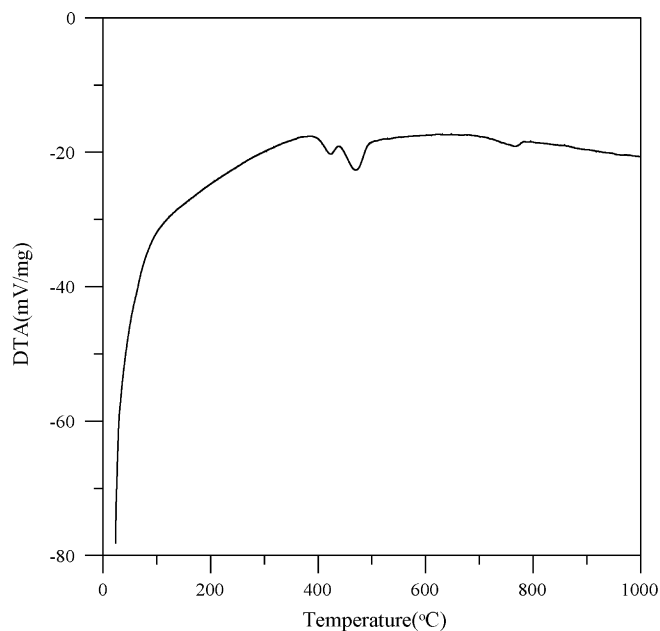


Fig. 1. DTA curve of the LSGM precursor from hydrothermal process.

And this stage, which corresponds to the transformation of large amount of non-perovskite phase to perovskite phase, occurred over a temperature range of 780–1000 °C. This means that the synthesis temperature of the LSGM using hydrothermal urea hydrolysis precipitation process may be lowered to 1000 °C.

Huang and Goodenough<sup>8</sup> have shown that the LSGM powders synthesized through the hydrothermal route utilizing the mixed acetates of the component and ammonia solution, then two endothermic peaks located around 100 and 280 °C, and one exothermic peak was around 330 °C from thermal analysis. For this hydrothermal reaction, the formed gel was used as the precursor of the hydrothermal treatment. The discrepancies

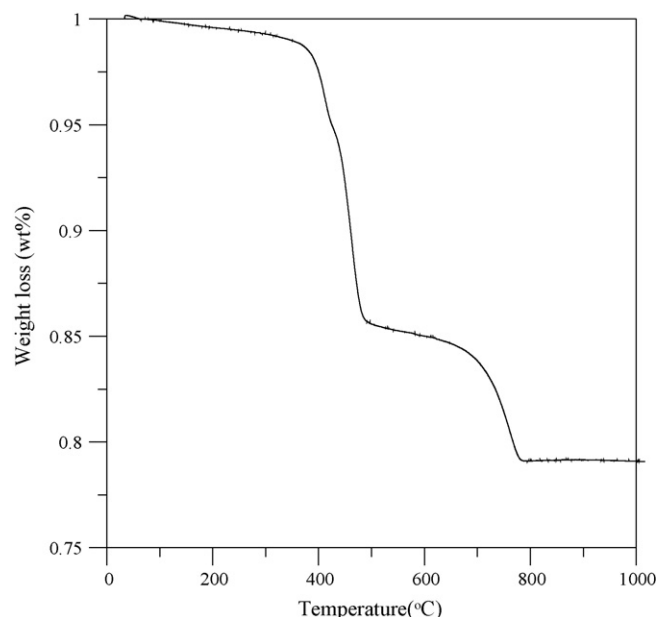


Fig. 2. TGA curve of the LSGM precursor from hydrothermal process.

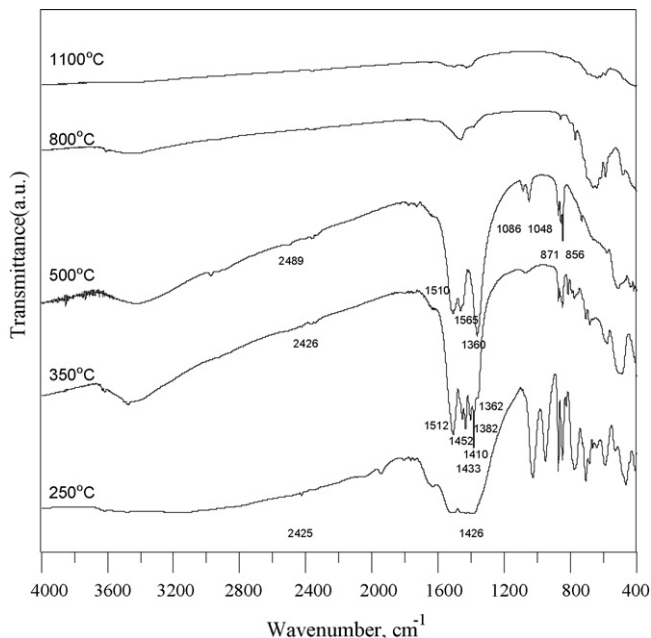


Fig. 3. FTIR spectra of LSGM powders at different calcination temperatures.

between Huang's work and the present study may be caused by the difference in the raw materials between acetates and nitrates.

The IR spectra of the precipitated powders plotted according to the calcination temperature are shown in Fig. 3. The broad band at  $3200\text{--}2600\text{ cm}^{-1}$  corresponds to the stretching vibration of the free hydroxyl group ( $-\text{OH}$ ), even though the hydrothermally synthesized products have been freeze-dried. Some water was still absorbed on the surface of the precipitate powders until they were heated to higher temperatures. The bands of  $1400\text{--}1300$ ,  $1580\text{--}1400$  and  $2500\text{--}2350\text{ cm}^{-1}$  indicated the presence of the N–H stretching vibration of  $\text{NH}_4^+$  in the precipitated powders. The presence of the N–H stretching vibration is due to the unwashed nitride ions remaining in the precipitated powders. With the increase of the calcination temperature (from 500 to  $800\text{ }^\circ\text{C}$ ), the intensity of the  $\text{CO}_3^{2-}$  band at  $876\text{--}856$  and  $1086\text{--}1047\text{ cm}^{-1}$  was enhanced. This contribution of the  $\text{CO}_3^{2-}$  band is due to the formation of  $\text{CO}_2$  at higher temperature. Eventually, when the calcined temperature was higher than  $800\text{ }^\circ\text{C}$ , no trace of  $\text{CO}_3^{2-}$  bonding was observed due to the formation of the oxides. Previous researches<sup>10,14</sup> on hydrothermal process of LSGM and LSGZ also show similar phenomena, respectively. Tas et al.<sup>14</sup> showed the structural  $\text{CO}_3^{2-}$  is observed by the broad bands at  $1330\text{--}1520\text{ cm}^{-1}$ , also at  $696\text{--}730$ ,  $805\text{--}858$ , and  $1028\text{--}1074\text{ cm}^{-1}$ . Splitting of the  $\text{CO}_3^{2-}$  bands is commonly observed in basic carbonates, and such splitting is clearly observed in our data.

The phase evolution in precipitated powders was investigated based on XRD traces (as a function of calcination temperatures for a period of 12 h) in Fig. 4. Note that the XRD of the sample calcined at  $800\text{ }^\circ\text{C}$  presents many intermediate phases. This result shows that the formation of the perovskite phase requires the undergoing of different intermediate stages. The powdery precipitates after the freeze-drying step were found

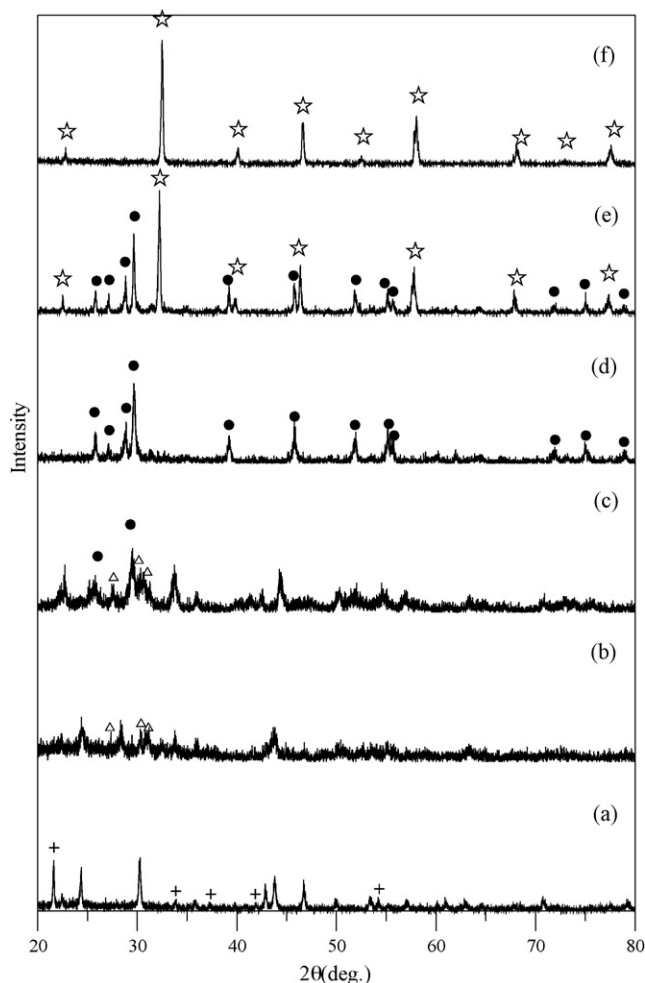


Fig. 4. XRD patterns of LSGM precursor after calcination at different temperatures for 12 h. (☆)  $\text{LaGaO}_3$ , (●)  $\text{La}_2\text{O}_3$ , ( $\Delta$ )  $\text{La}(\text{OH})_3$ , (+)  $\text{GaOOH}$ . (a)  $200\text{ }^\circ\text{C}$ ; (b)  $350\text{ }^\circ\text{C}$ ; (c)  $500\text{ }^\circ\text{C}$ ; (d)  $700\text{ }^\circ\text{C}$ ; (e)  $800\text{ }^\circ\text{C}$ ; (f)  $900\text{ }^\circ\text{C}$ .

to be crystalline,  $\text{GaO}(\text{OH})$  (JCPDS:06-0180). However, this  $\text{GaO}(\text{OH})$  phase completely disappeared after being heated to  $350\text{ }^\circ\text{C}$ , as shown in Fig. 4(b). At the same time, the crystalline of  $\text{La}(\text{OH})_3$  also gradually formed. As the temperature increased from 500 to  $800\text{ }^\circ\text{C}$ , the  $\text{La}(\text{OH})_3$  decomposed and turned into  $\text{La}_2\text{O}_3$ , as shown in Fig. 4(c and d). Finally, the precipitate powders transformed into a pure perovskite phase as shown in Fig. 4(f) after calcinations at temperatures higher than  $800\text{ }^\circ\text{C}$ . Based on the XRD analysis, the precipitate powders exhibit many intermediate phases, such as  $\text{GaO}(\text{OH})$ ,  $\text{La}(\text{OH})_3$  and  $\text{La}_2\text{O}_3$ , when heated from room temperature to  $800\text{ }^\circ\text{C}$ . Furthermore, these results indicate that the formation of pure LSGM perovskite from the hydrothermal urea hydrolysis precipitation process involves different intermediate stages. With the assistance of high pressure and heat from hydrothermal process, well-crystallized LSGM powder was obtained at temperatures significantly lower ( $900\text{ }^\circ\text{C}$ ) than those used in the solid-state reaction method (higher than  $1100\text{ }^\circ\text{C}$ ).<sup>2-4</sup>

Synthesis of single-phase LSGM has been a big challenge for many researchers. Stevenson et al.<sup>5</sup> have pointed out that  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$  powders were prepared by

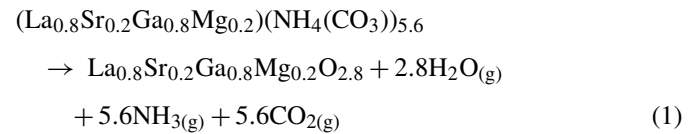


glycine/nitrate combustion synthesis with calcination at 1400 °C were almost fully perovskite with only a small amount (about 3 wt.%) of unidentified second phase remaining. It has also been claimed single-phase LaGaO<sub>3</sub> and La<sub>0.9</sub>Sr<sub>0.1</sub>GaO<sub>2.95</sub> powders were synthesized successfully after calcinations at temperatures of 850 and 1340 °C, respectively.<sup>10</sup> However, the LSGM powders still contained 4–5 wt.% second phase of LaSrGa<sub>3</sub>O<sub>7</sub> or LaSrGaO<sub>4</sub> after calcinations at 1400 °C for 8 h.

The present investigation used the nitrate solution with urea, under the hydrothermal treatment at 200 °C for 6 h, calcinations at 900 °C for 12 h. Subsequently, highly pure LSGM perovskite powders were obtained at significantly lower temperature compared to others' works.

Based on the consideration of the thermal analysis and IR spectra versus the calcination temperatures, the first (~430 °C) and second (~470 °C) endothermic peaks correspond to the removal of H–O and N–H bonding, and the third (~780 °C) endothermic peak represents the removal of carbon dioxide. Furthermore, based on the results of thermal analyses, XRD and IR,

the following reaction may be expressed to describe the final conversion of the precipitated powders to the LSGM powder during calcinations in air at 1000 °C:



From Eq. (1), the percentage of total weight loss due to the removal of H<sub>2</sub>O, NH<sub>3</sub> and CO<sub>2</sub> from the freeze-dried powder in the above-mentioned reaction was estimated to be around 22%, which is in good agreement with the TGA trace. The EDS analyses performed on these calcined powders (at 1000 °C) show that the fractions of La, Ga, Sr and Mg cation on lattice sites are 81.82, 83.91, 18.18 and 16.09 at%, respectively. These values are also consistent with the content of the starting reactants.

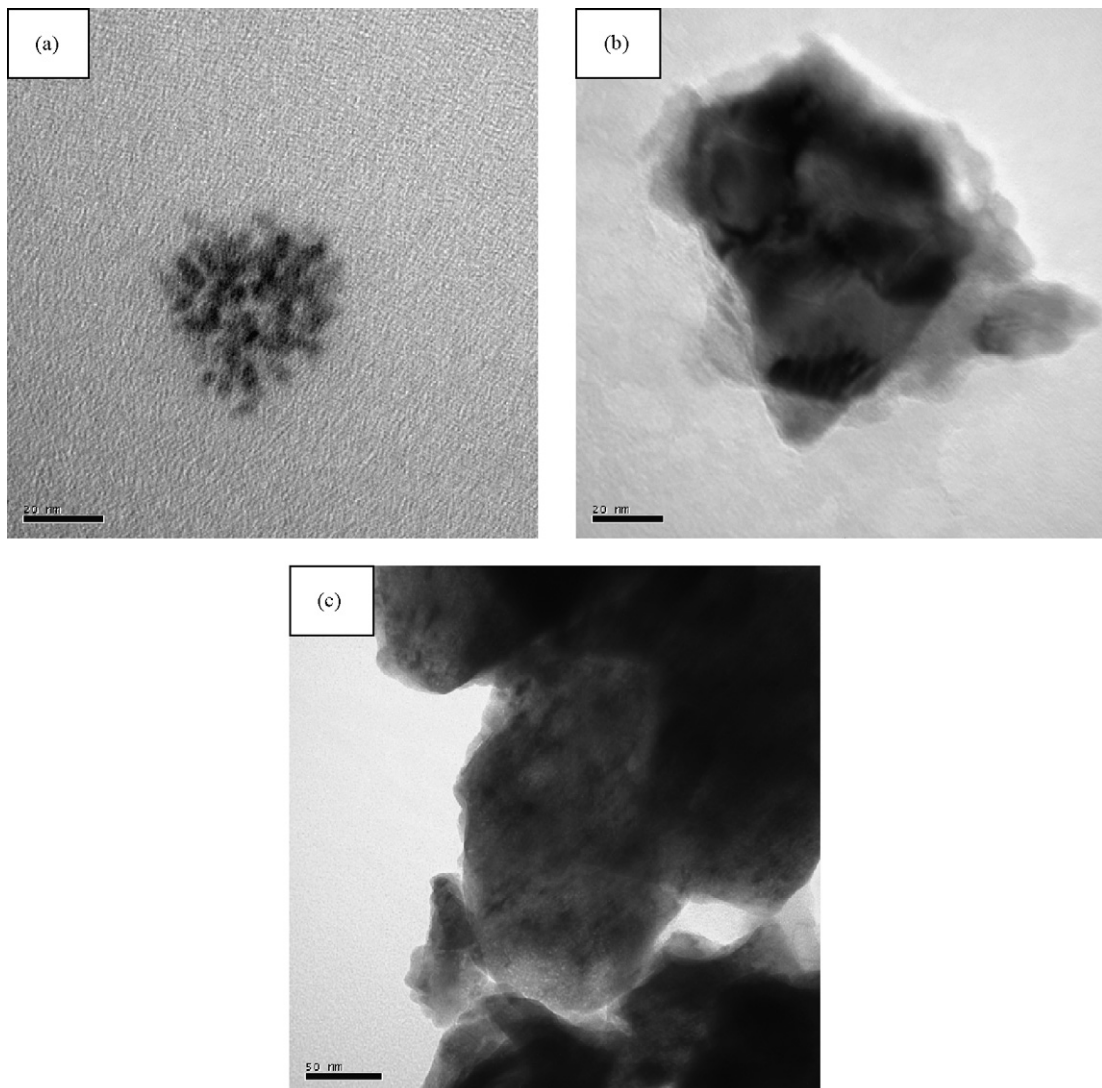


Fig. 5. TEM photographs of LSGM (a) precursor, (b) after calcined at 800 °C for 12 h and (c) after calcined at 900 °C for 12 h.

### 3.2. TEM observation and particle size analysis

Fig. 5(a) shows the typical TEM images of the LSGM precipitated powders obtained from hydrothermal urea hydrolysis precipitation method after freeze-drying. The precipitated powders consist of agglomerates of nanosized particles. The average diameter of the precipitated powder is as small as 5 nm. But the size of the agglomerate is around 45 nm. Fig. 5(b and c) shows the TEM micrographs of precipitated powders after being calcined at 800 and 900 °C for 12 h, respectively. After calcination at 800 °C for 12 h, the precipitated powders showed an average diameter close to 80 nm. LSGM precipitated powders calcined at 900 °C also have a similar appearance. The powders clearly exhibit crystalline particles with a size averaging 150 nm, with agglomeration, probably due to the partial sintering when calcined at 900 °C. However, the grain size increased from 50 to 150 nm. This result showed good agreement with the BET measurement, as shown the following calculation. The diameter of particle ( $d$ ) may be obtained from BET measurement based on the following equation<sup>21</sup>:

$$d = \frac{6}{S\rho} \quad (2)$$

where  $S$  and  $\rho$  are the specific surface area ( $\text{m}^2/\text{g}$ ) and the particle density ( $\text{g}/\text{cm}^3$ ), respectively. The measured specific surface area of LSGM powder is  $6.3965 \text{ m}^2/\text{g}$ . From Eq. (2), the particle size of the calcined LSGM powder is about 142 nm. This result indicates that the sinterability of LSGM may be improved due to the higher surface area of smaller particle size.

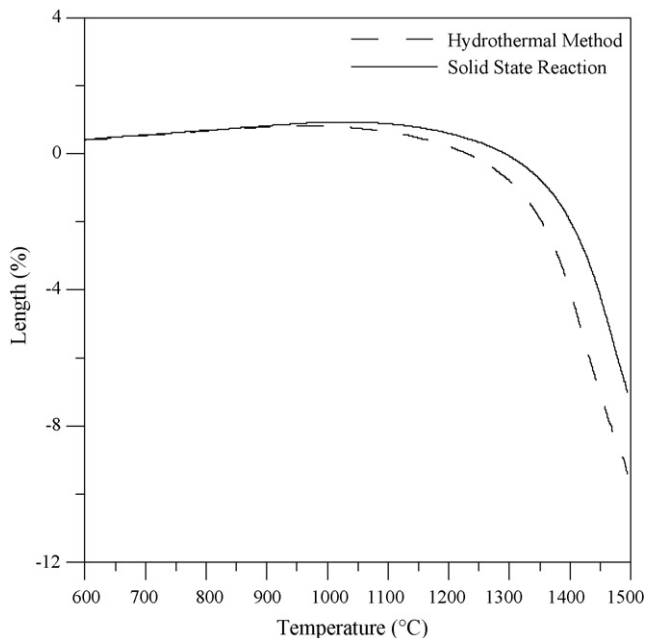


Fig. 6. Linear shrinkage of the LSGM green body during sintering from different synthesis methods, dash line (---) and solid line (—) are hydrothermal method and solid-state method, respectively.

### 3.3. Densification of LSGM precipitate

The dilatometry of the LSGM green compact was measured under a constant heating rate of 10 K/min from 600 to 1500 °C. The result is shown in Fig. 6. The solid line (—) and the dashed line (---) represent the hydrothermal urea hydrolysis precipitation method and solid-state reaction method at a constant heating rate of 10 K/min, respectively. The beginning of sintering temperature was estimated to be 1087 °C for hydrothermal urea hydrolysis precipitation method. However, the sintering onset temperature of SSR sample occurred at 1137 °C. The accumulated shrinkage being 9.16 and 7.01% at 1400 °C, respectively, indicate LSGM from hydrothermally treated show higher density than SSR samples. The hydrothermally treated LSGM shows the relative density of LSGM bulk sintered at 1400 °C for 3 h as high as 98% that is higher than that prepared using the SSR after sintering at 1420 °C for 15 h (95%) by Gorelov et al.<sup>22</sup> This result indicates that the powder from hydrothermal urea hydrolysis precipitation method give better densification behavior.

Fig. 7(a and b) shows SEM micrographs of LSGM powders that were obtained from the hydrothermal urea hydrolysis precipitation reaction and followed by the calcination at 900 and 1100 °C for 12 h, respectively. Fig. 7(a) shows that nanosize spherical particles of LSGM powder were obtained at 900 °C,

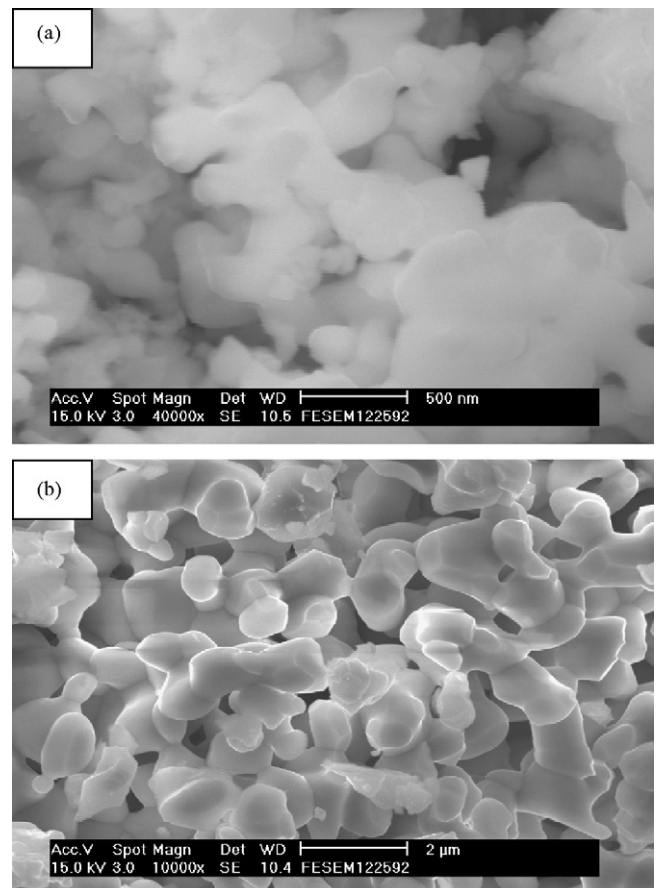


Fig. 7. SEM micrographs of LSGM powder calcined at (a) 900 °C and (b) 1100 °C for 12 h.

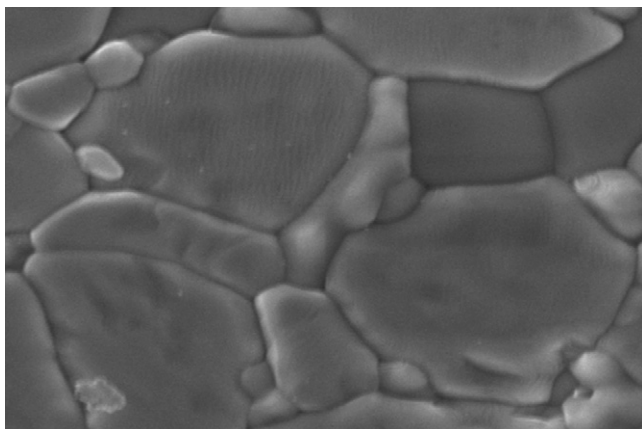


Fig. 8. SEM micrograph of LSGM bulk sintered at 1400 °C for 3 h with calcined at 900 °C for 12 h by hydrothermal process.

although some particles were agglomerated. By increasing the calcination temperature to 1100 °C, these LSGM particles reveal partial necking and bonding. This result is in good agreement with its shrinkage from dilatometry curve, as shown in Fig. 6, and its sintering onset temperature is about 1087 °C. This morphological observation of LSGM calcined powder, a round shape and about 1 μm, indicates that the hydrothermally reacted powders are highly reactive and easy to densify into a single, orthorhombic perovskite.

Fig. 8(a) shows an SEM micrograph of hydrothermally processed LSGM bulk samples after sintering at 1400 °C for 3 h. The relative density (98%) of the hydrothermal sample was higher than the solid state's ones (95% at 1420 °C and 98% at 1520 °C).<sup>18</sup> No cracks, pores or pin holes were seen on the surface of LSGM sample prepared from hydrothermally derived powder. Based on these microstructure evolutions, it may be concluded that LSGM with enhanced densification and microstructure may be obtained by using the hydrothermally processed powder derived from hydrothermal urea hydrolysis precipitation process.

#### 3.4. Conductivity measurement of LSGM

Fig. 9 shows Arrhenius plots of electrical conductivity of LSGM samples synthesized using hydrothermal urea hydrolysis precipitation process and solid-state reaction.<sup>6</sup> Both samples were sintered at 1500 °C for 3 h. The conductivity was measured from 500 to 900 °C in air. The relative density of samples is also shown in parentheses. As expected, the conductivity of these LSGM samples increased with the increasing temperature. Apparently, the conductivity of hydrothermal urea hydrolysis precipitation processed sample exhibits the higher conductivity of 0.056 S/cm at 800 °C. However, the sample from solid-state reaction showed lower conductivity of 0.035 S/cm at the same temperature. The conduction behavior for hydrothermally processed LSGM are in good agreement with the published data based on the same compositions.<sup>2–8</sup> Therefore, the low conductivity of sample prepared from solid-state-reacted powder may be due to poor densification at 1400 °C for 3 h (85% relative density).

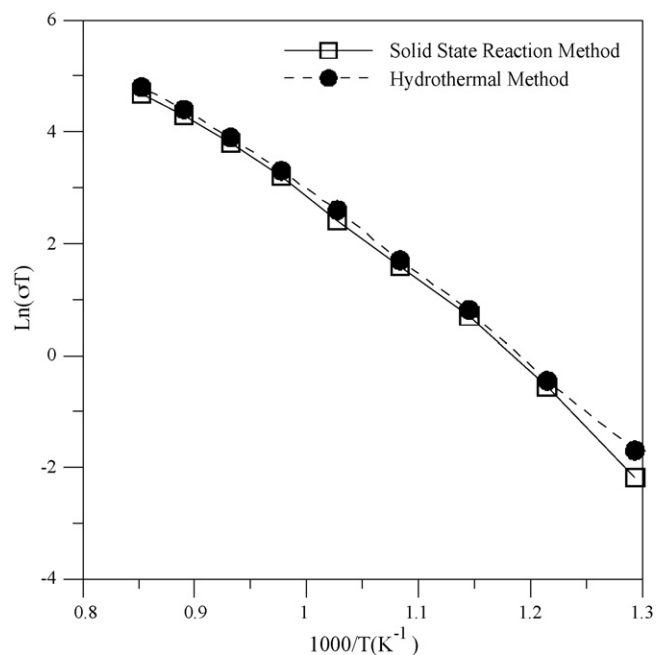


Fig. 9. Conductivity of LSGM bulk by hydrothermal and solid-state process as a function of 1000/T.

Although the conductivity of LSGM from solid-state reaction is slightly lower than that of the hydrothermal urea hydrolysis precipitation processed one, it is still higher than that of YSZ. Summarily, the hydrothermally process is an excellent technique to obtain homogeneous and nanosized LSGM powder that provides great sinterability at reduced temperature. Such a highly reactive powder gives better opportunity for LSGM to become a practical solid electrolyte for SOFC applications.

#### 4. Conclusions

The synthesis and densification of oxygen-conducting  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$  (LSGM) nano powder from a hydrothermal urea hydrolysis precipitation process has been investigated using DTA/TG, TMA, XRD, SEM and TEM. The following conclusions may be drawn based on this study.

- (1) A nanosized powder of LSGM was obtained at 900 °C by hydrothermal urea hydrolysis precipitation technique. The calcined powders of the precursor were shown to have the stoichiometric and single-phase LSGM after calcinations at 900 °C for 12 h.
- (2) LSGM was able to densify to 98% of theoretical density at 1400 °C for 3 h. When LSGM powder with diametric of ~150 nm was obtained from the hydrothermal urea hydrolysis precipitation process.
- (3) To investigate the effect of the hydrothermal urea hydrolysis precipitation process on the ionic conduction and densification of LSGM powder, both solid-state-reacted and hydrothermal-processed LSGM powder was sintered at the same temperature of 1400 °C for 3 h. The conductivity of LSGM derived from the hydrothermal urea hydrolysis pre-

precipitation process shows significant higher conductivity of 0.056 S/cm than 0.035 S/cm of solid-state-reacted counterpart simply due to its low density (85% of theoretical density) at 1400 °C.

### Acknowledgment

This work is financially supported by the Council of Agriculture, Executive Yuan, Taiwan; Grant 96AS-10.1.1-AD-U1.

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