Influence of molar ratio of citric acid to metal ions on preparation of La$_{0.67}$Sr$_{0.33}$MnO$_3$ materials via polymerizable complex process

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Abstract

Polycrystalline La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO) nanometric sized powders and thin films are obtained from the resins synthesized by the polymerization of citric acid and ethylene glycol. Molar ratios of citric acid to metal ions were varied, and the resulting effects on the powder's properties were studied using TGA/DTA, FTIR, SEM and X-ray diffraction (XRD). The results indicated that with the molar ratio of citric acid/metal ions at 4, the resin contained a lower fraction of monodentate ligand and a higher portion of C−C−O structure obtained from ethylene glycol, which made it possible to synthesize the perovskite phase at temperature as low as 500 °C. The powder calcined at 550 °C exhibited a pure phase of perovskite, had a particle size of about 20–50 nm and a specific surface area of 25.24 m^2/g. Thin films were prepared by using the as-prepared sols for spin coating on (1 0 0) Si substrate to investigate the properties of the films. As a result of the molar ratio of citric acid/metal cations at 3–4, the transformation of rhombohedral structure to cubic structure was observed.
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1. Introduction

Polycrystal lanthanum manganate (LaMnO$_3$) perovskite and related materials have been of considerable interest because of their exceptional magneto transport properties,[1–3] their applications in automotive exhaust control,[4,5] and as eliminators of CO environment pollutants.[6] Furthermore, La$_{1−x}$Sr$_x$MnO$_3$ oxides are used as the cathode in the solid oxide fuel cell (SOFC) because of their excellent electric, thermal, chemical and mechanical properties.[7,8] Therefore, considerable interest has been shown in the synthesis of LSMO perovskite materials.

Various wet-chemical methods have been developed to prepare high quality and homogenous products utilized in high technology applications.[9] These methods are based on the principle that the reactants are mixed in the molecular level. Low calcination temperature is then needed to produce fine powders with higher surface area and high purity. For the rapidly progressing development of very large scale integrated (VLSI) circuits, high purity thin films are required for manufacturing high performance electronic devices.

In recent years, chemical methods for the deposition of thin films have found broader application and have been replacing physical methods. Chemical methods include sol–gel techniques,[10] metallo-organic decomposition (MOD),[11] and chemical vapor deposition (CVD).[12] Temperatures used in the application of chemical processes are usually lower (400–800 °C) than the ones used in physical methods. Another advantage is that large surface area films can be produced without the need for extra high vacuum environment.

A simple powder/film preparation method was developed by Pechini,[13] where citric acid was used to chelate metal ions, ethylene glycol was used as solvent for the process of polymerization between citric acid and ethylene glycol, and an intermediate of polyester-type resin was obtained.

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Ethylene glycol greatly inhibits metal ions segregation and achieves a homogeneous precursor in the polymerization of citric acid–metal complexes.[14–16] Some studies concerning the synthesis of other similar perovskite oxide materials by the mentioned methods have been reported, recently.[17–19] In the process, the properties of the synthesized product were crucially affected by the molar ratio of citric acid/ethylene glycol.[20,21] Although the process is simple, it can have wide applications. A citrate precursor containing La, Sr and Mn can be prepared, then dried, and calcined, and a LSMO powder/film are obtained. This is an important method for preparing a high quality LSMO material. However, until now the literature does not, to the best of our knowledge, cover an investigation comparing the influence of the molar ratios of citric acid to metal ions on the properties of the LSMO perovskite materials from this system.

In the present study, a Pechini-type polymerized complex route based on polyesterification between citric acid and ethylene glycol has been successfully used to synthesize perovskite LSMO nanometric sized powders. LSMO thin film on Si (1 0 0) substrate of exceptionally high-phase purities at 600–800 °C is also prepared. Our method allows an easy control over the final stoichiometry, low processing temperature and without intermediate grinding. In addition, molar ratio of citric acid/metal ions had been studied for its effects on the film properties and microstructure of LSMO films.

2. Experimental procedure

2.1. Preparation of LSMO perovskite powders

Procedures adopted for the synthesis of $La_{0.67}Sr_{0.33}MnO_3$ are schematically shown in Fig. 1. First, analytical grade $La(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2$ and $Mn(NO_3)_3 \cdot 6H_2O$ were weighed accurately and dissolved in deionized water to obtain a clear solution in such a way that 100 ml of resultant solution contains 0.04 M of metal ions (La^{3+}, Sr^{2+} and Mn^{4+}). Various amounts of citric acid ($HOOCCH_2C(OH)(COOH)CH_2COOH$) were weighed, according to the molar ratios of citric acid/total metal ions (defined as R) being 2–5, and mixed with 10 ml ethylene glycol ($C_2H_6O_2$) to produce various citric acid–ethylene glycol solutions. Then, the citric acid–ethylene glycol solution was mixed with the above solution containing metal ions and agitated vigorously to obtain a homogeneous yellow solution. After achieving complete dissolution, the resultant solution was heated with continuous stirring, at 90 °C for 4 h in order to evaporate the excess solvents and promote polymerization. After being heated at 85 °C for several hours, the solution became highly viscous, with a change in color from yellow to orange, and finally it gelled to a glassy resin. The gels prepared at various molar ratios of citric acid/metal ions (2–5) were dried and calcined to obtain powders or sub-
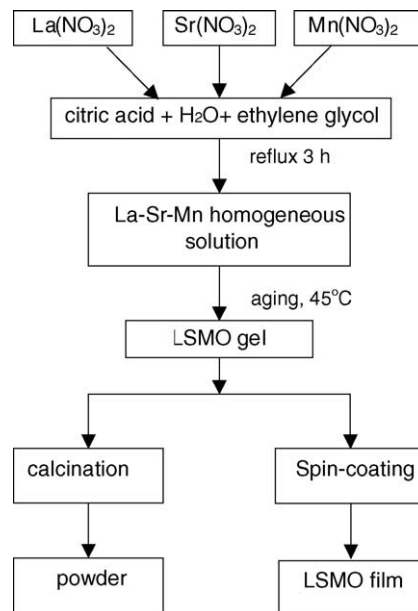

Fig. 1. Schematic illustration of the preparation of LSMO powders or films by the polymerizable complex process.

jected for spin coating on Si (1 0 0) substrate to produce a thin film.

2.2. LSMO spin coating on Si (1 0 0) substrate

Prior to coating, the substrate (10 mm × 10 mm × 525 μm) was thoroughly cleaned. Contaminations were removed by soaking in acetone, isopropanol and 10% HF, respectively. Finally, the substrates were washed with deionized water and dried.

LSMO sols were spin-coated on Si (1 0 0) substrates using a spin coater at 6000 rpm and 30 s for each coating. The as-deposited films were dried in an oven at 85 °C for 3 h, and then dried on a hot plate at 300 °C for 3 min to evaporate residual organic species. The films were synthesized by 3-layer coating, usually. The films were heat-treated at 600–800 °C for 2 h with heating rates of 1 °C/min, and a cooling rate of 1 °C/min, respectively, to prevent the cracking of thin films. The crystalline phase and orientation of the LSMO films formed on Si (1 0 0) substrates were examined by using X-ray diffraction (XRD).

2.3. Testing methods

Physical properties of both dried citric acid–ethylene glycol–metal ion gels and calcined powders were investigated by FTIR spectroscopy, TGA/DTA, X-ray powder diffraction, laser particle size distribution analyzer and BET specific surface area analyzer. Furthermore, the crystalline phase of the LSMO films formed on Si (1 0 0) substrates were examined by using XRD. The microstructures of the films were observed using a SEM, and phases also determined by XRD.

3. Results and discussion

3.1. The effect of preparatory conditions on LSMO powders

3.1.1. Preparation of LSMO dried gels and powders

The amount of citric acid used as a chelating ligand plays an important role in keeping the homogeneity of precursor. To prevent the precipitation occurring over the whole concentration process and to maintain the homogeneity of the metal ions in the resin on a molecular scale, the molar ratio of citric acid to metal ions should be high enough.[22] Therefore, the minimum molar ratio of chelating ligand to total metal ions in the precursor of LSMO system was investigated.

The suggested values of R (the molar ratios of citric acid/metal ions) and characteristics of the obtained gels and powders are prepared and observed. It was found that maintaining the metal ions dissolved in homogeneous solution during the drying process with the precursor prepared from R lower than 3 was difficult. However, when the precursor was heated to remove water and solvents, because of the lack of sufficient citric acid, precipitation would occur. When the molar ratios of citric acid to metal ions were 3–4, no visible precipitation was observed during the polymerization process.

It was found that the chelating ability of citric acid is proven by the formation of stable precursor during the drying process, and revealed that a severe concentration condition is required in the citric acid/ethylene glycol process. The precipitation occurred as the water and solvents evaporated. According to our studies, the drying rate should be moderate and drying temperature should not be above 90 °C for producing a transparent intermediate resin by citric acid/ethylene glycol process, which was utilized to produce an LSMO thin film.

The powder properties of the nanometer-size LSMO prepared from molar ratios of citric acid/metal ions at 4 and calcined at various temperatures are shown in Table 1. It is indicated that the LSMO perovskite powders have BET surface areas between 10 and 25 m^2/g. The surface areas of powders prepared from this process are much more than those prepared by solid-state reaction method (<1 m^2/g), and also more than those by citrate complexing method (<5 m^2/g). A higher surface area perovskite-type powder with higher catalytic activity could be applied as a sensor of exhausted gases.
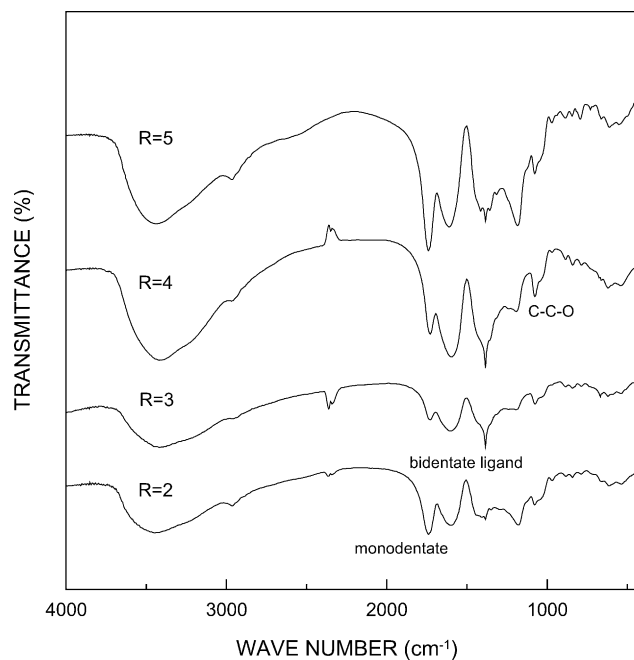

Fig. 2. FTIR spectra of LSMO-resins prepared from various molar ratio of citric acid/metal ions and dried at 120 °C for 24 h. Molar ratio of citric acid/metal ions at: (a) 2; (b) 3; (c) 4; and (d) 5.

3.1.2. FTIR analyses

The FTIR spectra of the resin prepared from various molar ratios of citric acid/metal ions and dried at 120 °C are shown in Fig. 2. As seen from Fig. 2, a broad adsorption band around 3400 cm^{-1} appeared in the IR spectra of all citric acid–ethylene glycol–salt resins, which are the characteristic of absorbed water or hydroxyl group in alcohol. It also shows that the sharp absorption bands appear at the vicinities of 1725 and 1190 cm^{-1}, which can be attributed to the monodentate ligand of metal ion with carbonyl groups (COO$^-$).[23,24] And there are also two absorption bands at the vicinities of 1380 and 1600 cm^{-1}, which were due to symmetric and asymmetric vibration of the carbonyl groups. Furthermore, a strong absorption band appears at around 1180 cm^{-1}, attributed to the C–C–O structure from ethylene glycol in the polymerization process.[25] The resin was characterized to have both monodentate and bidentate ligand of carbonyl group, which may be due to the fact that the resin contains the chelating of carbonyl group with metal ions.

Table 1
The powder properties of nanometer-size LSMO prepared from molar ratios of citric acid/metal ions at 4 and calcined at various temperatures

Temperature (°C)	D_{SEM} (nm)	S_{BET} (m^2/g)	D_{BET}[a]	D (crystalline)	D_{LPD} (nm)	D_{LPD}/D_{SEM}
550	20–50 (35 ± 15)	25.24	36.1	30	76.20	2.17
600	30–60 (45 ± 15)	18.03	50.6	43	110.38	2.45
700	40–80 (60 ± 20)	13.76	66.3	52	159.61	2.65
800	50–90 (70 ± 20)	10.16	89.8	64	196.25	2.80

[a] The BET particle sizes were calculated by $D_{BET} = (6/\rho) \times S_{BET}$, where ρ is the theoretical density of La$_{0.67}$Sr$_{0.33}$MnO$_3$, is about 6.58 g/cm^3, calculated based on Chen's study [2].
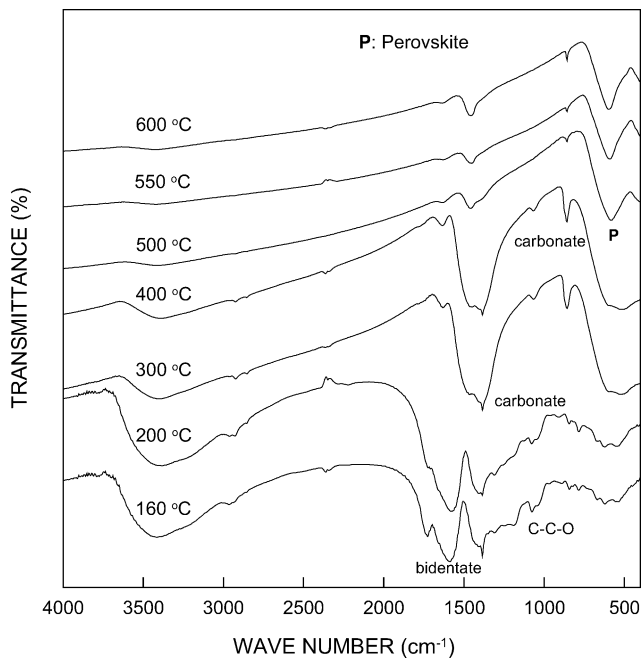
Fig. 3. FTIR spectra of LSMO-resins prepared from molar ratio of citric acid/metal ions at 4 and calcined at various temperatures.

Fig. 4. The result of the TGA/DTA analysis of the dried LSMO-resin prepared from molar ratio of citric acid/metal ions at 4.

According to the FTIR analyses (Fig. 2), the resins prepared from $R = 3$ or 4 contain a relatively low fraction of monodentate ligand and a relatively high fraction of C–C–O structures. The lower decomposition temperature of monodentate ligand makes the chelating of metal ions with carbonyl group to collapse easily. Hence, the metal ions ligand with monodentate COO$^-$ would be much more easy to segregate with the heating process. Furthermore, the lower decomposition temperature of C–C–O structure, which is constituted in the resin obtained from the raw material of ethylene glycol, makes it possible for the formation of much small fractional pieces in the dried gel during the heat treatment process. Thus, it could be predicted that a small and chemically homogeneous perovskite powder could be prepared under such conditions as the lower fraction of monodentate ligand and the existence of more C–C–O structure. It could also be predicted that the perovskite powders, prepared from $R = 3$ or 4, should have a small size and homogeneous chemical composition, and these results are also in agreement with the results of BET and SEM (not shown).

Fig. 3 shows the FTIR spectra of the dried resin prepared at $R = 4$ and after heat-treatment at various temperatures between 160 and 600 °C. It shows two strong adsorption bands appearing in the vicinities of 1600 and 1380 cm^{-1}, which can be attributed to the stretching vibration of COO$^-$. However, the intensities of the characteristic bands for complex bidentate ligands of carbonyl group do not seem to change much during the heat treatment temperatures below 200 °C. In contrast, the monodentate ligands of COO$^-$ and C–C–O structure are decreased dramatically and the intensities of characteristic peaks for C–C–O structure diminished signif-
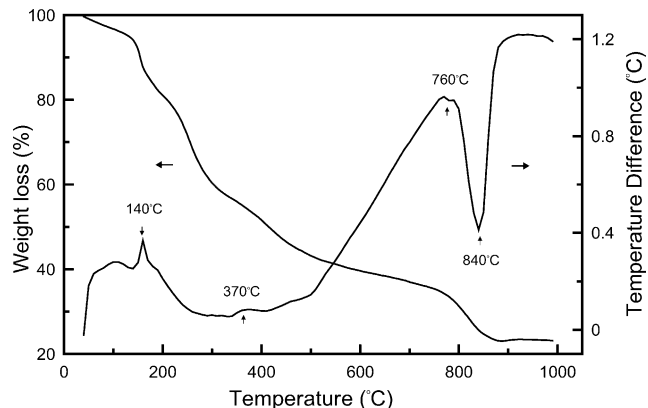
icantly after treatment at 300 °C. Additionally, the absorption bands at 860, 1060 and 1460 cm^{-1} reveal the existence of carbonate.[23] From the characteristic stretching vibration peaks of carbonyl group the presence of a lot of carbonate can be noticed. When calcination temperature was increased to 400 °C, the characteristic peaks of complexes COO$^-$ almost disappeared with a concomitant appearance of adsorption for carbonate. From the FTIR analyses, it can be suggested that the ethylene glycol (C–C–O) readily undergoes oxidation than citric acid.

As the dried gel calcined above 500 °C, the 1460 cm^{-1} absorption peak decreased, indicating the decomposition of carbonate. The wide absorption band at 560 cm^{-1} of the gel calcined at 500 °C, suggests perovskite formation. A perovskite band at 560 cm^{-1} accompanied with a few carbonate is observed, as shown in Fig. 3, which is in accordance with the XRD results discussed later part of this article.

3.1.3. TGA/DTA studies

The weight loss and temperature difference versus temperature (TGA/DTA analysis) for the pyrolysis process of the complex LSMO dried gels are shown in Fig. 4. The weight loss profile of TGA could be divided into four stages. The first stage of the TGA profile, with the weight loss of about 13% at a range of 60–160 °C is attributed to the loss of water and low boiling organic species where, the precursor was not dried enough as a result, might have absorbed water. The second stage, a fast weight loss stage of about 30% in the range of 240–490 °C, is attributed to the decomposition of the related coordination species, corresponding to the exothermic peaks at 370 °C in DTA curves. The third stage, a weight loss of about 12% between 500 and 800 °C is observed. By comparing with XRD analysis, it has been revealed that this is due to the formation of perovskite phase in this temperature range. During the stage, it is also found that a small exothermic peak existed at 760 °C, which is presumably due to the formation of pseudo-cubic perovskite phase from rhombohedral perovskite. Further studies of XRD from the LSMO thin film (Fig. 7) also support this argument. It is also found that the
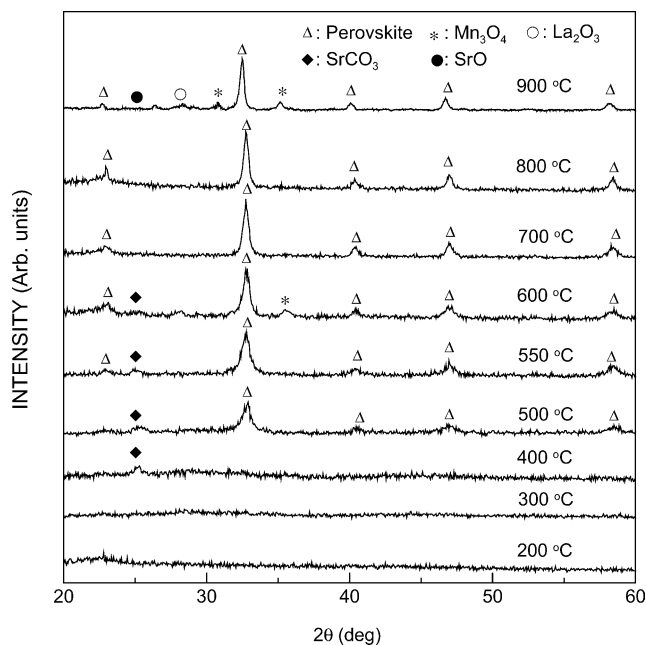
Fig. 5. The XRD patterns of LSMO-resins prepared from molar ratio of citric acid/metal ions at 4 and heat-treated at various temperatures.

peak positions (the conversion temperature from rhombohedral to pseudo-cubic perovskite) is affected by the preparatory condition of molar ratio of citric acid/metal ions.

In the fourth stage, a visibly strong exothermic peak occurred at 840 °C accompanied by about 10% of weight loss. Compared with the analysis of XRD studies, it is revealed that LSMO powder cannot be only a perovskite structure at 900 °C. Instead, a lot of other phases were examined by XRD and mentioned below.

3.1.4. XRD analysis

The LSMO precursor prepared at $R = 4$ and calcined at different temperatures for 4 h are characterized by XRD as shown in Fig. 5. The powders were amorphous if calcined at temperatures between 200 and 400 °C. Combining the XRD results with the FTIR-spectra indicate that the precursors were decomposing to carbonate prior to the formation of perovskite powder at 500 °C, and at this temperature there is still some unreacted carbonate existed. At 600 °C the precursor contained a higher amount of perovskite phase and fewer unreacted $SrCO_3$, La_2O_3 and Mn_3O_4.

According to the studies of FTIR and XRD, it revealed that a polycrystal LSMO perovskite phase accompanied with a few $SrCO_3$ was obtained during the resins calcined at 500–600 °C. As the calcined temperature increased, $SrCO_3$ reacted with the formed perovskite into a pure LSMO perovskite structure. Furthermore, the peak due to the perovskite phase is getting stronger and sharper as the calcination temperature increased from 600 to 800 °C, indicating an increase in the degree of long-range order in the perovskite lattice.

As seen from the XRD patterns in Fig. 5, there is a little amount of $SrCO_3$ and only trace of La_2O_3 and Mn_3O_4

observed as intermediate phases prior to the formation of pure LSMO perovskite phase during the decomposition of the resin. Only trace of La_2O_3 and Mn_3O_4 should be considered as almost perfect mixing of the constituent cations in the resin. This would be understood to mean that LSMO perovskite phase obtained from the amorphous powder precursor without significant segregation of the individual metals directly.

Calcined at 900 °C, the powder could not be a pure LSMO perovskite phase again. In contrast, a lot of other phases (SrO, La_2O_3 and Mn_3O_4) were examined as shown in Fig. 5. The LSMO perovskite is not stable as calcined at 900 °C. It might be postulated that the phase of this case was identified to be a cubic phase, having relatively smaller unit cell volume than rhombohedral phase,[2] and resulting in an unstable condition as calcined at 900 °C. The results are inconsistent with Kakihana et al. study,[26] who has synthesized $LaMnO_3$ by the Pechini-type polymerizable complex based on in situ polyesterification between citric acid and ethylene glycol. The powder heat-treated at 900 °C was characterized to be a monophase perovskite with a rhombohedral symmetry.

LSMO powders obtained from resins calcined at various temperatures for 4 h, were characterized by XRD using diffraction angles of 2θ between 31° and 33° as also shown in Table 1. The diffraction angle $2\theta = 32.6°$ represents the (1 1 0) plane of perovskite phase. The average crystalline size (D) is determined using the Scherrer equation[27] as shown below:

$$D = \frac{\lambda}{\beta} \times \cos\theta$$

where λ is the incident X-ray wave length (in Å, $\lambda_{Cu} = 1.5418$ Å), β the integral board (rad) of the diffraction pattern at $2\theta = 32.6°$, and θ represents the diffraction angle in degrees. The average crystalline size (D) of the LSMO samples obtained between 550 and 800 °C were between 30 and 64 nm.

Fig. 6 shows the SEM images of the LSMO samples prepared at $R = 4$ and calcined at 550, 600, 700 and 800 °C, respectively. It is obvious that the LSMO powders calcined at various temperatures appear to be agglomerated. In which, the primary particles are small and uniform, having particle sizes of 20–50 nm, 30–60 nm, 40–80 nm and 50–90 nm, respectively. This result confirms that the primary particles of the LSMO powders prepared by the citric acid/ethylene glycol sol–gel method in the present works are perovskite phase materials of nanometer sizes.

Inspection of the data of Table 1 and of the SEM micrographs of Fig. 6 shows that: (1) particles are generally formed by agglomerates of nanosized LSMO crystals; (2) the smallest particles visible in Fig. 6 correspond to the primary LSMO crystallites; (3) aggregation of crystallites is of fundamental importance in determining the particle size distribution (PSD) of final powder; and (4) the calcination temperature influences the agglomeration process, leads to a bigger particle; and has also an effect on nucleation and growth of the nanosized crystallites. Table 1 shows that the
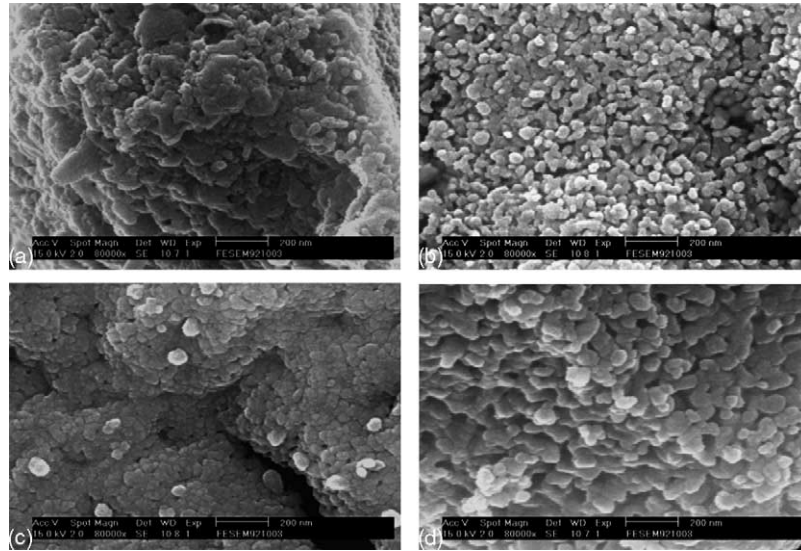
Fig. 6. SEM micrographs of LSMO powder prepared from molar ratio of citric acid/metal ions at 4 and calcined at various temperatures. Calcined at: (a) 550 °C; (b) 600 °C; (c) 700 °C; and (d) 800 °C.

mean particle size obtained by SEM (D_{SEM}) is smaller than that obtained by the laser particle size distribution analyzer (D_{LPD}) for the calcined LSMO powders. Besides, the ratio of D_{LPD}/D_{SEM} of the LSMO is also increased as the increase of calcination temperature. This mean that the higher calcination temperatures lead to the formation of larger crystals, the agglomeration process is also promoted.

3.2. The effects of preparatory conditions on LSMO thin films

3.2.1. Molar ratio of citric acid/metal ions

The films prepared from various molar ratios of citric acid/metal ions ($R = 2, 3, 4$ and 5), were heat treated at 700 °C for 4 h and examined by XRD, as shown in Fig. 7. It shows that a rhombohedral phase of LSMO with a perovskite structure accompanying with a little amount of $SrCO_3$, Mn_3O_4 and La_2O_3 is observed at molar ratios of citric acid to metal ions being 2 and 3. As the molar ratio of citric acid/metal ions increased up to 4, there is much more cubic phase of LSMO with a perovskite structure and only trace of the second phases in the synthesized film. It is revealed that the ligand of citric acid to metal ion is influenced by the molar ratio of citric acid; therefore, the crystal phase of film is changed depending on the amount of citric acid. At a lower molar ratios of citric acid/metal ions ($R = 2$ and 3), a less ligand of citric acid to metal ions causes a more segregation of metal ions, and results in the formation of second phases. Furthermore, the segregation of metal ions alters the compositions of metal ions in the main resin structure deviated from the original design of La:Sr = 0.67:0.33. Mahendiran et al. have reported that the structure is rhombohedral phase when the composition of Sr is in the 0.1–0.3 range and cubic phase when $x = 0.4$ and 0.5 in the $La_{1-x}Sr_xMnO_3$ system.[28] In our study,

owing to the segregation of metal ions, the Sr composition in the LSMO films synthesized at lower molar ratios of citric acid/metal ions would be reduced and near to 30%. Therefore, a rhombohedral phase would be produced easier than a cubic perovskite in the LSMO film. However, it is necessary to have a further investigation.
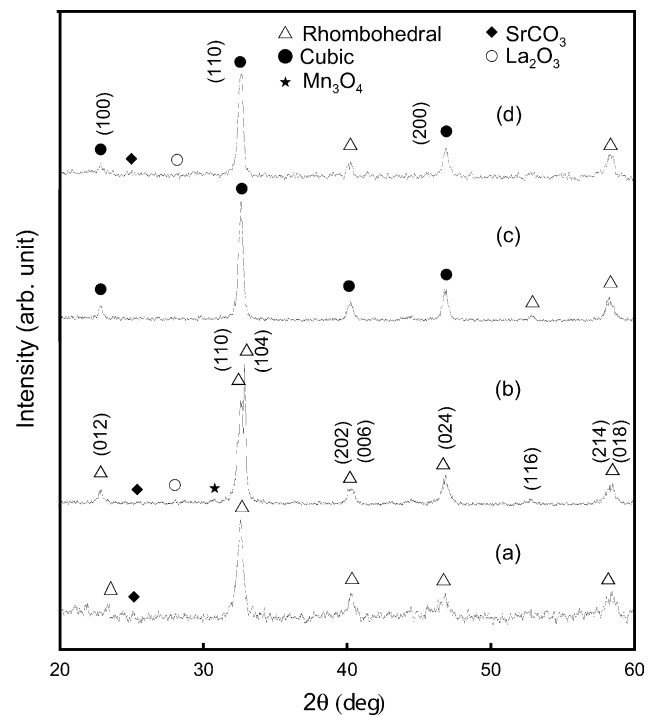

Fig. 7. The XRD patterns of LSMO thin films prepared from various molar ratios of citric acid/metal ions and heat-treated at 700 °C for 4h. Molar ratio of citric acid/metal ions at: (a) 2; (b) 3; (c) 4; and (d) 5.
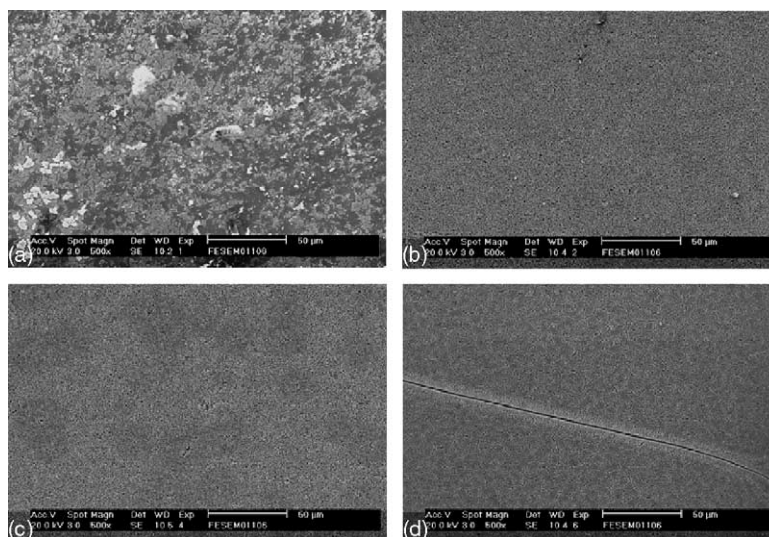
Fig. 8. SEM micrographs of LSMO thin films obtained from various molar ratios of citric acid/metal ions and heat-treated at 700 °C for 4 h. Molar ratio of citric acid/metal ions at: (a) 2; (b) 3; (c) 4; and (d) 5.

SEM was used to examine the surface morphology of film prepared from various molar ratios of citric acid to metal ions ($R = 2, 3, 4, 5$), as shown in Fig. 8. The film prepared from $R = 2$, it is obviously found that there are serious crack on the film surface, and accompanied with some avulsions between film and substrate were also observed somewhere (Fig. 8a). It is also found that with the films prepared at $R = 3$ or 4, the surface seems smooth and contains fewer crack on the film surface. In contrast, with higher molar ratio of citric acid to metal ions at $R = 5$, there are some cracks and cavities present on the film.

It can be explained that the higher molar ratio of citric acid to metal ions applied in the citric acid polymerizable complex process, the more crosslinked polyesterification occurs at higher molar ratio of citric acid/metal ions, which is caused by the higher ratio of COOH (carbonyl acid group) reacted with hydroxyl from ethylene glycol. The more crosslinked film containing a large portion of organic species, leads to greater shrinkage of film and cracks happening when treated at high temperature.

4. Conclusions

Polycrystalline $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) materials, including nanometric-sized powders and thin films, can be obtained from the resins synthesized from the polymerized complex technique based on Pechini method. Mixtures of nitrates dissolved in a water solution containing citric acid, and ethylene glycol were used to produce the resin of chelate from polyesterification between citric acid and ethylene glycol. Molar ratios of citric acid to metal ions were varied in the range of 2–5, and the resulting effects on powder's properties were studied using TGA/DTA, FTIR, SEM, BET surface area analyzer and X-ray diffraction. The results of the present study indicated that the molar ratio citric acid/metal ions at 4, the resin contained a lower fraction of monodentate ligand and a higher portion of C–C–O structure obtained from ethylene glycol, caused to obtain a small size perovskite structure synthesized at temperature as low as 500 °C. The powder was calcined at 550 °C to have a pure phase of perovskite, exhibited a nanometric sized LSMO powder of about 20–50 nm and a specific surface area of 25.24 m^2/g. Thin films were prepared by using the as-prepared sols spin coating on (1 0 0) Si substrate annealed at 600–800 °C. As a result of the molar ratio of citric acid/metal cations at 3–4, the transformation of rhombohedral structure to cubic structure was observed. The surface seems smooth and contained fewer crack. In contrast, with a higher molar ratio of citric acid to metal ions at 5, there were some cracks and cavities present on the film.

Acknowledgement

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