Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 34 (2008) 443–446
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Short communication

Synthesis of $LaAlO_3$ powder using triethanolamine

Songlin Ran, Lian Gao *

State Key Lab of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Science, Shanghai 200050, PR China

Received 10 May 2006; received in revised form 28 August 2006; accepted 20 October 2006
Available online 2 January 2007

Abstract

$LaAlO_3$ powders were successfully synthesized by pyrolysis of complex compounds of lanthanum and aluminum with triethanolamine (TEA). The precursors and the derived powders were characterized by simultaneous thermogravimetry analysis (TG) and differential scanning calorimetry analysis (DSC), X-ray diffractometry (XRD), specific surface area measurements, and transmission electron microscopy (TEM). Pure $LaAlO_3$ phase was obtained at 775 °C for 2 h or 750 °C for 4 h, without formation of any intermediate phase. Pores were found from TEM images of $LaAlO_3$ powders prepared at 800 °C for 2 h.

Keywords: A. Powders: chemical preparation; A. Precursors: organic

1. Introduction

Lanthanum aluminate ($LaAlO_3$) ceramic with its high quality factor, high dielectric constant and zero temperature coefficient of resonant frequency is widely used as a substrate for high temperature superconductor [1] and ferroelectric thin films [2]. Due to its high surface area and catalytic activity, $LaAlO_3$ powders have also been used as catalyst for oxidative coupling of methane and hydrogenation and hydrogenolysis of hydrocarbons [3].

Traditional synthesis of $LaAlO_3$ powders from stoichiometric mixed oxide powders usually requires a temperature higher than 1500 °C [4]. This solid-state reaction process presents several drawbacks, such as high reaction temperature, large particle size, limited chemical homogeneity and low sintering ability. Various low temperature (750–900 °C) chemical routes have evolved for preparing finer and homogeneous powders such as co-precipitation [5], sol–gel [6], aerosol-furnace technique [7] and citrate-combustion route [8]. Sahu et al. have synthesized $LaAlO_3$ powders from low cost metal chlorides precursors by gelation–precipitation technique at a temperature of 600 °C [9]. It is well known that chlorine ions are very difficult to be rinsed off. Adak et al. prepared pure lanthanum aluminate powders by the evaporation of polyvinyl alcohol added to a mixed metal nitrate solution at 675 °C [10]. However, the size of the particles was not described. The sizes of cerium(IV) oxide and cordierite particles prepared by this method are >200 nm and 1–100 μm, respectively [11,12].

Recently triethanolamine (TEA) has been used to prepare nanosized oxide powders [13,14]. In this route, triethanolamine is used as a complex agent, keeping the metal ions in a homogeneous solution, which leaves sufficient flexibility for the system to exist homogeneously throughout the reaction without undergoing precipitation. The route involves dehydration of the solution of metal–TEA complex, followed by decomposition of the TEA complex. Complete dehydration of the resulting solution to dryness results in a voluminous, organic-based, black, fluffy mass. The dried carbonaceous mass is ground to fine powders to produce the precursor material. Heat treatment of the precursor results in nanosized powders [15]. In this paper we describe the synthesis of $LaAlO_3$ powders by the TEA gel route for the first time.

2. Experimental

The raw materials that were used for the preparation of $LaAlO_3$ were Al $(NO_3)_3{\cdot}9H_2O$, La_2O_3, HNO_3 and triethanolamine (TEA). First, $Al(NO_3)_3$ and La $(NO_3)_3$ solutions (La_2O_3

---

* Corresponding author. Tel.: +86 21 52412718; fax: +86 21 52413122.
E-mail address: liangaoc@online.sh.cn (L. Gao).

0272-8842/$34.00 © 2006 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2006.10.012

powders dissolved in nitric acid) were mixed to maintain the La:Al molar ratio at 1:1. Then, TEA was added into the mixed solution with constant stirring. At the beginning, TEA formed precipitates with metal ions. This precipitate dissolved, and a clear solution was obtained by adding concentrated HNO_3 to maintain a final pH value of 3–4. The clear solutions of TEA complex metal nitrates were evaporated at 100 °C with constant stirring for dehydration. Thereafter, it was placed on a hot plate at about 200 °C, leaving behind voluminous, organic-based, black, fluffy powders. This precursor powders were ground and calcined at various temperatures for different times. Other researches [14,15] have indicated that the particle size decreases with an increase in the amount of TEA. Thus the TEA to total metal ion ratio was fixed to 6:1 in the present experiment.

The powder phase composition was identified using X-ray diffractometry (XRD; Model D/MAX-2550V, Rigaku Co., Tokyo, Japan). Simultaneous thermogravimetry (TG) and differential scanning calorimetry (DSC) analysis (Model NETZSCH STA 409 PC/PG, Bayern, Germany) at a heating rate of 10 °C/min in static air were employed to analyze the oxidation and decomposition process of the precursor. The morphologies of the powders were examined using transmission electron microscopy (TEM; Model 200, JEOL, Tokyo, Japan). The specific surface area measurements were performed by the conventional BET technique with a nitrogen adsorption apparatus (Model ASAP 2010, Micromeritics Instruments, Norcross, USA).

3. Results and discussion

TG/DSC curves of the $LaAlO_3$ precursor are shown in Fig. 1. There are two exothermic peaks in the DSC curve. The sharp peak at 382 °C is assigned to the major decomposition of the metal–TEA complexes. Another exothermic peak is at 456 °C, corresponding to the oxidation of carbonaceous matters which are obtained from the decomposition of the metal–TEA complexes present in the system. A total weight loss of 69.4% is indicated by the TG curve, caused by the burning and decomposition of the precursor, which release a large amount of gases such as CO_2, NH_3, NO_2, and water vapor.

Fig. 2 shows XRD patterns of the powders heated at various temperatures for 2 h. After calcined at 700 °C for 2 h, only a broad arciform continuum could be found at about 30°, no sharp crystal phase peak exists, which means that the powders are still amorphous. When calcined at 775 °C for 2 h, all the peaks in the XRD pattern are in accordance with those of $LaAlO_3$ (JCPDS No. 85-0848). Then, after calcined at 800 °C for 2 h, the diffraction peaks are sharper, which implies that the crystalline structure tends to be more integrated. Fig. 3 shows XRD patterns of the powders heated at 750 °C for different times. After calcined at 750 °C for 2 h, only (1 1 0) peak appears. When the calcination time is prolonged to 4 h, all the peaks exist. The intensity of the peaks increased with the prolonged calcination time. From Figs. 2 and 3, it could be seen clearly that rising temperature and prolonging dwelling time are two effective ways to the formation of $LaAlO_3$ phase.

Although La_2O_3, Al_2O_3 and $LaAl_{11}O_{18}$ might present as intermediate phases in the course of synthesis of $LaAlO_3$ powders, only $LaAlO_3$ phase (with the resolution limit of XRD) is detected and no intermediate phase is observed in the present situation. Therefore, it could be considered that $LaAlO_3$ crystallized directly from the amorphous precursor without the formation of any intermediate phase. The reason is that the chelation between complex cations and TEA can result in a uniform distribution of La^{3+} and Al^{3+} in the molecular level,

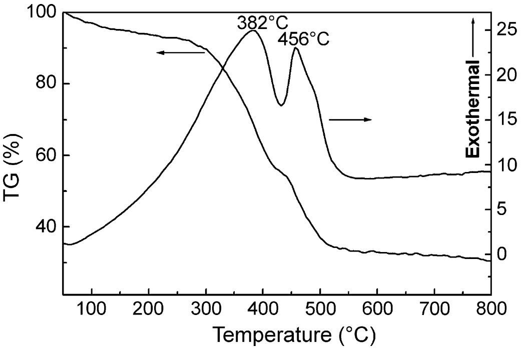

Fig. 1. TG/DSC curves of the $LaAlO_3$ precursor.

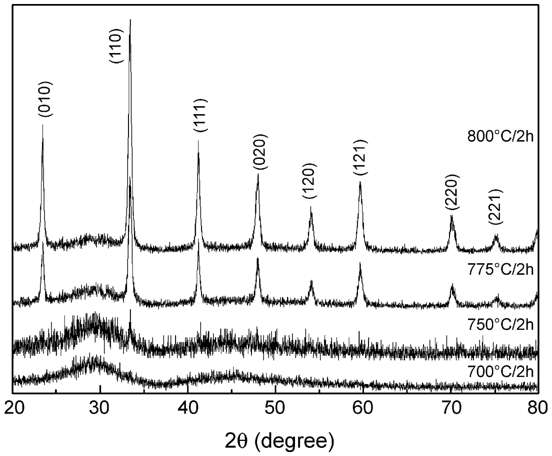

Fig. 2. XRD patterns of the powders heated at various temperatures for 2 h.

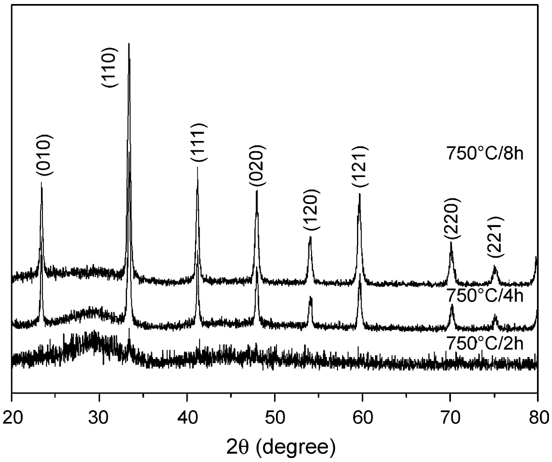

Fig. 3. XRD patterns of the powders heated at 750 °C for different times.

Table 1
Variation of BET surface area and average particle size with different calcination temperatures

Calcination temperature (°C)	S_{BET} (m^2/g)	D_{BET} (nm)
800	21.25	43
900	15.60	59
1100	13.17	70
1300	9.92	93

which could be maintain in the precursor after dehydration and decomposition.

Table 1 shows the variation of BET surface area and average particle size of the powders heated at different temperatures for 2 h. The average particle size (D_{BET}) obtained from surface area was calculated based on the equation:

$$D_{\mathrm{BET}} = \frac{6}{\rho S_{\mathrm{BET}}},$$

where ρ is the theoretical density of the powders (6.529 g/cm^3); S_{BET} is the BET surface area of the powders. It is shown that the specific surface area of the powders decrease with increasing calcination temperature, indicating the growth and aggregation of the powders at higher temperature.

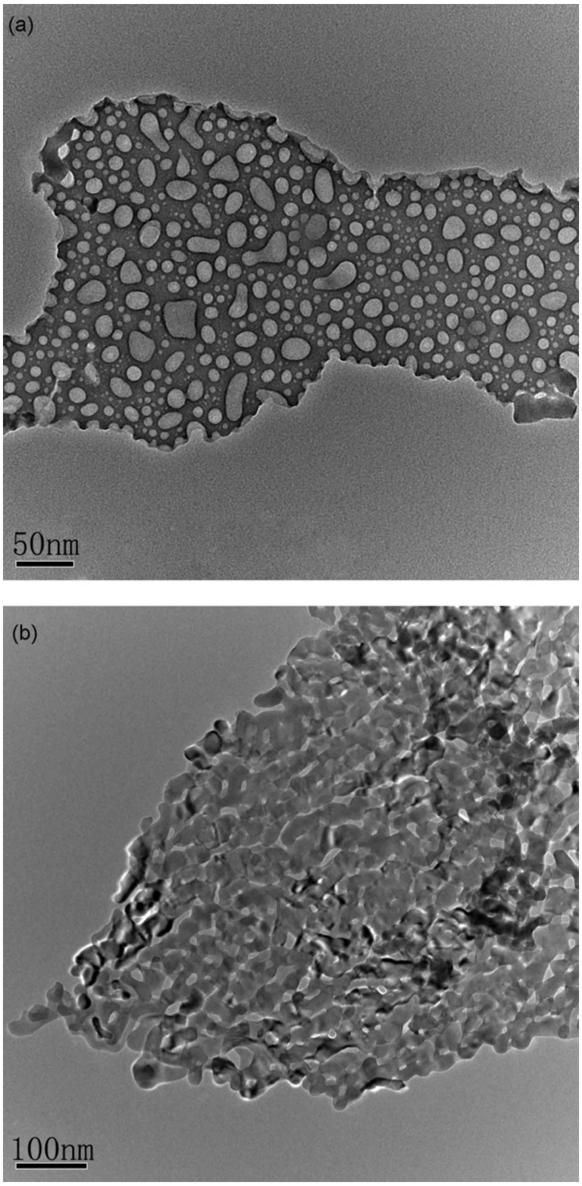

Fig. 4. TEM micrographs of the $LaAlO_3$ powders obtained at 800 °C for 2 h.

Fig. 4 gives TEM micrographs of the $LaAlO_3$ powders obtained at 800 °C for 2 h. Fig. 4a and b shows two different kinds of porous networks. The porous networks shown in Fig. 4b are the aggregation and combination of those of Fig. 4a. During the decomposition, the metal–TEA complexes expand rapidly and give off a large amount of gases which result in a loose and porous structure. These porous powders can be used as carrier for catalyst or honeycomb substrate material.

4. Conclusions

$LaAlO_3$ powders were successfully prepared through the thermal decomposition of metal–TEA complexes at 775 °C for 2 h or 750 °C for 4 h, without formation of any intermediate phase. The formation of porous $LaAlO_3$ powders in the present process is attributed to two factors: (1) strong complexing ability of TEA with the metal ions enables a homogeneous distribution of the metal cations throughout the liquid phase during the dehydration process; (2) rapid expansion of the metal–TEA complexes and the evolution of a large amount of gases during pyrolysis help to produce porous powders.

References

[1] R.W. Simon, C.E. Platt, A.E. Lee, G.S. Lee, K.P. Daly, M.S. Wire, J.A. Luine, M. Urbanik, Low-loss substrate for epitaxial growth of high-temperature superconductor thin films, Appl. Phys. Lett. 53 (1988) 2677–2679.

[2] Y. Gim, T. Hudson, Y. Fan, C. Kwon, A.T. Findikoglu, B.J. Gibbons, B.H. Park, Q.X. Jia, Microstructure and dielectric properties of $Ba_{1-x}Sr_xTiO_3$ films grown on $LaAlO_3$ substrates, Appl. Phys. Lett. 77 (2000) 1200–1202.

[3] R. Spinicci, P. Marini, S.D. Rossi, M. Faticanti, P. Porta, Oxidative coupling of methane on $LaAlO_3$ perovskites partially substituted with alkali or alkali-earth ions, J. Mol. Catal. A: Chem. 176 (2001) 253–265.

[4] G.Y. Sung, K.Y. Kang, S.C. Park, G.Y. Sung, K.Y. Kang, S.C. Park, Synthesis and preparation of lanthanum aluminate target for radio-frequency magnetron sputtering, J. Am. Ceram. Soc. 74 (1991) 437–439.

[5] K. Vidyasagar, J. Gopalkrishnan, C.N.R. Rao, Synthesis of complex metal oxides using hydroxide, cyanide, and nitrate solid solution precursors, J. Solid State Chem. 58 (1985) 29–37.

[6] P. Peshev, V. Slavova, Preparation of lanthanum aluminate thin films by a sol–gel procedure using alkoxide precursors, Mater. Res. Bull. 29 (1994) 255–261.

[7] B.C. Lux, R.D. Clark, A. Salazan, L.K. Sveumand, M.A. Krebs, Aerosol generation of lanthanum aluminate, J. Am. Ceram. Soc. 76 (1993) 2669–2672.

[8] M.D.S. Kumar, T.M. Srinivasan, P. Ramasamy, C. Subramanian, Synthesis of lanthanum aluminate by a citrate-combustion route, Mater. Lett. 25 (1995) 171–174.

[9] P.K. Sahu, S.K. Behera, S.K. Pratihar, S. Bhattacharyya, Low temperature synthesis of microwave dielectric $LaAlO_3$ nanoparticles: effect of chloride on phase evolution and morphology, Ceram. Inter. 30 (2004) 1231–1235.

[10] A.K. Adak, P. Pramanik, Synthesis and characterization of lanthanum aluminate powder at relatively low temperature, Mater. Lett. 30 (1997) 269–273.

[11] P. Duran, F. Capel, D. Gutierrez, J. Tartaj, C. Moure, Cerium (IV) oxide synthesis and sinterable powders prepared by the polymeric organic complex solution method, J. Eur. Ceram. Soc. 22 (2002) 1711–1721.

[12] S.J. Lee, W.M. Krivene, Crystallization and densification of nano-size amorphous cordierite powder prepared by a PVA solution–polymerization route, J. Am. Ceram. Soc. 81 (1998) 2605–2612.

[13] R.N. Das, A. Pathak, P. Pramanik, Low-temperature preparation of nanocrystalline lead zirconate titanate and lead lanthanum zirconate titanate powders using triethanolamine, J. Am. Ceram. Soc. 81 (1998) 3357–3360.

[14] R.K. Pati, J.C. Ray, P. Pramanik, Synthesis of nanocrystalline α-alumina powder using triethanolamine, J. Am. Ceram. Soc. 84 (2001) 2849–2852.

[15] Y.Q. Liu, L. Gao, Low-temperature synthesis of nanocrystalline yttrium aluminum garnet powder using triethanolamine, J. Am. Ceram. Soc. 86 (2003) 1651–1653.