Journal of Alloys and Compounds 509 (2011) 1984–1988

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Effects of heating atmosphere on formation of crystalline citrate-derived $LaAlO_3$ nanoparticles

Hsuan-Fu Yu*, Yu-Man Guo

Department of Chemical and Materials Engineering, Ceramic Materials Laboratory, Tamkang University, Tamsui, Taipei Hsien 25137, Taiwan

ARTICLE INFO

Article history:
Received 26 June 2010
Accepted 24 October 2010
Available online 4 November 2010

Keywords:
Lanthanum aluminate
Citrate precursor method
Thermal analysis
Calcination atmosphere
Ceramic synthesis

ABSTRACT

Crystalline $LaAlO_3$ nanoparticles were synthesized at relative low temperatures, using a citrate-precursor technique. $La(NO_3)_3$, $Al(NO_3)_3$, and $C_3H_4(OH)(COOH)_3$, in a molar ratio of 1:1:1, were dissolved in deionized water. NH_4OH was used to adjust the aqueous solution to pH 7. After drying, the citrate precursors were charred at 350 °C, followed by calcination at different temperatures, in air or oxygen atmosphere. The thermochemical properties of the resultant particles were analyzed using thermogravimetric and differential thermal analysis, X-ray diffractometry, infrared spectroscopy, scanning electron microscopy, and transmission electron microscopy. Effects of calcination temperature and heating atmosphere on the formation of crystalline $LaAlO_3$ nanoparticles were investigated. In O_2 atmosphere, clacining the citrate-derived charred solid precursor at 700 °C for 3 h can decompose all intermediates to produce pure $LaAlO_3$ nanoparticles (particle sizes ≤ 100 nm) with an average crystallite size of about 24 nm and possessing high sinterability.

1. Introduction

Lanthanum aluminate ($LaAlO_3$) has good dielectric characters: high relative permittivity (ε_r = 23), high quality factor ($Q \times f \approx 65{,}000$ GHz; $Q = \tan\delta^{-1}$; f: measuring frequency) and very small temperature coefficient of resonant frequency ($\tau_f = -44$ ppm/K) [1], which attracts a great attention in recent years because of its variety of applications [1–8]. Conventionally, $LaAlO_3$ powder is synthesized via solid-state reaction routes. The solid-state synthesis of lanthanum aluminates from the corresponding metallic oxides or salts usually requires extensively mechanical mixing and lengthy thermal treatments in the temperature range of 1300–1700 °C [2,9,10]; consequently, the resultant powder may have several drawbacks, such as limited chemical homogeneity, large particle sizes and low sinterability.

To produce $LaAlO_3$ powder with high quality, various wet chemical routes have been developed or under investigation, such as co-precipitation [8,11,12], sol-gel conversion [13–15], polyvinyl alcohol evaporation [16], mechanochemical alloying [17], molten salt [18], and organic metal-precursor [7,19–23]. These wet chemical methods are all designed to produce $LaAlO_3$ with better physical characters (e.g., small particle sizes, narrow size distribution, monodispersed particles, large specific surface area, and high sinterability) and chemical properties (e.g., homogeneous composition and high purity) at temperatures as low as possible. The citrate-precursor technique is one of the organic metal-precursor methods. In this technique, the required metallic ions are uniformly mixed in a proper solution and then the different metallic ions in the solution are co-chelated by carboxyl groups ($-COO^-$) of citric acid to form metal complexes. These metal complexes may continuously react with the polyalcohol, if it exists in the solution, to form the corresponding polyesters. After drying, the obtained solid precursors are calcined to form the oxides.

Fu et al. [7] used the citrate precursor technique (or called Pechini method) to prepare Sr/Mn-substituted $LaAlO_3$, which was evaluated as potential anode materials for solid oxide fuel cells. They used the metallic nitrates as the sources of the required metallic ions and found that single phase perovskite structures of $(La_{0.8}Sr_{0.2})_{1-y}Al_{1-x}Mn_xO_{3-\delta}$ (x = 0, 0.3, 0.5; y = 0 or 0.06) were obtained after firing at 1300 °C for 5 h in air. Kuo et al. [8] prepared $LaAlO_3$ powder by chemical coprecipitation using $La(NO_3)_3{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ aqueous solutions as the starting materials. For the $LaAlO_3$ precursor gels precipitated at pH 9 and calcined at 700 °C for 6 h, the formation of the perovskite $LaAlO_3$ phase occurred and the presence of crystalline impurities was not found. The crystallite size of $LaAlO_3$ slightly increases from 37.8 to 41.5 nm with calcination temperature increasing from 700 to 900 °C for 6 h. Kakihana and Okubo [19] conducted polyesterification between (La, Al)–citrate complexes and ethylene glycol at 130 °C to form a transparent brown glass resin. After being charred at 350 °C, the obtained black powder precursor was subjected to heat treatment at 700–900 °C for 2–8 h in static air. They reported that pure per-

* Corresponding author.
E-mail address: hfyu@mail.tku.edu.tw (H.-F. Yu).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.10.109

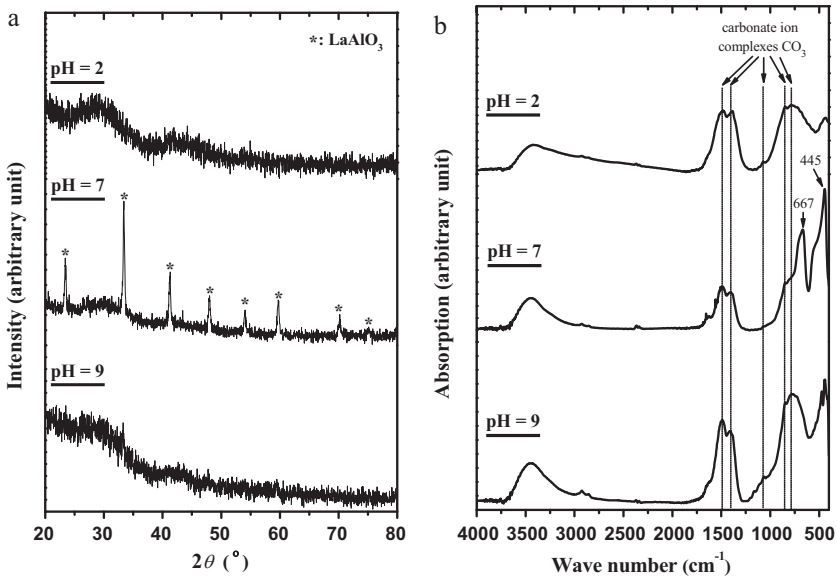

Fig. 1. (a) XRD patterns and (b) IR spectra for the specimens of pH 2 (without NH_4OH addition), 7 and 9 obtained at 600 °C for 9 h.

ovskite $LaAlO_3$ powders, with specific surface area in the range of 13–16 m^2/g, were formed at 700 °C for 8 h or at 750 °C for 2 h.

The citrate-precursor technique is one of potential methods to produce crystalline $LaAlO_3$ nanoparticles at relative low temperatures. Our previous work [23] demonstrated that pure crystalline $LaAlO_3$ particles with an average crystallite size of ~30 nm can be produced by calcining the citrate-derived solid precursor in air atmosphere at ≥800 °C. In this study, we tried to further reduce the forming temperature of crystalline $LaAlO_3$ particles by calcining the citrate-derived solid precursor in an oxygen-enriched atmosphere. Effects of calcination temperature and heating atmosphere on the formation of crystalline $LaAlO_3$ particles were investigated and discussed.

2. Experimental

A citrate-precursor method was used to prepare crystalline $LaAlO_3$ nanoparticles. $La(NO_3)_3{\cdot}6H_2O$ (98% purity, Janssen Chimica, Belgium) and $Al(NO_3)_3{\cdot}9H_2O$ (98% purity, Showa, Japan) were dissolved in de-ionized water to form an aqueous solution of 0.005 M. Citric acid [$C_3H_4(OH)(COOH)_3$; 95% purity, Showa, Japan] was added into the aqueous solution. The molar ratio of solutes in the solution was La^{+3}:Al^{+3}:$C_3H_4(OH)(COOH)_3$ = 1:1:1. The aqueous solution was stirred at room temperature for 3 h. Then, the pH of solutions was adjusted using NH_4OH (29 wt% purity, Fisher Scientific, USA); the solutions with three different pH values (i.e., pH 2 (without adding NH_4OH), 7, and 9) were prepared. After pH adjustment, the solution was continuously stirred for another 3 h, followed by evaporating water at 90 °C and then charring the organic contents at 350 °C for 1 h. The charred solid precursors were then calcined in air or oxygen atmosphere at temperatures ranging from 450 to 900 °C, using a heating rate of 5 °C/min.

Effects of pH of the starting solution, heating atmosphere, and calcination temperature on characteristics of the resultant particles were investigated using thermogravimetric and differential thermal analyses (TG and DTA; TG-DTA 2000, Mac Science, Tokyo, Japan), X-ray diffractometry (XRD; D8A, Bruker, Madison, WI, USA; X-ray wavelength = 0.154056 nm), and infrared spectroscopy (IR; Magna-IR spectrometer 550, Nicolet, Madison, WI, USA). Thermal analysis (TG and DTA) allows discovering the changes that occurred in the specimen during heating. By comparison with Joint Committee on Powder Diffraction Standards (JCPDS) files, XRD identified the crystalline phases and crystal structure that existed in the specimen. The average size (d) of $LaAlO_3$ crystallites in the specimen was estimated using Scherrer's equation (Eq. (1)):

$$d = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where λ is the wavelength of incident X-ray, β is the full width at half maximum (FWHM) value of the (1 1 0) XRD peak for $LaAlO_3$, and θ is the Bragg angle for the corresponding XRD peak. The sizes and morphologies of the citrate-derived $LaAlO_3$ particles were also observed by transmission electron microscopy (TEM; JEM-2100F, JEOL, Tokyo, Japan) and scanning electron microscopy (SEM; JSM-6500F, JEOL, Tokyo, Japan). IR analysis was used to distinguish the organic or inorganic functional groups that existed in the specimen.

3. Results and discussion

3.1. $LaAlO_3$ formation in air atmosphere

To find out the better pH condition to prepare crystalline citrate-derived $LaAlO_3$ particles, the reacting system was adjusted at three different pH values (i.e., pH 2 (without NH_4OH) addition, 7 and 9) and the resultant charred solid precursors were then calcined in air at 600 °C for 9 h. Fig. 1 shows the XRD patterns and IR spectra of the particles so obtained. The calcined particles at pH 2 and 9 were noncrystalline, but crystalline $LaAlO_3$ phase was detected for one obtained at pH 7 (see Fig. 1(a)). While IR analysis indicated the existence of bridging carbonate ion complexes CO_3 (the absorption bands at 1484, 1406, 1070, 852, and 785 cm^{-1}) [24] in all three specimens, the characteristic absorption bands for $LaAlO_3$ (the bands at 667 and 445 cm^{-1}) [23] were detected only in the specimen of pH 7, which was in agreement with the results obtained from XRD analysis. Accordingly, the condition of pH 7 was used to prepare citrate-derived $LaAlO_3$ particles and the thermal behavior of its charred solid precursor was investigated.

Fig. 2 shows the TG and DTA curves, being operated using a heating rate of 5 °C/min in a flowing air of 40 mL/min, of the charred solid precursor of pH 7. Below 350 °C, the weight of the specimen gradually decreased with increasing temperature, which was due to the evaporation of the physical absorbed water on the surface and in the pores of the solid. At 360–450 °C, the specimen experienced an exothermic change (DTA peak temperature at 410 °C), resulting in about 2.7% loss in weight. Starting from about 600 °C and ending at about 820 °C, two distinguishable exothermic changes were occurred in the specimen, resulting in more than 8.9% weight loss of the specimen.

To discover the effects of these exothermic changes on the compositions of the specimen, the charred solid precursor was calcined in air to the predesigned temperature (i.e., 600, 700 and 900 °C) for 3 h. The resultant solids were analyzed by XRD and IR. The corresponding XRD patterns and IR spectra are given in Fig. 3. While the charred solids and the specimens obtained at 600 °C were noncrystalline, the ones at ≥700 °C were composed of crystalline $LaAlO_3$. The IR spectra revealed that the charred solid contained

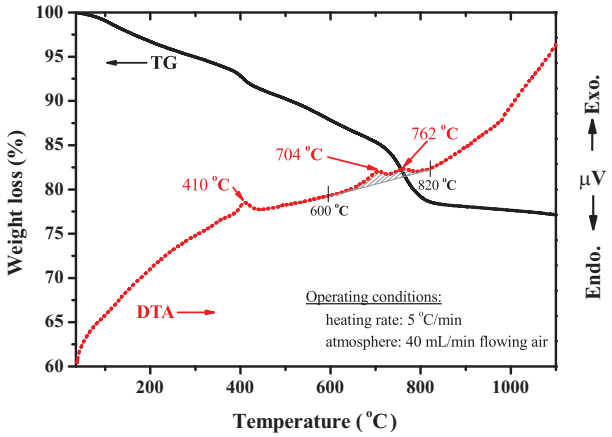

Fig. 2. Thermal behavior (TG and DTA curves) of the charred solid precursor of pH 7 in a flowing air atmosphere.

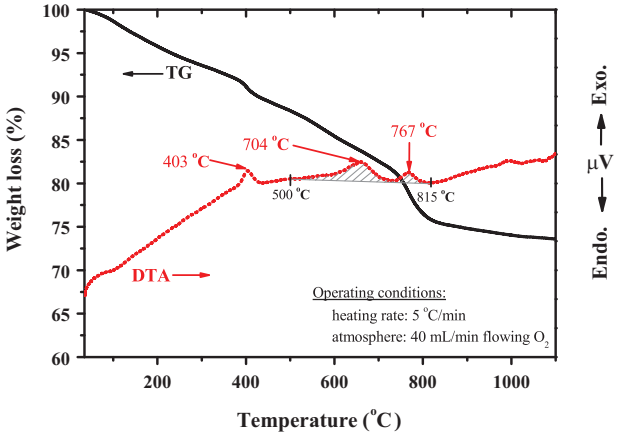

Fig. 4. Thermal behavior (TG and DTA curves) of the charred solid precursor of pH 7 in a flowing O_2 atmosphere.

bridging carbonate ion complexes CO_3 and some NO_3^- functional groups (1385 cm^{-1} for N–O stretching vibration) [24]. At 600 °C, the NO_3^- functional groups in the specimen were decomposed and the M–O (M = Al and/or La) bonding (the absorption bands at ~450 cm^{-1}) [23] was formed in the specimen. Heating up to 700 °C, the intensities of the characteristic absorption bands for bridging carbonate ion complexes CO_3 were greatly decreased and the absorption bands for crystalline $LaAlO_3$ (the absorption bands at 667 and 450 cm^{-1}) [23] were appeared in the IR spectrum. At 900 °C, the characteristic absorption bands for carbonate ion complexes CO_3 were not detected. Combining these XRD and IR results with the results from thermal analysis (i.e., TG and DTA curves in Fig. 2), it can be concluded that the exothermic change occurred at 360–450 °C is not only due to the oxidation of the char but also the removal of NO_3^- functional groups. The two successive exothermic changes taking place at 600–820 °C should be ascribed to the formation of crystalline $LaAlO_3$ and the oxidation/decomposition of bridging carbonate ion complexes, respectively.

The above analysis indicated that in air atmosphere the formation of crystalline $LaAlO_3$ from the charred solids of pH 7 was started at about 600 °C; however, the crystallization rate at this temperature was so slow that the specimen calcined at 600 °C with soaking time much less than 9 h was still noncrystalline (refer to Fig. 1(a) and Fig. 3(a)). On the other hand, the calcination temperature of 900 °C in air was required to completely remove the bridging carbonate ion complexes CO_3, as an intermediate, in the specimen to form pure crystalline $LaAlO_3$. At the heating course to form crystalline $LaAlO_3$ from the citrate-derived charred solid precursor, three major exothermic changes occurred in the specimen and most of these changes consumed oxygen from its ambient environment. If an oxygen-enriched atmosphere is provided during the calcination of the charred solid precursor, it should accelerate the corresponding reaction and probably lower the reaction temperatures. Accordingly, an attempt to lower the production temperature of pure crystalline citrate-derived $LaAlO_3$ nanoparticles was conducted by calcining the charred solid of pH 7 in an oxygen atmosphere.

3.2. $LaAlO_3$ formation in O_2 atmosphere

Fig. 4 shows the thermal behavior (i.e., TG and DTA curves) of the charred solid precursor of pH 7 in a flowing O_2 of 40 mL/min. Similarly to the one observed in a flowing air atmosphere (see Fig. 2), the charred solid precursor in O_2 atmosphere experienced successively three major exothermic changes at the heating course to 1100 °C, which corresponded to oxidation and decomposition of the char and the NO_3^- functional groups, formation of the crystalline $LaAlO_3$ and oxidation/decomposition of the bridging carbonate ion com-

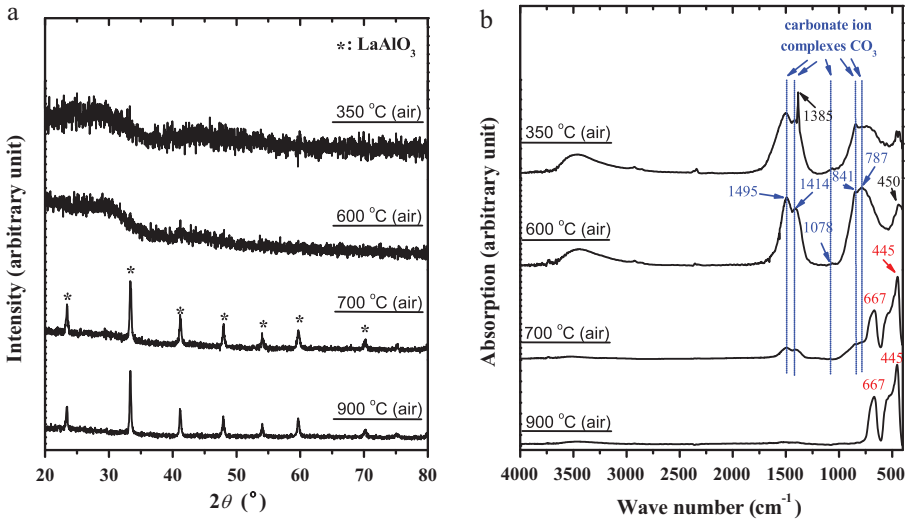

Fig. 3. (a) XRD patterns and (b) IR spectra for the charred solids (350 °C) of pH 7 and the solids obtained by heating the charred solids at three different temperatures.

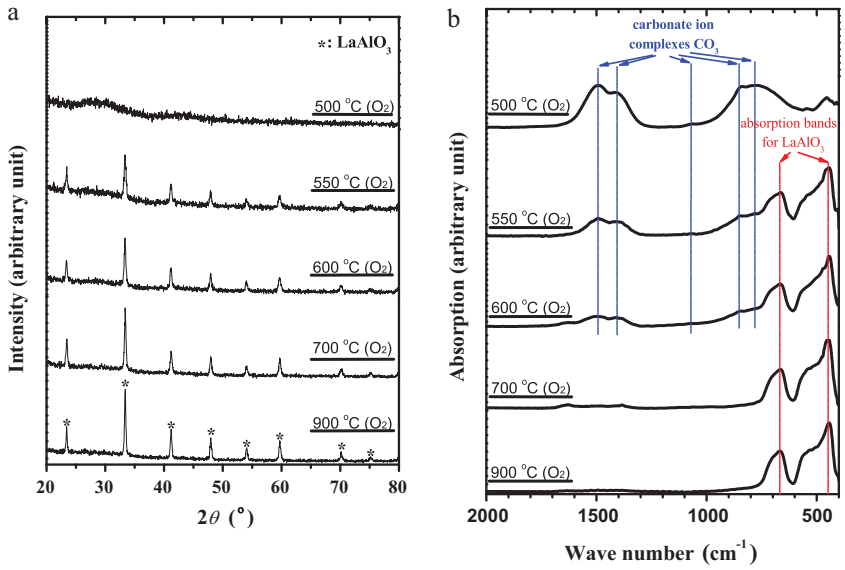

Fig. 5. (a) XRD patterns and (b) IR spectra for the charred solids of pH 7 calcined at five different temperatures for 3 h in an O_2 atmosphere.

plexes, respectively. However, the oxygen atmosphere triggered the reactions at lower temperatures. For example, the formation of crystalline $LaAlO_3$ was begun at about 500 °C, which is 100 °C lower than that in air. Based on the results obtained from the thermal analysis and the consideration of reaction rates, the charred solid precursor was heated, in an O_2 atmosphere, up to five different temperatures, ranging from 500 °C to 900 °C, for 3 h. The specimens so obtained were analyzed by XRD and IR. The corresponding XRD patterns and IR spectra are given in Fig. 5. Although soaking the solid at 500 °C in oxygen atmosphere for 3 h was not able to form crystalline $LaAlO_3$, $LaAlO_3$ crystallites was formed at ≥550 °C. It is to be mentioned that by heating the charred solid precursor at 500 °C in O_2 atmosphere for 4.5 h, $LaAlO_3$ crystalline phase was detected by XRD in the resultant specimen, but the degree of crystallinity of $LaAlO_3$ was low. Fig. 5(b) indicated that the carbonate ion complexes started to decompose at 550 °C in O_2 atmosphere and were completely removed to form pure crystalline $LaAlO_3$ particles at 700 °C in O_2 atmosphere.

Fig. 6 gives the average sizes (d) of $LaAlO_3$ crystallites obtained at different calcination temperatures. $LaAlO_3$ crystallites had an average size about 21 nm at 550 °C and grew linearly with increasing calcination temperature. At 900 °C, the $LaAlO_3$ crystallites reached an average size of about 28.3 nm. As mentioned previously, the value of d was estimated using Scherrer's equation (see Eq. (1)); to check the accuracy of the estimated d, the specimen at 900 °C was selected to conduct TEM measurement. Fig. 7 gives the TEM image of the citrate-derived $LaAlO_3$ crystallites at 900 °C, which reveled that the average size of the crystallites was in agreement with the estimated value of d.

Fig. 8 shows the SEM images of the $LaAlO_3$ particles obtained by calcining the charred solid precursor at four different temperatures in O_2 atmosphere. At 550 °C, the particles obtained were heavily agglomerated and were composed of the larger secondary particles. It is suspected that the agglomeration of particles should be due to the existence of the bridging carbonate ion complexes CO_3 in the specimen. At 600 °C, the amount of the carbonate ion complexes in the specimen was decreased (see Fig. 5(b)), resulting in a reduction of the degree of particle agglomeration. After being calcined at 700 °C in oxygen atmosphere, distinct pure $LaAlO_3$ nanoparticles (≤100 nm) were produced. At 900 °C, the $LaAlO_3$ nanoparticles tended to spheroidize in shape and the necking between the particles was observed, implying the citrate-derived

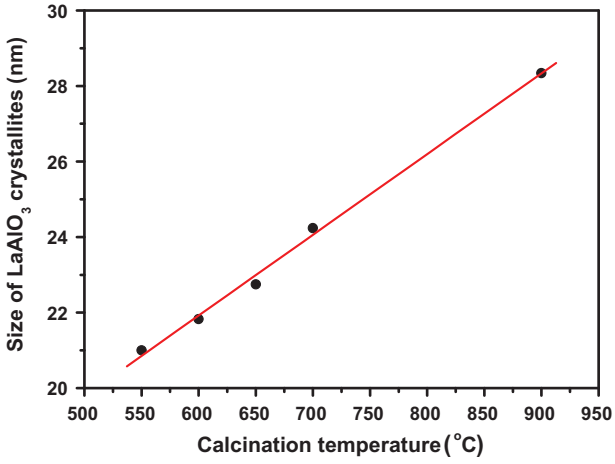

Fig. 6. Average sizes of $LaAlO_3$ crystallites obtained at different heating temperatures in O_2 atmosphere.

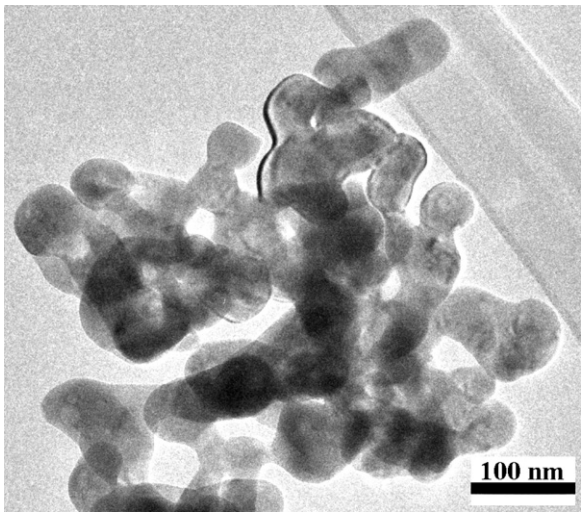

Fig. 7. TEM image of the citrate-derived $LaAlO_3$ crystallites obtained by calcining the charred solid precursor at 900 °C in O_2 atmosphere.

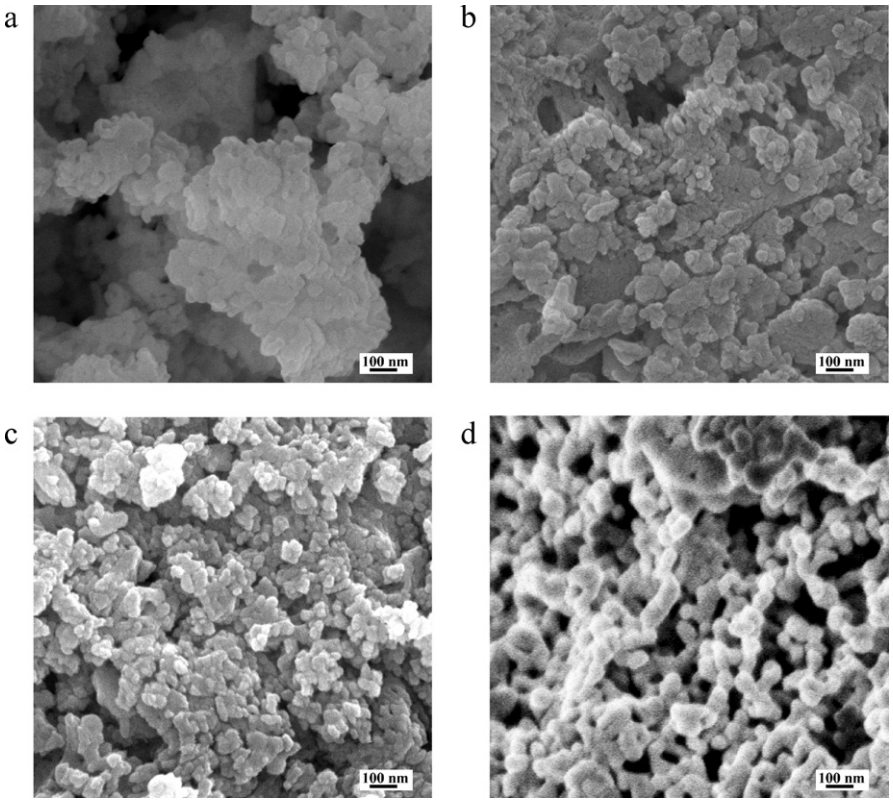

Fig. 8. SEM images of the citrate-derived $LaAlO_3$ particles obtained at (a) 550 °C, (b) 600 °C, (c) 700 °C, and (d) 900 °C in O_2 atmosphere.

$LaAlO_3$ nanoparticles in oxygen atmosphere possess high sinterability.

4. Conclusions

Pure $LaAlO_3$ nanoparticles were synthesized at temperature as low as 700 °C in an oxygen atmosphere, using a citrate-precursor technique. In air atmosphere, although crystalline $LaAlO_3$ can be formed by calcining the citrate-derived charred solid of pH 7 at 600 °C for 9 h, the calcination temperature much higher than 700 °C is required to remove all the intermediates and to produce pure $LaAlO_3$ particles. However, pure $LaAlO_3$ nanoparticles can be produced at 700 °C by simply changing the calcination atmosphere of the citrate-derived charred solid from air to oxygen. The $LaAlO_3$ nanoparticles so obtained had particle sizes less than 100 nm and possessed high sinterability.

References

[1] S.-Y. Cho, I.-T. Kim, K.S. Hong, J. Mater. Res. 14 (1999) 114.
[2] T. Tagawa, H. Imai, J. Chem. Soc. Faraday Trans. 1. Phys. Chem. Condens. Phases 84 (1988) 923.
[3] G.Y. Sung, K.Y. Kang, S.-C. Park, J. Am. Ceram. Soc. 74 (1991) 437.
[4] D.A. Atwood, B.C. Yearwood, J. Organomet. Chem. 600 (2000) 186.
[5] C.-S. Hsu, C.-L. Huang, Mater. Res. Bull. 36 (2001) 1939.
[6] M. Nieminen, T. Sajavaara, E. Rauhala, M. Putkonen, L. Niinistö, J. Mater. Chem. 11 (2001) 2340.
[7] Q.X. Fu, F. Tietz, P. Lersch, D. Stöver, Solid State Ionics 117 (2006) 1059.
[8] C.-L. Kuo, C.-L. Wang, T.-Y. Chen, G.-J. Chen, I.-M. Hung, C.-J. Shih, K.-Z. Fung, J. Alloys Compd. 440 (2007) 367.
[9] R. Elsebrock, C. Makovicka, P. Meuffels, R. Waser, J. Electroceram. 10 (2003) 193.
[10] T.A. Vanderah, C.K. Lowe-Ma, D.R. Gagnon, J. Am. Ceram. Soc. 77 (1994) 3125.
[11] W. Li, M.W. Zhuo, J.L. Shi, Mater. Lett. 58 (2004) 365.
[12] P.K. Sahu, S.K. Behera, S.K. Pratihar, S. Bhattacharyya, Ceram. Int. 30 (2004) 1231.
[13] M. Chroma, J. Pinkas, I. Pakutinskiene, A. Beganskiene, A. Kareiva, Ceram. Int. 31 (2005) 1123.
[14] S.N. Koc, F. Oksuzomer, E. Yasar, S. Akturk, M.A. Gurkaynak, Mater. Res. Bull. 41 (2006) 2291.
[15] A. Barrera, S. Fuentes, M. Viniegra, M. Avalos-Borja, N. Bogdanchikova, J. Campa-Molina, Mater. Res. Bull. 42 (2007) 640.
[16] A.K. Adak, P. Pramanik, Mater. Lett. 30 (1997) 269.
[17] Q. Zhang, F. Saito, J. Am. Ceram. Soc. 83 (2000) 439.
[18] Z. Li, S. Zhang, W.E. Lee, J. Eur. Ceram. Soc. 27 (2007) 3201.
[19] M. Kakihana, T. Okubo, J. Alloys Compd. 266 (1998) 129.
[20] D. Zhou, G. Huang, X. Chen, J. Xu, S. Gong, Mater. Chem. Phys. 84 (2004) 33.
[21] D. Hreniak, W. Strek, P. Dereń, A. Bednarkiewicz, A. Łukowiak, J. Alloys Compd. 408–412 (2006) 828.
[22] P.J. Dereń, M.A. Weglarowicz, P. Mazur, W. Strek, J. Lumin. 122–123 (2007) 780.
[23] H. Yu, J. Wang, S. Wang, Y. Kuo, J. Phys. Chem. Solids 70 (2009) 218.
[24] G. Socrates, Infrared and Raman Characteristic Group Frequencies—Tables and Charts, third ed., John Wiley and Sons, New York, 2001.