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Deterioration and film forming abilities of the slurries used for preparing $La_{0.8}Sr_{0.2}MnO_3$ films through composite sol–gel method

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ABSTRACT

The slurries, used for preparing $La_{1-x}Sr_xMnO_3$ (LSM) films through composite sol–gel method with citric acid, were made up of LSM particles and precursor sol with different pH values. The reasons and key factors for the deterioration of the acidic slurry were analyzed by XRD, SEM and TG/DSC. Furthermore, the LSM films were fabricated with different slurries for studying their film forming abilities. It has been found that the deterioration of the acidic slurry is determined by the abundant H^+ ions, generated from ionization of the citric acid. Discoloration of the alkaline sol and slurry is considered as a result of complicated complexes of Mn^{2+} ions, which have a good effect on the film forming ability of the alkaline slurry, together with the complexes of La^{3+} and Sr^{2+} ions. The alkaline slurry has better long-term stability than the acidic slurry, and the films made from it are more homogeneous, thicker and have lower sheet resistance.

1. Introduction

Lanthanum manganate doped with calcium, strontium or barium ($La_{1-x}A_xMnO_3$, A = Ca, Sr or Ba) have received much attention for several years, due to the fine electric conductivity, catalytic, mechanical and colossal magnetoresistance (CMR) properties [1–3]. Their film forms are of more interest than the bulk and single-crystal forms due to their potential application for the cathode in solid oxide fuel cells (SOFCs) [1], electrocatalyst in air–metal hydride (MH) battery system [4], electric heating film, thermal sensitive element [5], novel all-oxide p–n junctions, magnetic-field sensors [6], etc.

For the preparation method of $La_{1-x}A_xMnO_3$ films, such as RF-sputtering technique [7], plasma deposition [8], pulsed laser deposition [9], screen-printing [10,11], MOCVD (Metallo-Organic Chemical Vapor Deposition) [12], FAVD [13] and the sol–gel method have all been successfully used. As one of the most frequently used method for ceramic film or coating, the sol–gel method has several advantages, such as excellent homogeneity, easy control of film thickness, ability to coat large and complex shapes, simple and low-cost processing, etc., [14]. But it is very difficult to get rid of crack formation in a coating layer during the preparing process, until the composite sol–gel method was proposed and used by Barrow [15]. He dispersed fine lead zirconate titanate (PZT) particles as the seeds in a sol–gel PZT solution to form a composite slurry, and produced high quality, dense, crack-free and thick ceramic films. And his extensive research indicated that these films had similar results with dielectric, ferro-electricity and piezoelectricity. Using this method, Olding et al. deposited electrically insulative alumina and silica-based coating up to 500 μm in thickness on steel substrates [16]. In the authors' former work, some $La_{0.8}Sr_{0.2}MnO_3$ (LSM) films on alumina substrate were fabricated using this method, and the effects of some influencing factors, such as the concentration of seeds, the number of dip-coatings, the technology of pre-fired and calcining, etc., on the properties of the films were discussed [17]. However, besides the poor suspending ability, some deterioration phenomena were observed in the composite slurry after being placed in air at room temperature for about 5 h. The transformed slurry is not suitable to keep on the substrate, and the sintered film has a low bonding strength and conductivity, with a white color while the LSM film is black.

Li et al. found that LSM particles dissolved in its acidic suspending liquid [18], and Ding et al. also achieved similar results with the acidic suspending liquid of $BaTiO_3$ [19]. In addition, they described an inverse relationship between the ion separation amount and the pH of the suspending liquid, but they did not give the reason. Up to now, the related systemic research on the deterioration of the composite slurry has been rarely reported. In this paper, the reason for deterioration of the slurry is discussed, and the microstructure and electrical conductivity of the LSM films prepared with different slurries are analyzed.

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Table 1
pH value and account of the compositions of the sol precursor, slurries and various solutions involved in this paper.

Solutions and slurries	pH value	Primary composition	Concentration of the primary composition
Acidic precursor sol	1	LSM composition	0.2 (M)
Acidic slurries	1	LSM powder	0, 17.8, 56.4 or 66.0 (wt%)
Alkaline sol	9	LSM composition	Slightly lower than 0.2 (M)
Alkaline slurries	9	LSM powder	0, 17.8, 56.4 or 66.0 (wt%)
Aqueous solution of citric acid	1	Citric acid	0.48 (M)
Ammonium citric acid solution	9	Ammonium citric acid	0.48 (M)
Mixed nitrate solution of La^{3+}, Sr^{2+} and Mn^{2+} with the mol ratio 0.8:0.2:1	1	Metal cation composition	0.4 (M)
De-ionized water	7	Water molecule	100 (wt%)
Hydrochloric acid solution	1	Hydrochloride	1.5 (M)
Complexing solution of citric acid and lanthanum nitrate	1	Complexing and free ions of La^{3+}	0.16 (M)
Complexing solution of citric acid and stronium nitrate	1	Complexing and free ions of Sr^{2+}	0.04 (M)
Complexing solution of citric acid and manganese nitrate	1	Complexing and free ions of Mn^{2+}	0.2 (M)

2. Experimental

LSM films were deposited on the 95% alpha-alumina (α-Al_2O_3) substrate by the composite sol–gel process using the dip-coating method. The first step of this process was the synthesis of a precursor sol for LSM, according to the stoichiometric formula $La_{0.8}Sr_{0.2}MnO_3$, $La(NO_3)_3{\cdot}6H_2O$ ($\geq$99.0%), $Sr(NO_3)_2$ ($\geq$99.5%), $Mn(NO_3)_2$ solution (49.0–51.0 wt%) were the starting materials with analytical citric acid ($\geq$99.5%) as the complexing agent. All the starting materials were dissolved in the de-ionized water while the mol ratio of citric acid to metal ions was 1.2:1, to form a stable and acidic precursor sol with about pH 1 after heated in a water bath at 80 °C for 30 min, the concentration of LSM in which was 0.2 mol L^{-1} (0.2 M). The next step was synthesis of the LSM powder and preparation of the acidic and alkaline slurries. The fabricated precursor sol was divided into three parts. First part was used as the acidic sol for making the acidic slurries. Second part was regulated by aqua ammonia of 25–28 wt% to alkaline sol with pH 9, the concentration of LSM composition in which was slightly lower than 0.2 M. And the others were used to fabricate LSM powder, proceeding gelation and calcination at 800 °C for 2 h. Then different amounts of the LSM powder were added into the two kinds of sol as the seeds in weight percentages of 0, 17.8, 56.4 and 66.0. After being milled for 30 min, a series of composite slurries for dip-coating were obtained. The α-Al_2O_3 substrates were first cleaned with ultrasonically in acetone for 5 min followed by ethanol for 5 min by acetone, and then dipcoated with the slurries using a homemade dip-coating apparatus at a withdrawal rate of 1 cm min^{-1}. After coating, the films were dried at 120 °C for 5 min, calcined at a ramp rate of 1 °C min^{-1} in a programmable box furnace (Chang Da) with air atmosphere, kept at 600 °C for 10 min and cooled down naturally. This procedure was repeated 10 times and after final coating, the samples were annealed at 800 °C for 4 h in air to decompose the residual organic substance, to crystallize the perovskite phase and to densify the film.

The reason of deterioration, discovered in the acidic slurry during the resting period, was analyzed through comparing with some related experiments. Various solutions were respectively used instead of the sol for the composition of slurry, including an aqueous solution of citric acid, ammonium citric acid solution, a mixed nitrate solution of La^{3+}, Sr^{2+} and Mn^{2+} with the mol ratio 0.8:0.2:1, de-ionized water and a hydrochloric acid solution. In addition, some phenomena were present in the preparation of the alkaline sol from the acidic precursor sol. Moreover, the color of the placed alkaline sol and slurries gradually became darker and deeper. In order to determine these behaviors, three kinds of complexing solutions were prepared with citric acid, individually mixed with lanthanum nitrate, manganese nitrate or strontium nitrate. All the chemicals used were purchased from Qiguang Company. Table 1 shows the pH value and account of the compositions of the sol precursor, slurries and various solutions in this paper.

The characterization techniques in this present work are as follows: To determine the phase composition of the LSM powder, deposition and films, X-ray diffraction (XRD) of the samples at room temperature were recorded using Cu-Kα radiation source (Rigaku/Dmax-rB) for normal scan mode. Thermal decomposition of the deposition was characterized with Thermo gravimetry/Differential scanning calorimetry (TG/DSC, NETZSCH STA 449 C) instruments under flowing air (heated at 10 °C min^{-1} from ambient temperature to 900 °C). The surface and cross-section of the films were sputter-coated with gold and visualized by a scanning electron microscope (SEM, JEOL JSM-6380LA). Four-point probe analysis (SX1934) was performed on all samples to determine the sheet resistance of the LSM films at room temperature in air.

3. Results and discussion

In the present work, the phenomena of deterioration in the composite slurry with the acidic sol were observed as a decrease of the amount of LSM particles, appearance of white deposition and discoloration of sol, as shown in Fig. 1(a)–(c). However, in the alkaline slurries with pH 9, the white deposition and the decrease of the LSM particles were not observed after 6 months, and the color of upper sol become darker and deeper, as shown in Fig. 1(d)–(f). Different phenomena were observed with the related experiments. After the LSM powder was added into the aqueous solution of citric acid, the deterioration was observed in the slurry during a 48 h

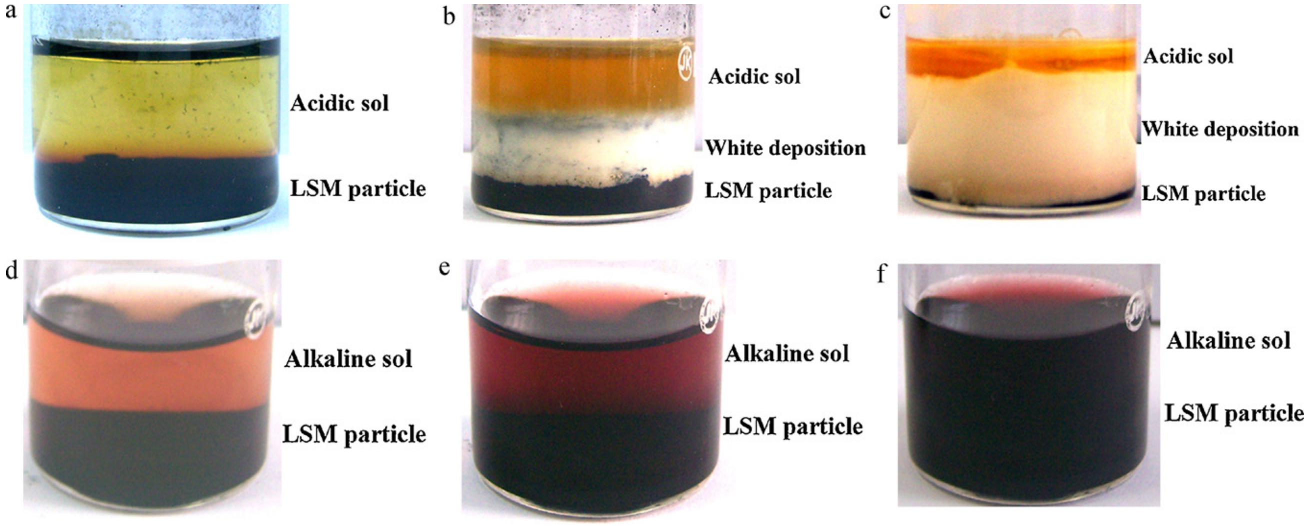

Fig. 1. Discoloration of the two kinds of slurries with standing time which was placed in air at room temperature: (a) acidic slurry after 1 h; (b) acidic slurry after 5 h; (c) acidic slurry after 72 h; (d) alkaline slurry after 1 h; (e) alkaline slurry after 5 h; and (f) alkaline slurry after 72 h.

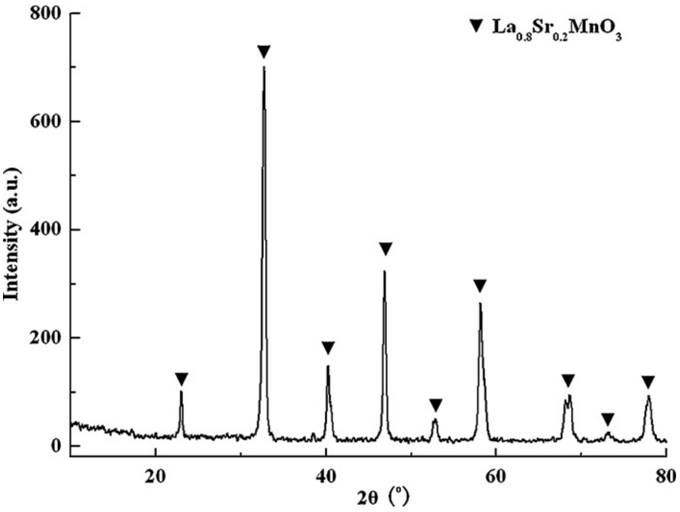

Fig. 2. XRD pattern of LSM powder.

period, but the color of the upper solution changed from colorless to ruby red gradually. When the ammonium citric acid solution with pH 9, the mixed nitrate solution of La^{3+}, Sr^{2+} and Mn^{2+} or deionized water was used as the substitution of the sol, there was no evidence of deterioration during about 6 months. In addition, the added particles decreased gradually in a hydrochloric acid solution with 1.5 M after being mixed. By this token, the dissolution of the LSM particles occurs in the acidic condition, and the appearance of white deposition is probably due to the citrate groups in the acidic condition.

It is well-known that as a complexing agent of the $La_{1-x}Sr_xMnO_3$ precursor solution, the citric acid ($C_6H_8O_7$) has three –COOH and one –OH presenting triplex ionization with the pH increasing, as follows: $H_4Cit \xleftrightarrow{K_1} H_3Cit^- \xleftrightarrow{K_2} H_2Cit^{2-} \xleftrightarrow{K_3} HCit^{3-} \xleftrightarrow{K_4} Cit^{4-}$ ($H_4Cit = C_6H_8O_7, K_1 = 8.32 \times 10^{-4}, K_2 = 4.07 \times 10^{-5}, K_3 = 3.24 \times 10^{-6}, K_4 = 2.51 \times 10^{-12}$). Thus, La^{3+} and the citrate groups are likely to obtain multiplicate complex compounds, due to the variety of the pH of the solutions and the ratio of La^{3+} ions to the citrate groups [20]. In this paper, the mol ratio of citric acid to metal ions was 1.2:1 in the sol, the pH of which was around 1. Soluble ions, $[La(H_3Cit)]^{2+}$, $[Sr(H_3Cit)]^+$ and $[Mn(H_3Cit)]^+$, were formed by the reaction between the excessive citric acid and the metal ions, La^{3+}, Sr^{2+} and Mn^{2+}. However, these complex ions usually generate citrate coordination polymers with water molecules, as the three metal ions are sexadentates [21].

As shown in Fig. 2, the powder presented a single LSM perovskite phase after being calcined at 800 °C for 2 h. The perovskite bulk material usually possesses good physicochemical stability, and has the advantage of strong ability of acid and base resistance. However, the powder prepared by the sol–gel method usually has plenty of superfine particles (<100 nm) with a small size effect and surface effect [22,23]. Therefore, the reaction between the particle and the sol is likely to originate from strong surface activity of the powder. The dissolution of the particle reported by Ref. [18] and [19] is probably because ball milling of the suspending liquid results in some small particles with high surface activity. In the present work, citric acid was excessive in the sol, so a conceivable reaction process in the acidic slurry occurred during a period of time, tentatively described as Eq. (1).

$$LSM + 6H^+ \rightarrow 0.8La^{3+} + 0.2Sr^{2+} + 0.8Mn^{3+} + 0.2Mn^{4+} + 3H_2O \quad (1)$$

After the acidic composite slurry was ground for 30 min, some changes gradually presented. The LSM particles subsided to the bottom of the slurry about 1 h later, and the upper liquid was yellow and transparent, as shown in Fig. 1(a). After about 3 h, a small quantity of white deposition began to appear. Meanwhile, the color of the liquid with pH 2 became orange yellow. It was probably induced by the Mn^{3+} and Mn^{4+} ions as the generations of Eq. (1), which have the similar color. About 5 h later, a large amount of white deposition appeared at the interface between the sol and bottom particles, as shown in Fig. 1(b). At this time, the pH value of the upper liquid was about 3. And the bottom LSM particles decreased as the white deposition increased. After about 72 h, the content of the white deposition did not increase with only a little residual particles, and the color of the liquid on the top of the deposition stayed orange yellow with about pH 4, which were illustrated in Fig. 1(c).

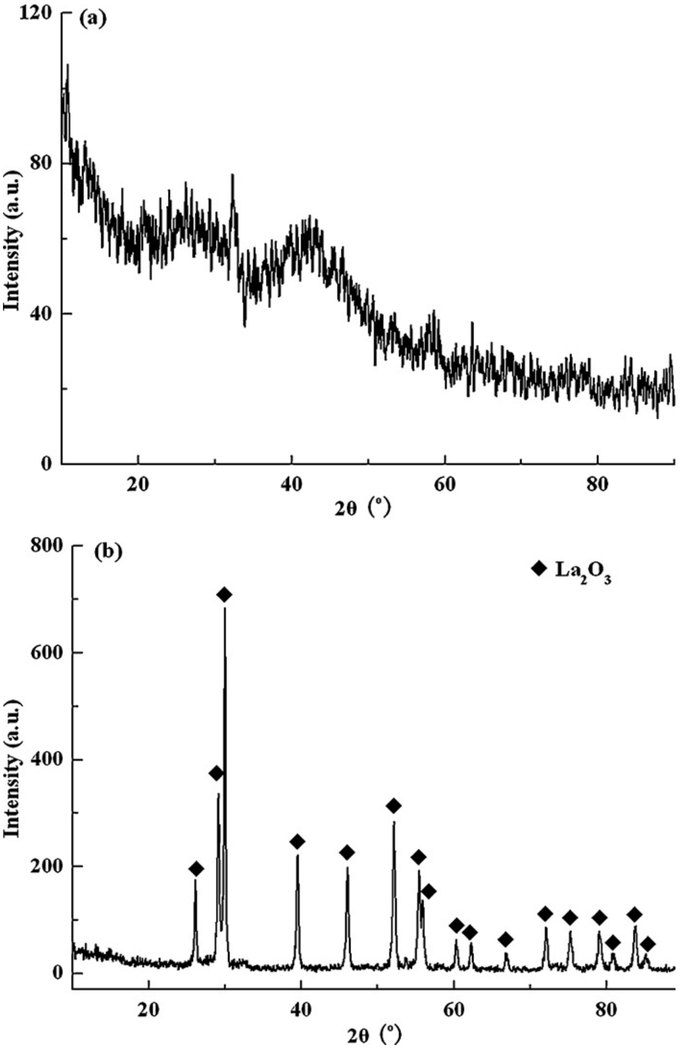

Fig. 3. XRD pattern of the white deposition, generated from the acidic slurry, dried at 80 °C for 5 h (a); calcined at 800 °C for 15 min (b).

The XRD pattern of the dried white deposition is shown in Fig. 3(a), and the calcined one at 900 °C for 15 min in Fig. 3(b). It can be seen that the calcined deposition is crystallized phase of La_2O_3, while the uncalcined one is amorphous. The white deposition could not be metal hydroxides because the sol is pH 3. And the soluble metal nitrates are also excluded. Abundant white deposition $LaHCit \cdot 6H_2O$ was obtained in the citrate solution of La^{3+} ions by Xu et al., while the pH value of the solution was adjusted to about 3.5 with NaOH [24]. Similarly, Feng et al. suggested that, in a weak acid condition, the white deposition $LaHCit \cdot nH_2O$ was the main citrate complex compounds of La^{3+} with $La^{3+}:HCit^{3-} = 1:1$ [25]. For our

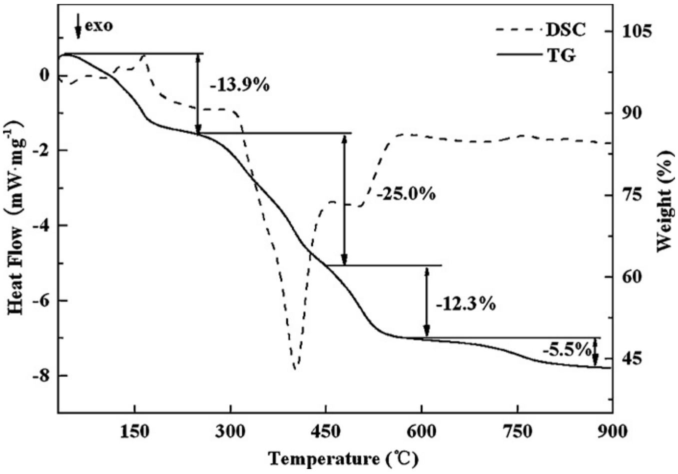

Fig. 4. TG/DSC curves for the decomposition of the white deposition, generated from the acidic slurry, under flowing air (10 °C min^{-1}) from ambient temperature to 900 °C.

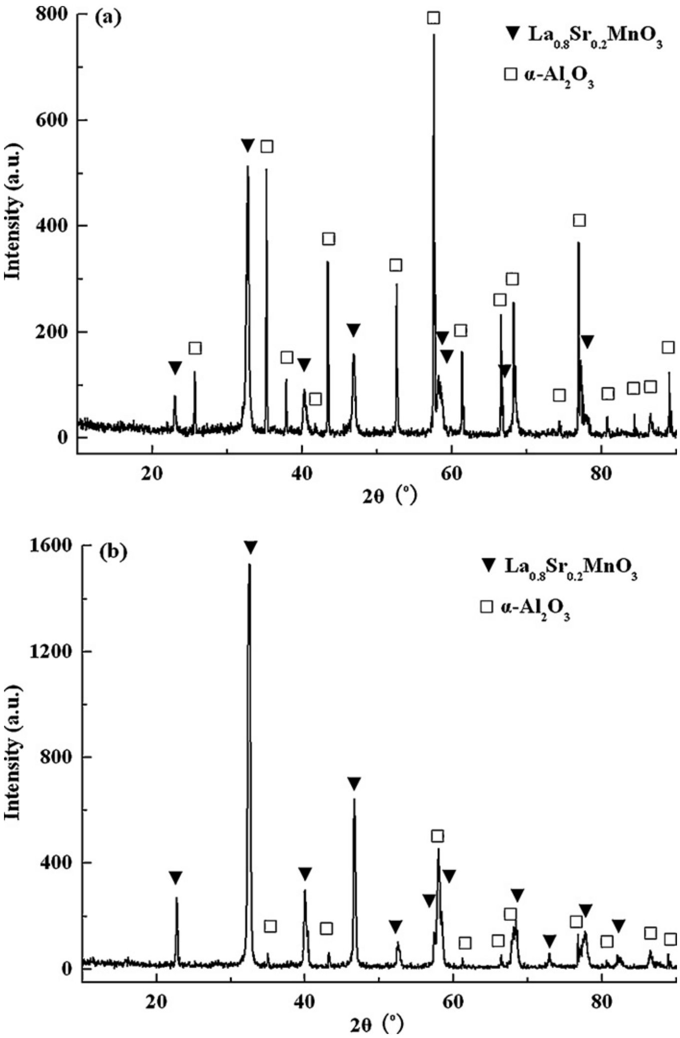

Fig. 5. XRD patterns of LSM films prepared with the acidic slurry (a) and the alkaline slurry (b) dip-coated for 10 times.

part, the dissolution of LSM particles increased the concentration of La^{3+} ions of the upper sol. In addition, H$^+$ ions in the sol were gradually consumed due to the Eq. (1). This induced the further ionization of the citric acid in the sol, which increased concentration of the citrate groups. In the citric acid solution, Cit^{4-} usually formed at pH > 10, and HCit^{3-} ions were present at pH > 4 [26]. So in the upper sol of this work, it was also possible to achieve plenty of HCit^{3-} ions at pH 3. Therefore, it is concluded that the white deposition is LaHCit·nH$_2$O.

In our work, the TG/DSC curves (shown in Fig. 4) of the white deposition LaHCit·nH$_2$O were performed from 30 °C to 900 °C and the analysis results were similar to Ref. [27], which reported that the thermal decomposition of lanthanum citrate trihydrate La[(C$_6$H$_5$O$_7$)(H$_2$O)$_2$]·H$_2$O synthesized with La$_2$O$_3$ and citric acid was characterized by means of FTIR, TGA; moreover, the related reaction equations of each stage are presented in Table 2.

It is obvious that the experimental results are basically consistent with the calculated results. According to the total weight loss of −56.7%, it can be calculated that molecular weight of the initial compound is about 382 g mol^{-1}. With the experimental error, three water molecules (n = 3) should be present in the crystal structure in order to arrive at the calculated molecular weight. The first decomposition stage probably indicates three successive dehydration steps (1a, 1b and 1c) corresponding to the three small endothermic peaks shown in the DSC curve, at about 80.0 °C, 125.9 °C, 163.6 °C respectively. These steps indicate that the 3 water molecules probably have different bonding modes with La^{3+} in the crystal structure due to the sexadentate La^{3+}. The second stage and the third stage denote the formation of La$_2$(CO$_3$)$_3$ and La$_2$O$_2$CO$_3$, respectively. The DSC curve displays two obvious exothermic peaks corresponding to the two stages, which should be attributed to the decomposition of the organic constituents and crystallization process [28]. La$_2$O$_3$ is formed at the fourth stage, which is testified to by Fig. 3(b). Therefore, the La$_2$O$_3$ phase probably appeared in the calcined film fabricated with the deteriorated slurry, which would have an impact on the phase composition and properties of the desired LSM film.

In order to study the discoloration of the sol, it is necessary to analyze species of the ions in the upper liquid. When all of the activated LSM particles are dissolved, the reaction Eq. (1) ends, and then the content of the white deposition will not increase with depletion of the La^{3+} or HCit^{3-} ions. After being filtered, a solution of lanthanum nitrate was added into the orange yellow filtrate. The white deposition was not observed. This indicates that there is no residual HCit^{3-} in the filtrate, so Mn^{2+}, Mn^{3+}, Mn^{4+}, Sr^{2+}, NO$_3$$^-$ and H$^+$ are the main ions, and there are probably La^{3+} ions left. Usually, the solution with Sr^{2+}, NO$_3$$^-$, H$^+$ and La^{3+} ions does not have color, and so does the diluted solution with Mn^{2+} ions. Thus, the orange yellow color of the filtrate would be due to Mn^{3+} and Mn^{4+} ions; moreover, it did not change for a long time.

Table 2
Stages of the thermal decomposition of LaHCit·3H$_2$O under flowing air.

Stage	Transformation reaction	Weight loss (%) calculated	Weight loss (%) observed	Temperature range (°C)
1a	$LaHCit\,3H_2O \rightarrow LaHCit{\cdot}2.5H_2O + 0.5H_2O$	–	−2.5	30–102.6
1b	$LaHCit\,2.5H_2O \rightarrow LaHCit{\cdot}1.7H_2O + 0.8H_2O$	–	−3.9	102.6–140.0
1c	$LaHCit\,1.7H_2O \rightarrow LaHCit + 1{\cdot}7H_2O$	–	−7.5	140.0–249.3
2	$2LaHCit + 9O_2 \rightarrow La_2(CO_3)_3 + 5H_2O\uparrow + 9CO_2\uparrow$	−25.9	−25.0	249.3–457.8
3	$La_2(CO_3)_3 \rightarrow La_2O_2CO_3 + 2CO_2\uparrow$	−11.5	−12.3	457.8–575.0
4	$La_2O_2CO_3 \rightarrow La_2O_3 + CO_2\uparrow$	−5.8	−5.5	575.0–900

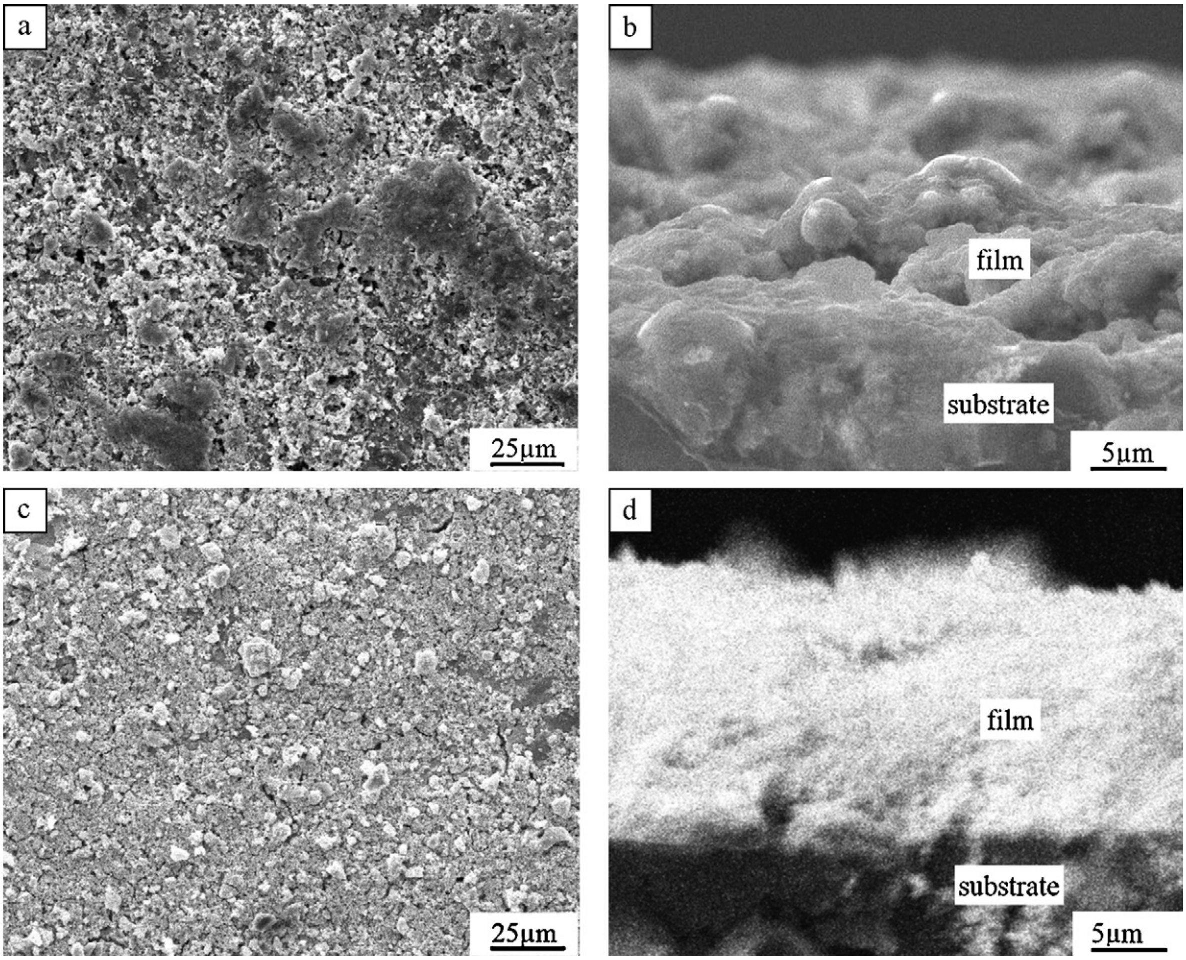

Fig. 6. Micrographs of La0.8Sr0.2MnO$_3$ films prepared with the slurry with 57.6 wt% dip-coated for 10 times. Secondary Electron Imagine (SEI) of surface by the acidic slurry (a); Backscattered Electron Imagine (BEI) of cross-section by the acidic slurry (b); SEI of surface by the alkaline slurry (c); SEI of cross-section by the alkaline slurry (d).

As a consequence, the deterioration of the composite slurry is mainly caused by H^+ and $HCit^{3-}$ ions. Moreover, the deposition of $HCit^{3-}$ and La^{3+} is only formed in the weak acidic condition, so these phenomena can be avoided by diminishing the extent of H^+ ions or increasing the pH value of the sol. This was evident in the former experiment with the alkaline slurry. In the alkaline slurry, the Eq. (1) hardly occurs because of a lack of the H^+ ions, and the extent of La^{3+} ions does not increase. Without the compensation of La^{3+} ions, the ratio of La^{3+} ions to $HCit^{3-}$ ions could not achieve 1:1 due to the excessive citric acid, and the white deposition of $LaHCit{\cdot}nH_2O$ is not generated.

While the acidic sol was regulated to the alkaline sol by the aqua ammonia of 25–28%, some changes were discovered with the pH value increasing. At pH 3, a large amount of white deposition is generated, which has similar characteristics as $LaHCit{\cdot}nH_2O$. At pH 6–7, the white deposition is entirely dissolved. Ref. [26] pointed out that the $HCit^{3-}$ ions are the primary citrate groups with pH 6–11. So the dissolved deposition probably transformed into soluble $[La_2(HCit)_3]^{3-}$ or $[La(HCit)_2]^{3-}$ ions [25]. The color of the sol changes from colorless to brick red, and then turns to ruby red as pH 9. Furthermore, while the three kinds of citrate solutions of individual La^{3+}, Mn^{2+} or Sr^{2+} were all regulated by the aqua ammonia, only the second one changed from colorless to brick red. A period of time later, the first transparent solution changed from colorless to yellow, and stayed stable for a long time. The second transparent solution changed from brick red to ruby red and tended towards darker and deeper during the resting period, while the third one kept colorless all the time. It is obvious that the discoloration of the sol is mainly due to the manganese ions. The electron configuration of Mn^{2+} ions is $3d^5$, which can form sexadentate complexes of inner orbit type or outer orbit type with different ligands [26]. According to the above discussion, in the alkaline sol with pH 9, the citrate groups are almost $HCit^{3-}$ ions. Thus $HCit^{3-}$ ions, H_2O and NH_3 with different coordination ability, probably generate various complicated complexes. According to Ref. [26], the change of the inner ligand would induce the change of the electron configuration of Mn^{2+}, thus causing the complexes with different colors. The brick red color of the alkaline sol with pH 9 is probably due to the complexes with this color.

In addition, similar to the discoloration of the citrate solution of manganese with pH 9, the color of the alkaline sol after a period of time became darker and deeper, and so did the alkaline slurry made up of the alkaline sol and LSM powder. Sun et al. suggested that Mn^{2+} ions were oxidized to brick red deposition of $MnO_2{\cdot}2H_2O$ in the air at pH 6 and 9 [29]. However, the brick red deposition was not observed in this experiment, so it was considered that the discoloration was not due to the oxidation of Mn^{2+} ions. For Mn^{2+}, the complexes of inner orbit type are insert, usually generated in several hours, while the generation of the outer orbit type only needs less than one minute [26]. So this discoloration during the resting period is probably because of the increase of the brick red complexes or the transformation among the complexes. In a word, it is considered that the complicated complexes of Mn^{2+} result in the discoloration of the alkaline sol and slurry. Also, the similar

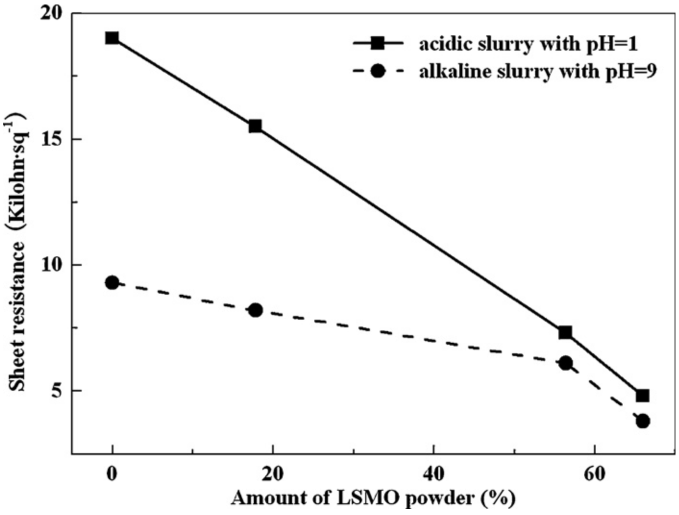

Fig. 7. Dependence of sheet resistance of LSM films as a result of the amount of LSM powder and pH value of the slurry.

complexes are generated by the complexation between La^{3+} ions or Sr^{2+} ions and $HCit^{3-}$, NH_3 or H_2O in the alkaline sol. Furthermore, these complicated complexes usually have a long-train structure or cyclic structure, and form the spatial network structure through mutual combination. It is a desired structure in the sol–gel method for fabricating dispersed nano-powder, which can induce the steric hindrance effect and improve the dispersion of ions [30]. Similarly, Ref. [18] reported that at pH > 8.0 of the suspending solution, the repulsive force of the electric double layer between the LSM particles reached maximum, the particles dispersed independently, and the suspending liquid had a good stabilization. Therefore, besides the dispersion of the ions in the sol, the dispersion of the LSM particles was probably benefited from the complicated complexes obtained in the alkaline slurry. Both of them can improve the uniformity of the slurry. In the acidic sol, the ligands are almost H_3Cit^{-} ions and H_2O, which usually have weaker coordination ability than $HCit^{3-}$ ions and NH_3. So the complexes formed by them with the metal ions have worse dispersibility than the complexes in the alkaline slurry. It was found that the alkaline slurry kept a longer suspending time than the acidic slurry. This would be beneficial to the uniform formation of film.

In order to determine the film forming abilities of different slurries, the phase composition, microstructure and electrical conductivity of a series of LSM films prepared with the acidic slurry and the alkaline slurry are studied. Fig. 5(a) and (b) are the XRD patterns of LSM films prepared with different slurries. The former was prepared with the acidic slurry of pH 1 before deterioration, and the latter was formed with the alkaline slurry after being regulated to pH 9. It can be seen that both kinds of films have a single phase LSM. Fig. 6 shows the micrographs of the two films. The film prepared with the alkaline slurry is more homogeneous. In addition, it is observed from Fig. 6(b) and (d) that both of them have a continuous and dense interface between the film and substrate. Although they have the same dip coating time, the latter is thicker than the former, so the alkaline slurry is beneficial to producing thick film. And in the process of dip coating, it was discovered that the former coating was easily eroded by the acidic slurry by virtue of the excess citric acid of the sol. It is supposed that the excessive citric acid can also induce dissolution of the LSM films without calcined at high temperature. So the thickness of the two films shows a little difference.

The dependence of sheet resistance of LSM films as a result of the amount LSM powder and pH value of the slurry was characterized in Fig. 7. It can be seen that the sheet resistance of the films prepared with the alkaline slurry is smaller than that of the acidic slurry, and is more stable and uniform. As previously discussed, the pH value of the slurry has an impact on the thickness and uniformity of the film, which influence the electric conductivity. Therefore, in order to obtain more homogeneous and thicker LSM film with lower sheet resistance, it is critical to regulate the slurry to alkaline.

4. Conclusion

Some phenomena of deterioration were observed in the acidic composite slurry with stoichiometric $La_{0.8}Sr_{0.2}MnO_3$ as pH 1, which included dissolution of the LSM particles, appearance of white deposition and discoloration of the sol. The dissolution of the LSM particles is due to the reaction between the activated particles and abundant H^+ ions. The white deposition is deemed to be a composition of $LaHCit·3H_2O$ and the Mn^{3+} and Mn^{4+} ions generated from the dissolution of LSM particles induces the discoloration of the acidic sol. The dissolution of the LSM particles and the white deposition were not observed in the alkaline slurry with pH 9 during about 6 months. It is considered that the discoloration of the alkaline sol and slurry is due to the complicated complexes generated by Mn^{2+} ions and various ligands. And the alkaline slurry has better dispersion ability than the acidic slurry due to the generation of the complicated complexes of La^{3+}, Mn^{2+} and Sr^{2+} ions. Consequently, the films prepared with the alkaline slurry were more homogeneous, thicker and had lower sheet resistance. In addition, a single LSM phase is the composite of films prepared with both slurries.

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References

[1] Teruhisa Horita, Katsuhiko Yamaji, Hideyuki Negishi, Natsuko Sakai, Harumi Yokokawa, Tohru Kato, Solid State Ionics 136–137 (2000) 897–904.
[2] Hae Jin Hwang, Masanobu Awano, J. Eur. Ceram. Soc. 21 (2001) 2103–2107.
[3] Y.D. Zhen, S.P. Jiang, S. Zhang, V. Tan, J. Eur. Ceram. Soc. 26 (2006) 3253–3264.
[4] M.V. Ananth, K. Manimaran, I. Arul Raj, N. Sureka, Int. J. Hydrogen Energy 32 (2007) 4267–4271.
[5] Xinde Zhu, Shengli Li, Hanzhou Liu, Qing Ao, Liangcheng Sun, Feng Wang, J. Chin. Ceram. Soc. 37 (2009) 1344–1350.
[6] M. Gunes, H. Gencer, V.S. Kolat, S. Vural, H.I. Mutlu, T. Seckin, S. Atalay, Mater. Sci. Eng. B 136 (2007) 41–45.
[7] Horita Teruhisa, Tsunoda Tatsuro, Yamaji Katsuhiko, Sakai Natsuko, Kato Tohru, Yokokawa Harumi, Solid State Ionics 152–153 (2002) 439–446.
[8] H.B. Wang, J.F. Gao, D.K. Peng, G.Y. Meng, Mater. Chem. Phys. 72 (2001) 297–300.
[9] S.W. Jin, X.Y. Zhou, W.B. Wu, C.F. Zhu, H.M. Weng, H.Y. Wang, X.F. Zhang, B.J. Ye, R.D. Han, J. Physics D: Appl. Phys. 37 (2004) 1841–1844.
[10] Wang Ying, J. Guo Lucun, Chin. Rare Earth Soc. 23 (2005) 62–65.
[11] J.Q. Li, P. Xiao, J. Eur. Ceram. Soc. 21 (2001) 659–668.
[12] O. Stadel, J. Schmidt, G. Wahl, C. Jlmenez, F. Weiss, M. Krellmann, D. Selbmann, N.V. Markov, S.V. Samoylenkov, O.Yu. Gorbonko, A.R. Kaul, Physica C 341–348 (2000) 2477–2478.
[13] S. Charojrochkul, R.M. Lothian, K.L. Choy, B.C.H. Steele, J. Eur. Ceram. Soc. 24 (2004) 2527–2535.
[14] L. Klein, Sol-Gel Technology for Thin Films, Fibers, Preforms, Electronics, and Speciality Shapes, Park Ridges, New Jersey, 1988, Part II.
[15] D.A. Barrow, T.E. Petroff, M. Sayer, Surf. Coat. Technol. 76–77 (1995) 113–118.
[16] Tim Olding, Michael Sayer, David Barrow, Thin solid films 398–399 (2001) 581–586.
[17] Xinde Zhu, Shengli Li, Xiaojie Yang, Jie Qiu, Appl. Surf. Sci. 2 (2007) 532–537.
[18] Guojun Li, Xiaoguang Liu, Daming Chen, J. Chin. Rare Earth Soc. 20 (2002) 126–128.
[19] Xiang Ding, Zhengfang Yang, Qiming Yuan, B. Chin. Ceram. Soc. 5 (2001) 3–6.
[20] Xinmu Zhou, J. Nanchang University (Natural Science) 26 (2002) 377–380.
[21] Wenguo Wang, Xiaofeng Zhang, Feng Chen, Chengbing Ma, Polyhedron 24 (2005) 1656–1668.
[22] Masato Kakihana, Momoko Arima, Masahiro Yoshimura, Noriko Ikeda, Yoshinori Sugitani, J. Alloy. Compd. 252 (1999) 102–105.

[23] M.A. Raza, I.Z. Rahman, S. Beloshapkin, J. Alloy. Compd. 485 (2009) 397–593.
[24] Xu Weimin, Wang Li, Wang Lufeng, Li Weisong, J. Chin. Rare Earth Soc. 3 (2006) 366–370.
[25] Zhijun Feng, Liefeng Ling, Qingwen Zong, J. Anqing Teachers College 2 (1999) 23–28.
[26] Fang Jingli, Electroplating of Multicomponent Complexes, National Defense Industry Press, Beijing, 1983.
[27] G. Vanhoyland, J. Pagnaer, J. D' Haen, S. Mullens, J. Mullens, J. Solid State Chem. 178 (2005) 166–171.
[28] T. Bataille, M. Louer, J.P. Auffredic, D. Louer, J. Solid State Chem. 150 (2000) 81–95.
[29] Hui Tong, Yubin Sun, Yongxi Chen, Liping Guo, Hui Wu, Jiaheng Lei, New Chem. Mater. 32 (2004) 33–35.
[30] Xuchen Lu, Tingxian Xu, J. Ceram. 19 (1998) 53–57.