

Short communication

Preparation of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.815}$ powders by microwave-induced poly(vinyl alcohol) solution polymerization

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Abstract

A new and simple chemical route, named microwave-induced poly(vinyl alcohol) (PVA) solution polymerization, has been used to prepare fine, homogeneous and high-density pellets of purer $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.815}$ (denoted as $\text{LS}_{0.2}\text{GM}_{0.17}$). The effect of different contents of PVA as the polymeric carrier, was studied and we obtained an optimal amount of PVA (1.65:1 ratio of positively charged valences of the cations (Me^{n+}) to negatively charged hydroxyl ($-\text{OH}^-$) groups of the organics), which could ensure homogenous distribution of the metal ions in the polymeric network structure and inhibit segregation. The behavior of the powder after calcination at different temperatures was studied. The PVA solution process consumed less organic material compared with the Pechini process, and consequently PVA was a more effective carrier in the preparation of LSGM. Higher heating rate and a more homogenous heating manner without thermal gradients in the microwave oven resulted in fewer secondary phases in the $\text{LS}_{0.2}\text{GM}_{0.17}$ powder after calcination at 1400 °C for 9 h and a smaller pellet grain size (2–3 μm) without segregation. The density of $\text{LS}_{0.2}\text{GM}_{0.17}$ pellet sintered at 1400 °C for 9 h was 6.19 g cm^{-3} .
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1. Introduction

Present development of intermediate temperature solid oxide fuel cells (IT-SOFCs) follows two strategies: one is to use an extremely thin yttria-stabilized zirconia (YSZ) membrane (<10 μm) to make the ohmic loss as small as possible. The other is to develop a new electrolyte material that shows oxide ionic conductivity higher than $10^{-2} \text{ S cm}^{-1}$ below 750 °C. Strontium-(Sr-) and magnesium-(Mg-) doped lanthanum gallate (LSGM) exhibits a high oxygen ionic conductivity at reduced temperature. Huang [1] reported that $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.815}$ (denoted as $\text{LS}_{0.2}\text{GM}_{0.17}$) 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, exceeded that of YSZ at the same temperatures. Thus, LSGM appears to be a promising electrolyte for IT-SOFCs [1–3].

The synthesis method of the material directly affects the density, microstructure and purity of the products. Conventional ceramic technique [3–5] (the solid state reaction), is unable to prepare LSGM powder with a particle size less than 1 μm . So, many researchers have turned to wet chemical synthesis methods such as sol-gel [6] or co-precipitation [7], hydrothermal synthesis [6], a glycine-nitrate combustion method [8,9], the amorphous citrate process [10] and the Pechini method [11,12] to prepare the LSGM powders with relatively small grain sizes. However, the complicating factors affecting the wet chemical process are difficult to control and usually result in low reproducibility. Recently, some researchers [13–16] have successfully synthesized various monophasic, fine, and purely mixed oxide powders by a novel solution polymerization route using poly(vinyl alcohol) (denoted as PVA) as the polymeric carrier. Unlike the Pechini process, which involves chelation and polymerization, the PVA process involves primarily the steric entrapment of cations in the polymer network. The long chains of PVA prevent the metal ions from contacting each other and ensure homogenous distribution of the metal ions in the polymeric network structure.

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To obtain purer and finer powders, our group recently used microwave heating to improve the conventional wet chemical synthesis to prepare fine, purer powders with small particle sizes. Different from the traditional heating mechanism by heat radiation from exterior to interior, the microwave process can provide a higher heating rate and more homogenous heating without thermal gradients. In this work, we attempted to use a novel microwave-induced PVA solution polymerization synthesis to prepare fine, homogeneous and high-density pellets of purer $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.815}$ (denoted as $\text{LS}_{0.2}\text{GM}_{0.17}$). A rather simple-structured and inexpensive polymer, PVA, was used as the polymeric carrier, the proper amounts of which could ensure the homogenous distribution of the metal ions in its polymeric network structure and inhibit segregation. Due to the narrow composition range for the stability of the perovskite phase, small deviations from the ideal composition result in secondary phases [1]. Thus, we studied the optimal amount of the polymer which can affect the purity of final powders, and studied the behavior of the powder after calcination at different temperatures. The products were characterized by X-ray diffraction (XRD), thermal analysis, Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM).

2. Experimental section

2.1. Materials and preparation

Stoichiometric amounts of Ga_2O_3 (99.99%), La_2O_3 (99.99%), MgO (98%) and SrCO_3 (99%) that corresponded to 2.5 g of $\text{LS}_{0.2}\text{GM}_{0.17}$ were, respectively, dissolved in $\text{HNO}_3:\text{H}_2\text{O} = 1:1$ to get nitrate solutions. Before weighing, MgO and La_2O_3 were calcined at 1000°C for 7 hours (h) to decompose carbonate and hydroxide secondary phases. The absence of secondary phases in reagents had been checked by XRD. The PVA solution was obtained by dissolving 5 wt.% poly(vinyl alcohol) $(-\text{CH}_2-\text{CH}(\text{OH})-)_n$, a degree of polymerization 1705, AR) in hot distilled water. These nitrate solutions were then mixed together in a glass beaker and then the PVA solution was added. The ratio of the PVA to cations in the solution were adjusted in such a way that the ratio of the positively charged cations (Me^{n+}) to the negatively charged hydroxyl ($-\text{OH}^-$) groups of the organics (denoted as $\text{Me}^{n+}/-\text{OH}^-$) were 1.25:1, 1.65:1, 2.5:1, 3:1, 4:1, 5:1, respectively. For example, in the case of 4:1, for 1 mol $\text{LS}_{0.2}\text{GM}_{0.17}$, the total positively charged cations was 5.63 mol, and thus 1.4075 mol hydroxyl ($-\text{OH}$) was required. One PVA monomer has one $-\text{OH}$ and the degree of polymerization is 1705, so that 1 mol PVA includes 1705 mol $-\text{OH}$. Consequently, the amount of PVA was 1.4075/1705 mol. The resulting clear solution (volume 150 ml) was stirred for 1 h at room temperature and then heated to polymerize it in a modified household microwave (MW) oven (2.45 GHz, 700 W) for 15 min. The PVA solution polymerization route was not sensitive to the pH of the solution [15]. The mixing solution showed a low pH of 1. The modified household microwave oven is shown in Fig. 1. The MW oven was operated at its maximum power setting. The solution was heated to evaporation, i.e. until a puffy yellow powder formed, which was then milled using an agate

mortar and pestle, and finally calcined in an air furnace over a temperature range of $250\text{--}1400^\circ\text{C}$ and characterized.

2.2. Sample characterization

The phases in the calcined powders were analyzed by X-ray diffraction (XRD) (Model x' Pert Pro, Phillips). Scans were taken with a 2θ step of 0.017° (over the range of $20\text{--}80^\circ$, 2θ) by $\text{Cu K}\alpha$ radiation (40 kV, 40 mA). The analysis work was done using Philips X'pert Highscore software (V1.0b). An environmental scanning electron microscope (ESEM) (Model Quanta 200, FEI) was used to study the morphology and microstructure. The powder was also studied by simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (NETZSCH STA 449C) with an air-flow and a $10^\circ\text{C min}^{-1}$ temperature rate. Fourier transform infrared (FT-IR) analysis was performed (Model VERTEX 70, Germany Bruker) in the range of $400\text{--}4000\text{ cm}^{-1}$ using dry KBr to form the pellets. The pellet (6 mm diameter) of $\text{LS}_{0.2}\text{GM}_{0.17}$ powders precalcined at 900°C for 6 h was made by uniaxially pressing with a compaction pressure of 200 MPa and sintering in air at 1400°C for 9 h. The density of the sintered pellet was measured via the Archimedes method.

3. Results and discussion

3.1. X-ray diffraction

X-ray diffraction patterns of $\text{LS}_{0.2}\text{GM}_{0.17}$ powders prepared with different ratios of $\text{Me}^{n+}/-\text{OH}^-$ annealed at 1400°C for 9 h are shown in Fig. 2. It was found that all the products had secondary phases in various amounts. By analysis, we determined that the main secondary phases were SrLaGaO_4 and $\text{SrLaGa}_3\text{O}_7$. Table 1 lists the comparative amounts of these two secondary phases by different ratios of $\text{Me}^{n+}/-\text{OH}^-$ preparation process.

The A_s/A_p 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.

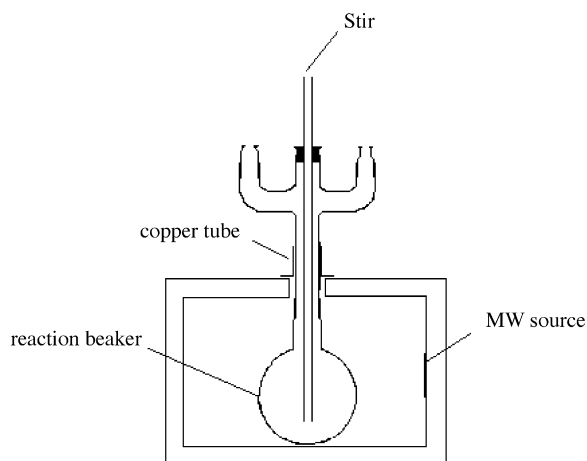


Fig. 1. Modified household microwave oven.

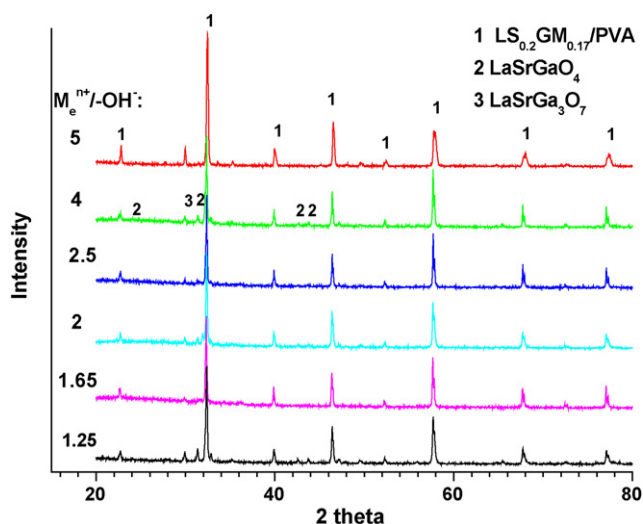


Fig. 2. XRD patterns of $\text{LS}_{0.2}\text{GM}_{0.17}$ powders prepared with different ratios of $\text{Me}^{n+}/\text{OH}^-$ calcined at 1400°C for 9 h.

Table 1

Estimation of the secondary phases in calcined powders

Ratio ($\text{Me}^{n+}/\text{OH}^-$)	As/Ap (%)
1.25	13.5
1.65	7.0
2	8.2
2.5	8.3
4	11.8
5	15.4

The data showed that the amounts of the secondary phases were the least when the ratio of $\text{Me}^{n+}/\text{OH}^-$ was 1.65:1. 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], thus the homogeneous mixing of the precursor is of great importance to the purity of the final products. The effects of the content of PVA may be attributed to the following considerations. The homogeneous mixing manner and the steric entrapment mechanism by large chain molecules of PVA resulted in a stoichiometric and homogeneous powder, shown in Fig. 3(a) [17]. A proper amount of PVA can ensure a homogenous distribution of the metal ions in the polymeric network structure. However, when the amount of PVA was not enough, the insufficiency of PVA resulted in an

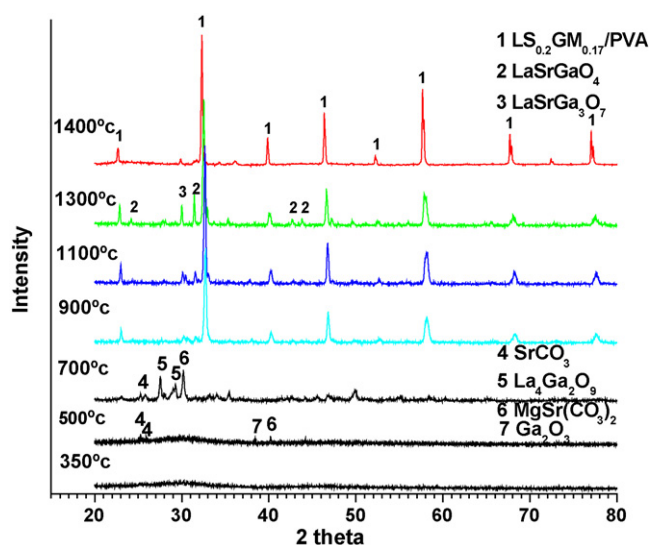


Fig. 4. XRD patterns of $\text{LS}_{0.2}\text{GM}_{0.17}$ powders prepared with the 1.65 ratio of $\text{Me}^{n+}/\text{OH}^-$ calcined at different temperatures.

uncomplete polymeric network structure and the secondary phases in the final product increased. On the other hand, when PVA was excessive, the solution viscosity increased caused by the entanglements of the long chains of the PVA molecules, as shown in Fig. 3(b). In this case homogeneity was difficult and the secondary phases of the final product increased also. From the above analysis, we concluded that 1.65 was the optimum ratio of $\text{Me}^{n+}/\text{OH}^-$ to synthesize the $\text{LS}_{0.2}\text{GM}_{0.17}$ powder and consequently we studied the evolution behavior (from amorphous to crystal phase) of the powder in this ratio after calcination at different temperatures.

XRD patterns of the as-received powders ($\text{Me}^{n+}/\text{OH}^- = 1.65:1$) annealed at different temperatures ($350, 500, 700, 900, 1100, 1300^\circ\text{C}$ for 6 h and 1400°C for 9 h) are shown in Fig. 4. It was found that the products remained amorphous up to 350°C and only low crystal secondary phases peaks could be detected at 500°C in the XRD patterns, such as SrCO_3 , Ga_2O_3 and $\text{MgSr}(\text{CO}_3)_2$. At 700°C , the clear diffraction peaks were still secondary phases, such as SrCO_3 , $\text{La}_4\text{Ga}_2\text{O}_9$ and $\text{MgSr}(\text{CO}_3)_2$. At 900°C , the most intense diffraction peaks were perovskite phases and the main secondary phases were SrLaGaO_4 and $\text{SrLaGa}_3\text{O}_7$. With the increase of the calcination temperature from 900 to 1300°C , the secondary phases became more and

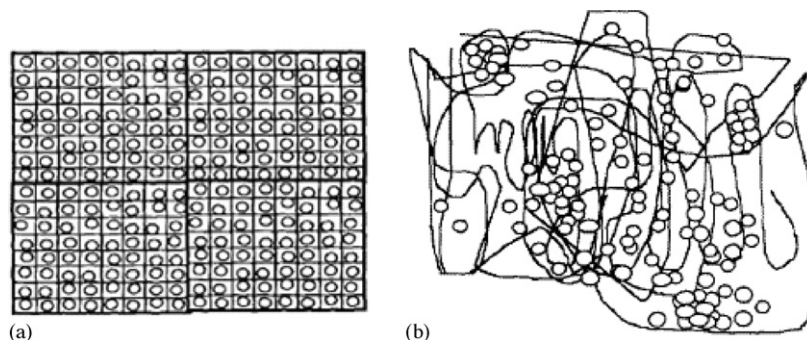


Fig. 3. Schematic representation of cation entrapment with: (a) optimal amount of polymer and (b) non-optimal amount of polymer.

more, which is not reported in the literature. This is possibly attributed to the metastable or thermodynamically stable conditions of the secondary phases and LSM [18] (some decomposition reactions of some of $LS_{0.2}GM_{0.17}$ and the transformation phase crystal process analyzed in TGA–DSC curves); our group found this phenomenon in the process by other microwave-induced wet chemical methods in previous studies. At 1400°C , the amounts of the secondary phases were the least ($As/Ap = 7.0\%$, showed in the above table) due possibly to the metastable or thermodynamically stable conditions, as with the published reports [11].

3.2. Thermal analysis

The TGA–DSC curve of $LS_{0.2}GM_{0.17}$ powder precursor ($Me^{n+}/-OH^{-} = 1.65:1$) is given in Fig. 5. The TGA–DSC analyses showed that most of the organics were removed at temperatures $<650^{\circ}\text{C}$. The large weight loss $<650^{\circ}\text{C}$, the exothermic peak at 336°C and the endothermic peak at 604°C were due to the complex decomposition reactions of the organics. The broad exothermic peak at $700\text{--}800^{\circ}\text{C}$ indicated that the amorphous $LS_{0.2}GM_{0.17}$ transformed to a perovskite phase, which agreed with the XRD results. The lower weight loss between 700 and 900°C could be due to the decomposition of carbonate intermediates. The clear exothermic peak observed at about 957°C , with little associated weight loss, was attributed to some decomposition reactions of some of the $LS_{0.2}GM_{0.17}$ and/or the crystal process of the secondary phases of $SrLaGaO_4$ and $SrLaGa_3O_7$, also found in XRD patterns. In the TGA curve, the total weight loss was 25.73% , lower than 55% by the traditional Pechini method [11]. This indicated that PVA solution process consumed less organics in comparison to the Pechini process. So PVA is a more effective carrier in the preparation of LSM.

3.3. IR spectra

The IR plots of the precursor ($Me^{n+}/-OH^{-} = 1.65:1$) at different calcination temperatures ($250, 350, 500, 700, 900, 1100^{\circ}\text{C}$

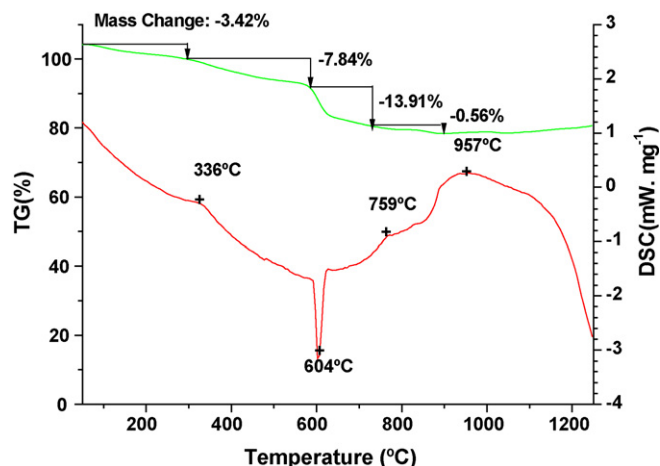


Fig. 5. TG–DSC spectra of $LS_{0.2}GM_{0.17}$ precursors with the 1.65 ratio of $Me^{n+}/-OH^{-}$.

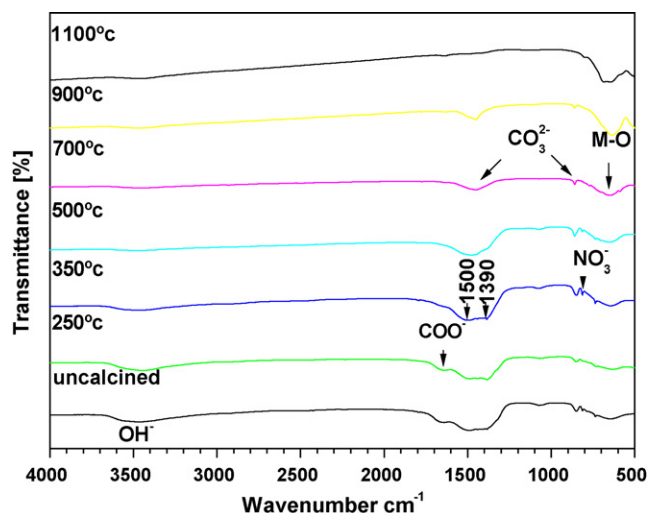


Fig. 6. IR spectra of $LS_{0.2}GM_{0.17}$ precursors with the 1.65 ratio of $Me^{n+}/-OH^{-}$ calcined as a function of different temperature.

for 6 h) are given in Fig. 6. The spectrum at 250°C presented similar bands to the uncalcined powder. The band at about 1650 cm^{-1} was associated with the acetate group in the initial PVA [13]. The double bands at 1500 and 1390 cm^{-1} were in the wavenumber region where carbonates usually have their absorption bands. However, the existence of the double bands instead of a single band, according to the XRD plots ($<500^{\circ}\text{C}$), was indicative of amorphous carbonate-like compounds [13]. At 500°C , the samples generally showed the presence of CO_3^{2-} (1455 and 865 cm^{-1}), as well as the carbonate crystal peaks in XRD plots. The broad band at about 645 cm^{-1} was for the vibration of M–O. After calcination at 1100°C , there were no anion vibrations.

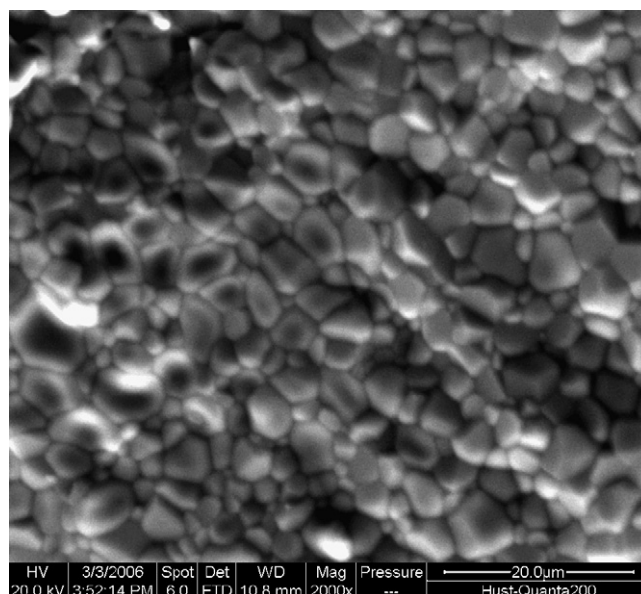


Fig. 7. SEM micrographs of $LS_{0.2}GM_{0.17}$ pellet (precursor with the 1.65 ratio of $Me^{n+}/-OH^{-}$) sintered at 1400°C , 9 h.

3.4. Microstructure and particle size

Fig. 7 shows the pellet sintered at 1400 °C for 9 h prepared by microwave-induced PVA solution polymerization. The surface of the pellet ($\text{Me}^{n+}/\text{-OH}^- = 1.65:1$) had a final grain size of about 2–3 μm and was homogeneous. The homogenous mixing mechanism of the precursor can prepare precursor powders with fine particles, which will in turn, result in small grain size of the final products. So, due to the higher heating rate and more homogenous heating manner without thermal gradients in the microwave oven, the grain size of the pellet was smaller than that of the pellet prepared by the traditional sol–gel method (8–15 μm)[10,19,20]. The density of the pellet was 6.19 g cm^{-3} measured by the Archimedes method.

4. Conclusions

The microwave-induced PVA solution polymerization route effectively used a long chain polymer PVA as the organic carrier for the precursor and was prepared in the modified microwave oven. Fine, homogeneous and high-density pellets of purer $\text{LS}_{0.2}\text{GM}_{0.17}$ were obtained after calcination at 1400 °C for 9 h. The homogeneous mixing manner and the steric entrapment mechanism by the large chain molecules of the PVA resulted in a stoichiometric and homogeneous powder. However, when the amount of PVA was not enough or was excessive, it was difficult for all the metal ions to be homogenous dispersed and in these cases, secondary phases of the final products increased. The long chains of the PVA prevented the metal ions from contacting each other and ensured homogenous distribution of the metal ions in the polymeric network structure, so that the optimum amount of PVA would result in a purer and more homogenous powder at the molecular level. We also determined the optimum amount of PVA ($\text{Me}^{n+}/\text{-OH}^- = 1.65:1$). The PVA solution process consumed less organics in comparison to the Pechini process, and consequently PVA was found to be a more effective carrier for the preparation of LSGM. A higher heating rate and more homogenous heating manner without thermal gradients in the microwave oven, also resulted in a $\text{LS}_{0.2}\text{GM}_{0.17}$ powder with less secondary phase after calcination at 1400 °C for 9 h and a smaller pellet grain size (2–3 μm) without segregations.

The density of $\text{LS}_{0.2}\text{GM}_{0.17}$ pellet sintered at 1400 °C for 9 h was 6.19 g cm^{-3} .

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