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# Synthesis of Sr- and Fe-doped $LaGaO_3$ perovskites by the modified citrate method

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Fine particle strontium and iron substituted lanthanum gallates $La_{1-x}Sr_xGa_{1-y}Fe_yO_{3-\delta}$, where $x = 0.2$, 0.4, and 0.6; $y = 0.2$, 0.4, 0.6, and 0.8, have been synthesized by a modified citrate method. The formation of these powders was confirmed by the X-ray powder diffraction (XRD) and the fine particle of $La_{0.6}Sr_{0.4}Ga_{0.2}Fe_{0.8}O_{3-\delta}$ was investigated by scanning electron microscopy (SEM), and particle size analysis. The single phase of $La_{0.8}Sr_{0.2}Ga_{0.4}Fe_{0.6}O_{3-\delta}$, $La_{0.6}Sr_{0.4}Ga_{0.2}Fe_{0.8}O_{3-\delta}$, and $La_{0.4}Sr_{0.6}Ga_{0.2}Fe_{0.8}O_{3-\delta}$ powders could be obtained both with and without calcination. The amount of the secondary phase increased when the amount of Sr in $La_{1-x}Sr_xFe_{0.6}Ga_{0.4}O_{3-\delta}$ was more than 0.2 ($x > 0.2$) and the amount of Fe in $La_{0.6}Sr_{0.4}Ga_{1-y}Fe_yO_{3-\delta}$ and $La_{0.4}Sr_{0.6}Ga_{0.2}Fe_{0.8}O_{3-\delta}$ was less than 0.8 ($y < 0.8$). The results indicated that in the pH range of 1.36–9.27, the single phase of $La_{0.6}Sr_{0.4}Ga_{0.2}Fe_{0.8}O_{3-\delta}$ was formed without calcination and the pH had negligible effects on the structure and lattice parameter. The fine particle of these calcined powders ($<4$ μm) was obtained with the average particle size 1.70 μm at pH = 1.36 and with the average particle size between 0.56–0.60 μm at pH range between 3.39–9.27, and with a lattice parameter about 3.9 Å. © *2004 Kluwer Academic Publishers*

## 1. Introduction

In recent years, the $LaGaO_3$based perovskite has been considered as a membrane to separate oxygen from air. Since it exhibits high $O^{2-}$ permeation at high temperatures, and the structure of this composition is very tolerant to the incorporation of foreign cations and a large number of cations can be used to partially substitute for either La or Ga [1–4].

Ishihara *et al.* [2, 3] reported that comparing with the undoped material, the Sr substitution increased the electrical and ionic conductivity of the $LaGaO_3$ based perovskite. It was found that the ionic conductivity, $\sigma_i$, increased with an increase in the amount of Sr additives and attained the maximum limit of the solid solution at $x = 0.1$ in $La_{1-x}Sr_xGaO_3$. They also concluded that iron was the most suitable dopant for $LaGaO_3$ due to its stability in a reducing atmosphere and the increase in the oxide ion conductivity. A high methane conversion rate was obtained when using $La_{0.8}Sr_{0.2}Ga_{1-y}Fe_yO_{3-\delta}$ where $y = 0.2$–0.5 as the oxygen-permeating membrane. Gharbage *et al.* [5] confirmed that Fe increased the chemical stability and the *p*-type conductivity in $La_{0.9}Sr_{0.1}Ga_{1-y}Fe_yO_{3-\delta}$ where $y = 0.05$–0.2 by the formation of $Fe^{4+}$ ions under oxidizing conditions. Ming *et al.* [6] found that the perovskite oxide $La_{0.5}Sr_{0.5}Ga_{0.2}Fe_{0.8}O_{3-\delta}$ maintained its cubic structure from 20 to 860°C in a reducing environment with an oxygen partial pressure of about $10^{-17}$ atm. Accordingly, $LaGaO_3$-based oxide doped with Sr and Fe could be a new candidate material for an oxygen permeation membrane, in particular, for air separation in the methane partial oxidation process.

The conventional method of solid state synthesis for producing ceramic powders involves the calcination of mixed metal oxides at high temperatures to obtain a single phase and mechanically milling the product to obtain the desired particle size. However, the high calcination temperature promotes crystal growth and resulting in a hard agglomeration [7]. Therefore, wet chemical syntheses have been developed to achieve the fine powder form. These methods include the citrate, spray-pyrolysis, and co-precipitation process [8]. It was reported that the membrane sample prepared by the co-precipitation method has a large strontium deficiency due to the filtration and aqueous washing steps involved in this method. The spray-pyrolysis method requires a special chamber for spraying aqueous solution of raw materials into it.

For the synthesis of Sr and Fe doped $LaGaO_3$, the conventional method has been used by many investigators using the calcination of metal oxides at 1,000–1,100°C for 6–12 h [3, 5, 9]. Recently, Ming *et al.* [6] reported a new method for the synthesis of $La_{0.5}Sr_{0.5}Ga_{0.2}Fe_{0.8}O_{3-\delta}$, using the self-propagating high temperature synthesis (SHS). They mixed metal oxide with $NaClO_4$, which acted as the internal oxygen for self combustion, and then pressed into pellet. To increase the homogeneity, after combustion, the pellet was immediately transferred to a pre-heated furnace kept at 1,400°C and cooled at a controlled cooling rate. The pellet with the large particle size (up to 30 $\mu$m) was finally obtained. Some other investigators used the sol-gel technique to synthesize this material by using metal acetates and forming a gel by ammonia solution. However, three days for aging the gel and eight hours for dehydration and drying [10] were needed, such method required a long synthesis time.

The citrate method has been chosen in this study for the synthesis of lanthanum based perovskites. The citrate method involves the complexing of metal ions with citric acid and the spontaneous combustion. The advantages of the citrate method include less energy consumption and potential to get fine particles and a single phase powder.

In this paper, the modified citrate method for the synthesis of fine particles of the single-phase $LaGaO_3$ based perovskites was investigated. Three series of oxide with the fixed components, $La_{1-x}Sr_xGa_{0.4}Fe_{0.6}O_{3-\delta}$ ($x = 0.2$, 0.4, and 0.6), $La_{0.6}Sr_{0.4}Ga_{1-y}Fe_yO_{3-\delta}$ ($y = 0.2, 0.4, 0.5, 0.6$, and 0.8), and $La_{0.4}Sr_{0.6}Ga_{1-y}Fe_yO_{3-\delta}$ ($y = 0.4$, 0.6, and 0.8), were selected in order to explore the influence of the amount of Sr and Ga for obtaining the single phase. The effect of the synthesis conditions, such as pH of the nitrate solution and calcination temperature, on the formation of a homogeneous product and on the particle size distribution was also studied.

## 2. Experimental

The powder preparation was modified from the citrate pyrolysis method [11, 12]. Stoichiometric amounts of highly purified lanthanum, strontium, iron, and gallium nitrates (based on 0.02 mole of perovskite powder) were dissolved in 10-ml ultrapure nitric acid (70%). Ultrapure metal nitrates (99.995–99.999%) were purchased from Aldrich. Then citric acid with an amount of two times of the total metal ions was added to the nitrate solution, which was then titrated with $NH_4OH$ at the controlled rate of 1.5–2.5 ml/min. The pH of the solution was adjusted to either 1–3.5 (acidic method) or ~9 (basic method), depending on the perovskite to be synthesized.

During the titration of the metal nitrate solution with $NH_4OH$, the solution changed from partially dissolved brown solution to clear brown solution (pH $\approx$ 1), to clear green solution (pH $\approx$ 1.5), to green precipitated solution (pH $\approx$ 3–6), to clear yellow solution (pH $\approx$ 7.5), and finally to completely dissolved brown solution (pH $\approx$ 9). Consequently, the pH of the solution was adjusted to (pH $\approx$ 1–3), and (pH $\approx$ 6–9) to obtain the homogeneous solution. $La_{1-x}Sr_xGa_{0.4}Fe_{0.6}O_{3-\delta}$ ($x =$ 0.2, 0.4, and 0.6), $La_{0.6}Sr_{0.4}Ga_{1-y}Fe_yO_{3-\delta}$ ($y = 0.2$, 0.4, 0.5, 0.6, and 0.8), and $La_{0.4}Sr_{0.6}Ga_{1-y}Fe_yO_{3-\delta}$ ($y = 0.4$, 0.6, 0.8) were synthesized from basic solutions. In addition, $La_{0.6}Sr_{0.4}Ga_{0.2}Fe_{0.8}O_{3-\delta}$ was synthesized from pH in the range of 1–9. The homogeneous solutions were agitated overnight.

The combustion of the homogeneous solution was carried out on a hot plate at around 200°C in a three-liter beaker covered with a fine sieve to prevent the loss of the fine powders. The water was evaporated until a sticky gel was obtained. Then it became a large swelling viscous mass and finally self ignited by $NH_4NO_3$. The combustion lasted for about 10–20 s with the sponge-like solid expanded to occupy almost 2/3 of the beaker volume at the end. The resulting powder was ground by mortar and pestle, and then calcined in the air at 800–1,300°C for 3–5 h with heating and cooling rate of 2°C/min to achieve phase purity or reduce the residual carbon. The particle was ground completely well by mortar and pestle before being subjected to characterization. The X-ray patterns were taken by using General Electric diffractometer model XRD-5 with a graphite monochromator, using Cu $K_\alpha$ radiation (50 kV/15 mA). The value of the lattice parameters (a) for the (110), (200), (211), (220), (310), (222), (400), (411), and (420) reflections was plotted against $\sin^2\Theta$. An estimation of the lattice parameter was obtained by a linear extrapolation of such a plot, to the value at $\sin^2\Theta = 1$ [13]. The morphology of the powder was carried out using the SEM manufactured by AMRAY, AMR1610. Particle size measurement was carried out using a centrifugal particle size analyzer by Shimadzu, SA-CP2.

## 3. Results and discussion

In the following discussion, $La_{1-x}Sr_xGa_{1-y}Fe_yO_{3-\delta}$ compositions are designated by the abbreviation LSGF. The numbers following the abbreviation refer to the proportions of La, Sr, Ga, and Fe in the material. For example, $La_{0.8}Sr_{0.2}Ga_{0.4}Fe_{0.6}O_{3-\delta}$ and $La_{0.6}Sr_{0.4}Ga_{0.2}Fe_{0.8}O_{3-\delta}$ are designated LSGF8246 and LSGF6428, respectively.

### 3.1. The effect of the amount of Sr on $La_{1-x}Sr_xGa_{0.4}Fe_{0.6}O_{3-\delta}$

$La_{1-x}Sr_xGa_{0.4}Fe_{0.6}O_{3-\delta}$ powder with different $x$ ($x =$ 0.2, 0.4, and 0.6) was synthesized from the basic solution and then calcined at 900°C. X-ray diffraction patterns of those powders are shown in Fig. 1. It can be seen that the single phase of LSGF8246 was obtained both with and without calcination. In other compositions, the amount of the secondary phase was slightly increased when the amount of Sr in $La_{1-x}Sr_xGa_{0.4}Fe_{0.6}O_{3-\delta}$ was more than 0.2 ($x > 0.2$). However, the intensity of

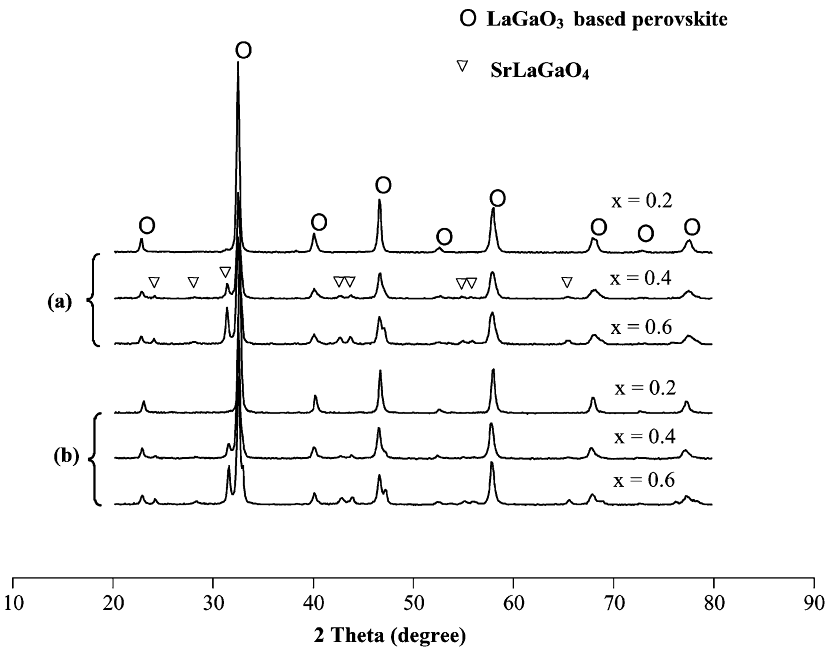


*Figure 1* XRD patterns of $La_{1-x}Sr_xGa_{0.4}Fe_{0.6}O_{3-\delta}$ ($x = 0.2$, 0.4, and 0.6): (a) calcination temperature at 900°C; (b) without calcination.

the highest peak ($2\theta \approx 31.4$) of the secondary phase did not exceed 13% of that ($2\theta \approx 31.2$) of the perovskite reflection. The phase identification has been done by comparing those patterns to the patterns of the possible secondary phases such as, $Ga_2O$, $La_2O$, SrO, $SrGaO_7$, $SrLaGaO_4$ and $La_4SrO_7$ [2, 14, 15]. The comparison showed that in addition to the $LaGaO_3$ based perovskite, the compound $SrLaGaO_4$ (JCPDS-database: 24-1208) was also present.

The XRD analysis of these materials indicated the formation of the perovskite-type phase with a cubic or distorted cubic structure. Therefore, the calculation of the lattice parameter was based on the cubic structure. Fig. 2 shows the lattice parameter of uncalcined powders and powders calcined at 900°C as a function of the amount of Sr. The results of the uncalcined powders indicated that the lattice parameter was about 3.91 Å for 20% Sr in the A-site and slightly increased with increasing the Sr content. Generally, a larger amount of Sr doped composition will lead to a larger unit-cell parameter due to the larger average A-site cation radius obtained on the partial replacement of $La^{3+}$ (ionic radii = 1.31 Å) with a $Sr^{2+}$ (ionic radii = 1.44 Å) [16]. After calcination, only LSGF8246 showed a single perovskite phase while all perovskites showed the smaller lattice parameters than uncalcined powders. The reason for these results is not clear yet, but the similar phenomenon was reported by Mori *et al.* [17] who synthesized $La_{1-x}Sr_xCrO_{3-\delta}$ ($x = 0$–0.3). In addition, the lattice parameter of the perovskites have a tends to decrease with the increasing amount of Sr.

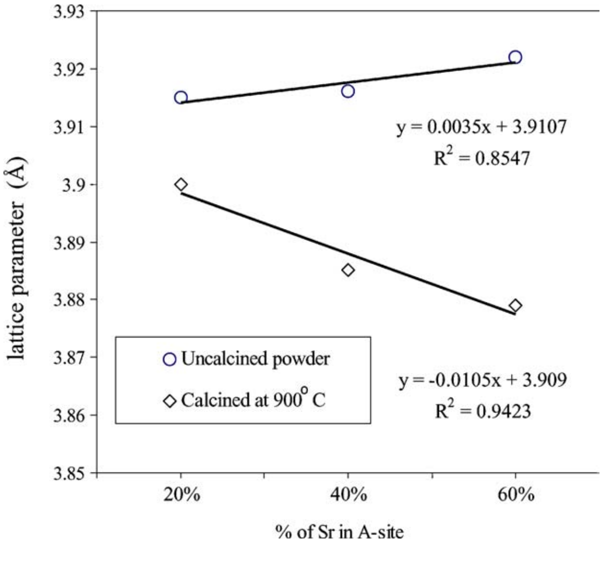


*Figure 2* The dependence of the lattice parameter on the amount of Sr in A-site.

For the case studied here, the lattice parameter of calcined powders estimated from the XRD analysis decreased depending on the amount of Sr and the amount of secondary phase. $SrLaGaO_4$ might be caused by the reduction of the amount of La and Sr in the perovskite structure, which provided the cation vacancies. Therefore, the average lattice parameter decreased in the unit cell. It could be concluded that the higher Sr content caused the higher amounts of secondary phase that resulted in the lower lattice parameters. This is confirmed by the increases of the peak intensity of the secondary phase in LSGF6446 and LSGF4646 from less than 4% of uncalcined powders to 10.8 and 12.7% of calcined powders, respectively.

Since a large amount of the Sr substitution enhanced the electronic and ionic conductivity of perovskite [18], $La_{0.6}Sr_{0.4}Ga_{1-y}Fe_yO_{3-\delta}$ and $La_{0.4}Sr_{0.6}Ga_{1-y}Fe_yO_{3-\delta}$ were chosen to obtain the single phase by varying the amount of Fe.

### 3.2. The effect of the amount of Fe on $La_{0.6}Sr_{0.4}Ga_{1-y}Fe_yO_{3-\delta}$, and $La_{0.4}Sr_{0.6}Ga_{1-y}Fe_yO_{3-\delta}$

$La_{0.6}Sr_{0.4}Ga_{1-y}Fe_yO_{3-\delta}$ ($y = 0.2$, 0.4, 0.5, 0.6, and 0.8) and $La_{0.4}Sr_{0.6}Ga_{1-y}Fe_yO_{3-\delta}$ ($y = 0.4$, 0.6, and

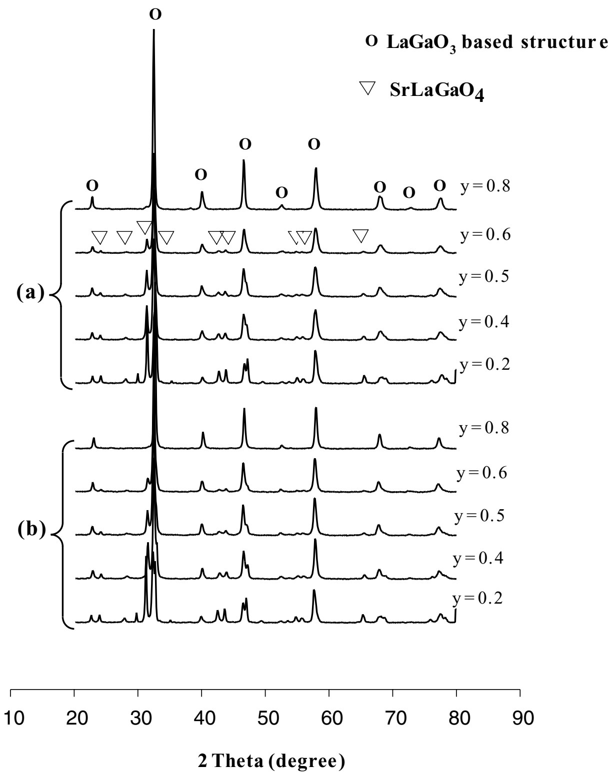


*Figure 3* XRD patterns of $La_{0.6}Sr_{0.4}Ga_{1-y}Fe_yO_{3-\delta}$ perovskite ($y$ = 0.2, 0.4, 0.5, 0.6, and 0.8): (a) calcination at 900°C and (b) without calcination.

0.8) powders were synthesized from the basic solution and then calcined at 900°C. Phase compositions of all samples with and without calcination were determined by the X-ray diffraction.

For $La_{0.6}Sr_{0.4}Ga_{1-y}Fe_yO_{3-\delta}$ series, as shown in Fig. 3, when the amount of Fe increased from 60 to 80%, a single phase of LSGF6428 was obtained. On the other hand, the secondary phase dramatically increased with the decreasing amount of Fe in both samples with and without calcination. $La_{0.4}Sr_{0.6}Ga_{1-y}Fe_yO_{3-\delta}$ series exhibited the similar phenomena as $La_{0.6}Sr_{0.4}Ga_{1-y}Fe_yO_{3-\delta}$ series leading to the single phase of LSGF4628. The XRD patterns of these series also revealed the pattern similar to the $La_{0.6}Sr_{0.4}Ga_{1-y}Fe_yO_{3-\delta}$ series, though XRD pictures are not shown here.

Although the diffraction peaks assigned to the secondary phases were observed in the XRD, the typical XRD patterns of $LaGaO_3$ based structure were exhibited for all powders. According to the XRD patterns, the secondary phase can be identified as $SrLaGaO_4$ [14].

## 3.3. The effect of the pH of the nitrate solution on $La_{0.6}Sr_{0.4}Ga_{0.2}Fe_{0.8}O_{3-\delta}$

LSGF6428 powders were synthesized by varying the pH of the nitrate solution in the range of 1 to 9. The metal-citrate complex solution was titrated with $NH_4OH$ until the desired pH was reached. The powders were ground by mortar and pestle before and after calcination at 900°C for 5 h.

Fig. 4 shows the XRD patterns of samples. The results show that a single $LaGaO_3$ perovskite phase was obtained in all powders except at pH = 1.10. All solutions were clear except at pH = 3.39, the precipitation was observed. It was due to the formation of metal-citrate complex, which did not disappear during the combustion process. The presence of this precipitation might cause the formation of the secondary phase after combustion. However, the obtained powder was still the single phase, the same as the others. It was possible that this powder could crystallize at the combustion temperature due to the presence of the sufficient fuel ($NH_4NO_3$).

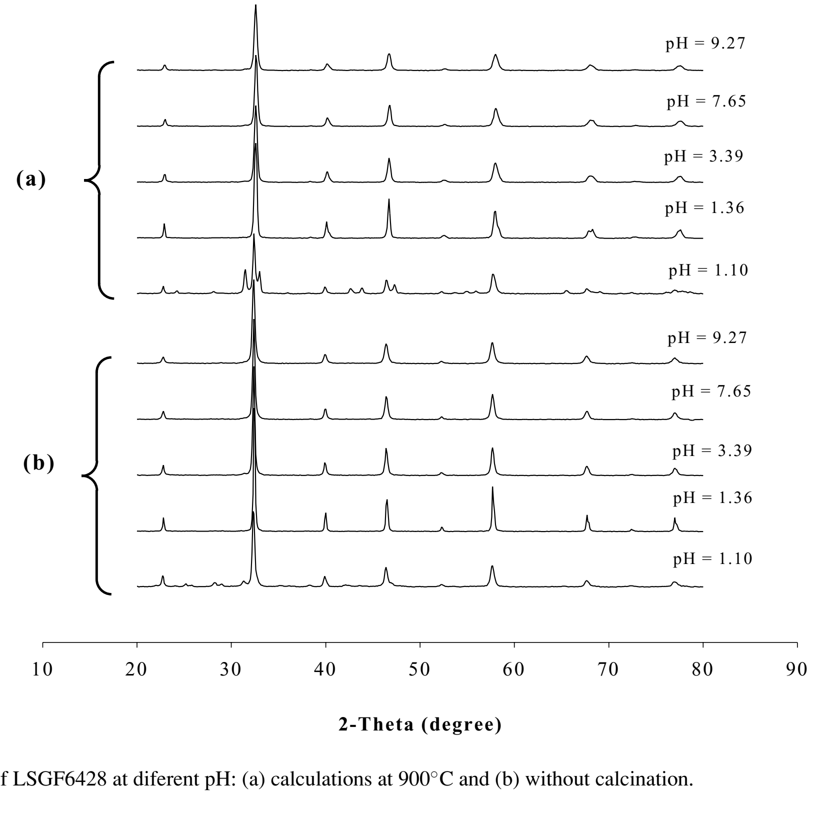


*Figure 4* XRD patterns of LSGF6428 at diferent pH: (a) calculations at 900°C and (b) without calcination.

XRD patterns of LSGF6428 at pH = 1.10 showed that the secondary phase of $LaSrGaO_4$ existed in both the uncalcined powder and the powder calcined at 900°C. It was possible that at pH = 1.10 the amount of the fuel ($NH_4NO_3$) for the combustion was not sufficient for developing the stable crystalline phase. Generally, the combustion involves two components, fuel and oxidant (normally air) which are heated to the suitable circumstance [19]. If there was sufficient amount of fuel, the combustion tended to give the high rate of flame propagation leading to the high temperature of the flame and less combustion time. Therefore, at pH = 1.10, the combustion may take place with the low rate of the flame propagation that caused the longer combustion time. This is substantiated by the fact that the combustion time for LSGF6428 was about 20 s, longer than those at higher pH compositions (about 10 s). The XRD data also provided the measurement of the lattice parameters for the uncalcined and calcined powders to be 3.90 and 3.88 Å, respectively.

The particle size distributions of calcined powders are shown in Fig. 5. It can be seen that significant differences existed between powders synthesized at pH in the range of 3.39–9.27 and the powder synthesized from pH = 1.36. The average particle size was around 0.60 $\mu$m at the pH higher than 1.36 while it was approximately 1.70 $\mu$m at pH = 1.36.

The SEM pictures of the calcined powder LSGF6428 synthesized at pH = 9.27 are shown in Fig. 6. It indicates that the particle size is about 0.6 $\mu$m. The particle sizes of other powders are similar to LSGF6428, though SEM pictures are not shown here. According to the results from Figs 5 and 6, the sizes are identical for the pH = 9.27. Therefore, it can be concluded that the average particle size is about 0.6 $\mu$m. In addition, it can be seen that powders calcined and ground by mortar and pestle include agglomerated powders.

The marked difference in the particle size of LSGF6428 prepared at pH = 1.36 and pH in the range of 3.39–9.27 can be probably attributed to the concentration of the nitrate solutions. It can be concluded that the high metal concentration in the nitrate solution tends to give larger particles than the lower one. Accordingly, the perovskite obtained at pH = 1.36 should consist of

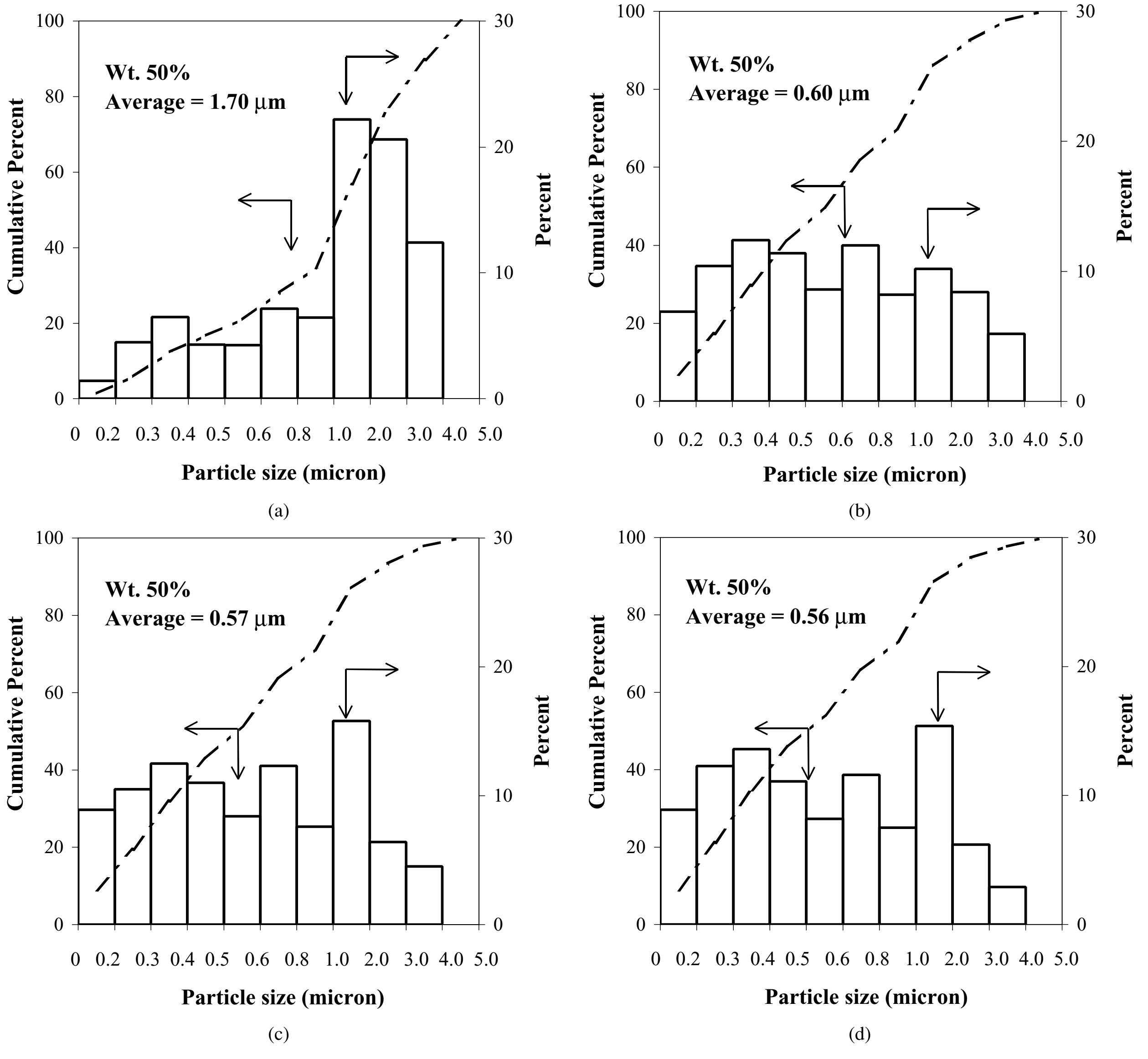
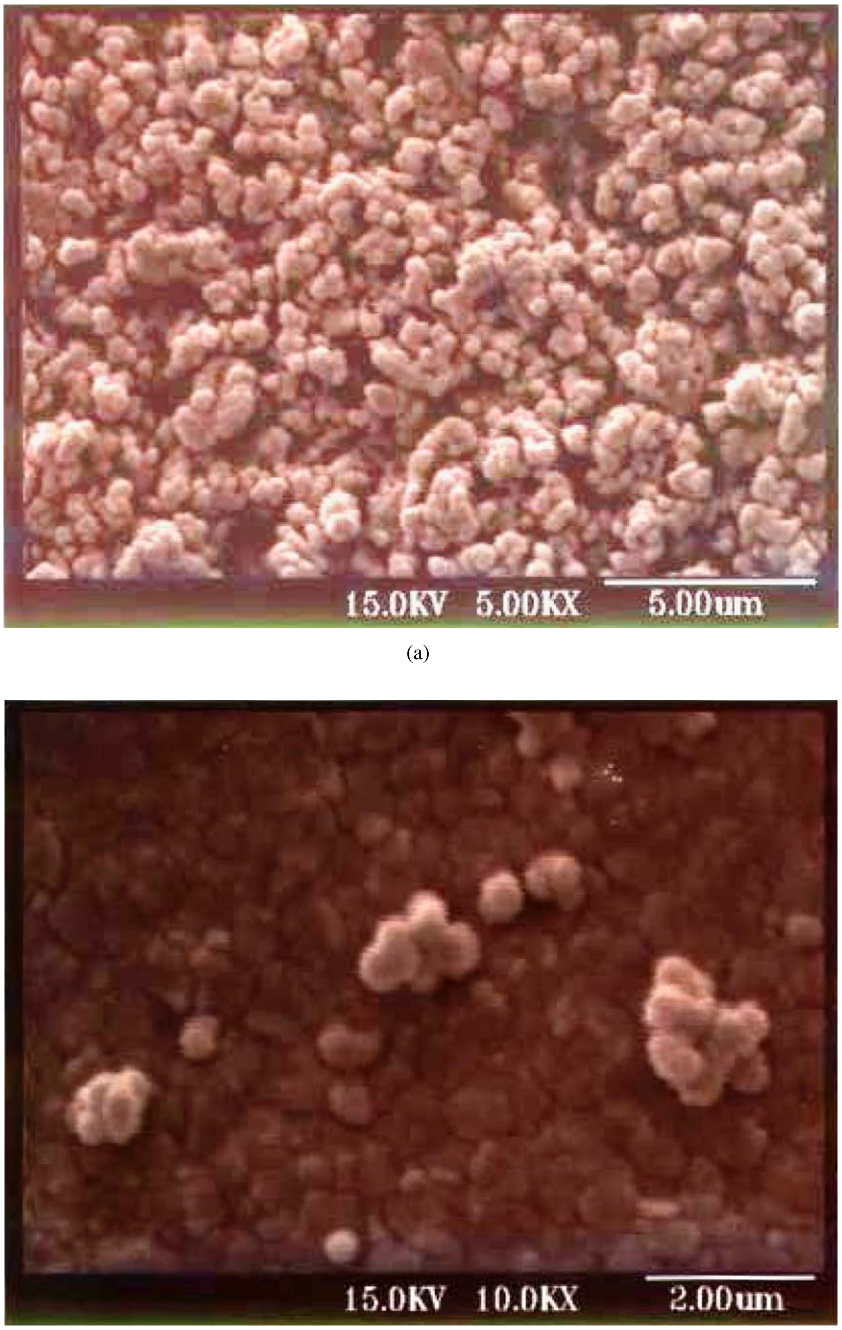


*Figure 5* Particle size distribution of calcined LSGF6428 a different pH: (a) pH = 1.36, (b) pH = 3.39, (c) pH = 7.65, and (d) pH = 9.27.



(a)

(b)

*Figure 6* SEM pictures of calcined powder LSGF6428 synthesized pH = 9.27: (a) cluster and (b) single powder.

the largest particle size since at pH = 1.36, the concentration of the solution was approximately 20% higher than the solution at pH = 9.27.

### 3.4. The effect of calcination temperature on the lattice parameter of LSGF6428

For the determination of the effects of the calcination temperatures, powders were calcined at 800, 900, 1,000, 1,100, and 1,300°C for 5 h. The characteristic XRD patterns of the LSGF6428, produced by the basic method, without calcination and after calcination are shown in Fig. 7. Lattice parameters are shown in Fig. 8. Table I shows the weight loss of powders as a function of the calcination temperature.

According to Figs 7, 8, and Table I, the powders calcined at 800–900°C showed a single phase of perovskite cubic structure with no significant change of lattice parameters and weight losses. When the temperatures were higher than 1,000°C, the lattice parameters were continuously decreasing while the weight losses were increasing as well as the amount of the secondary phase of $SrLaGaO_4$. Previous investigations by many researchers [14, 20, 21] showed that the secondary phase was the result of the volatilization of $Ga_2O$ from the $LaGaO_3$ based perovskite structure. This appears to be consistent with the result of the weight loss observed in the present study. The minor mass loss (0.15 and 0.16%), observed at calcination temperatures between 800–900°C, was probably due to the combustion of the carbon residue. While the increase of mass loss, occurred at calcination temperature higher than 1,000°C, was due to the vaporization of $Ga_2O$ as mentioned above. In addition, because we found traces of

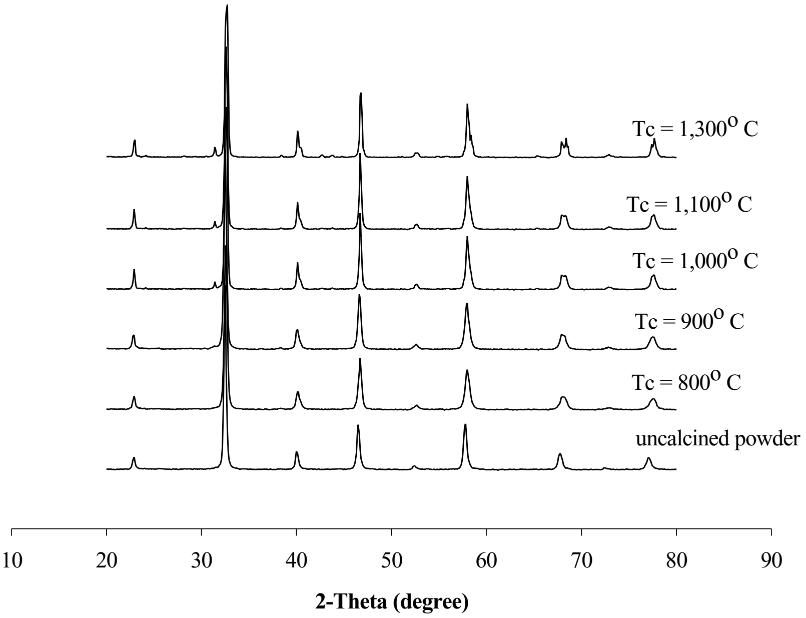


*Figure 7* XRD patterns of LSGF6428 without calcination and after calcination at 800, 900, 1,000, 1,100, 1,200, and 1,300°C.

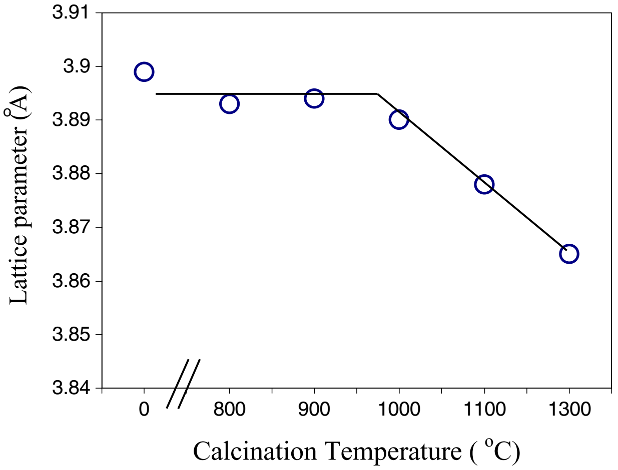


*Figure 8* Temperature dependence of lattice parameter of LSGF6428 powder.

solid sticking on the alumina crucible, the major loss at 1,300°C might also be due, in part, to the melting of $SrLaGaO_4$ which has the melting temperature about 1,400°C [14]. The decrease of the lattice parameter might have come from the consumption of $Ga^{3+}$ (ionic radii 0.62 Å) and $Sr^{2+}$ (ionic radii 1.44 Å) in the formation of the secondary phase. These cations have ionic radii bigger than $La^{3+}$ (ionic radii 1.31 Å) and $Fe^{3+}$ (ionic radii 0.55 Å) that caused the average unit cell parameter to decrease.

TABLE I The weight loss of powders as a function of calcination temperature

| Temperature (°C) | Weight before calcination (g) | Weight after calcination (g) | Percent of weight loss (%) |
|---|---|---|---|
| 800 | 0.9102 | 0.9088 | 0.15 |
| 900 | 0.9702 | 0.9686 | 0.16 |
| 1,000 | 0.9647 | 0.9608 | 0.43 |
| 1,100 | 0.9565 | 0.9500 | 0.68 |
| 1,300 | 0.5545 | 0.5452 | 1.67 |

As previously discussed, Ishihara *et al.* [2, 3] reported that a high methane conversion rate was obtained when using LSGF8264 as the oxygen-permeating membrane. Ming *et al.* [6] suggested that LSGF5528 might be a good membrane in a methane partial oxidation reactor due to its stability in both oxidizing and reducing environments. In this study, we obtained the single phases of LSGF8246, LSGF6428, and LSGF4628 with fine particles. The first composition, LSGF8264, closed to the perovskite obtained from Ishihara's method (LSGF8264) while the other compositions closed to the perovskite obtained from Ming's method (LSGF5528). Thus, these perovskites are expected to have the high mixed ionic and electronic conducting property and high stability that can be used as the membrane in the separation of oxygen from air. Moreover, when comparing this synthesis method with the Ishihara's method (conventional synthesis) and Ming's method (self-propagating high temperature synthesis), the modified citrate method consumes less energy and gives smaller particle sizes.

## 4. Conclusions

A modified citrate method can be used to prepare the single phase of LSGF8246, LSGF4628, and LSGF6428 both with and without calcination. The secondary phase of $LaSrGaO_4$ was slightly increased when the value of $x$ was larger than 0.2 in $La_{1-x}Sr_xGa_{0.4}Fe_{0.6}O_{3-\delta}$. The increase in the amount of Fe from 60 to 80% in $La_{0.6}Sr_{0.4}Ga_{1-y}Fe_yO_{3-\delta}$ and $La_{0.4}Sr_{0.6}Ga_{1-y}Fe_yO_{3-\delta}$, single phases were obtained. The pH range between 1.36–9.27, had insignificantly effects on the phase transformation including structure and lattice parameter of the single phase of LSGF6428. The fine particle size of the calcined LSGF6428 was less than 4 $\mu$m in this pH range and the average particle size was decreased from 1.70 $\mu$m at pH = 1.36 to 0.57 $\mu$m in the pH range between 3.39–9.27. Because the single phase powder could be obtained without calcination, the lower calcination temperature between 800–900°C was only for the combustion of the organic residue.

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