ELSEVIER

Ceramics International 32 (2006) 57–60

CERAMICS
INTERNATIONAL

www.elsevier.com/locate/ceramint

Synthesis of $La(Mg_{1/2}Ti_{1/2})O_3$ powder through ethylenediaminetetraacetic acid gel combustion

Yebin Xu [a,*], Xiao Yuan [a], Peixiang Lu [a], Guohua Huang [b], Chunlian Zeng [c]

[a] *The State Key Laboratory of Laser Technology, Huazhong University of Science and Technology, Wuhan, Hubei 430074, PR China*
[b] *Department of Physics, Nanning Teachers' College, Nanning, Guangxi 530001, PR China*
[c] *School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou, Guangdong 510275, PR China*

Received 29 October 2004; received in revised form 9 November 2004; accepted 3 January 2005
Available online 7 March 2005

Abstract

Single-phase $La(Mg_{1/2}Ti_{1/2})O_3$ has been prepared by ethylenediaminetetraacetic acid (EDTA) gel combustion synthesis process. The process starts with a pH adjusted aqueous solutions of $La(NO_3)_3$, $Mg(NO_3)_2{\cdot}6H_2O$, $Ti(OC_4H_9)_4$, and EDTA. Combustion reactions occur when heating the gel to 250 °C, which convert them to $La(Mg_{1/2}Ti_{1/2})O_3$ with traces of carbonaceous material directly. The derived powders were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, SEM and laser particle size distribution analysis.

Keywords: $La(Mg_{1/2}Ti_{1/2})O_3$; Ethylenediaminetetraacetic acid; Combustion synthesis

1. Introduction

Complex oxides with perovskite-like structures are attractive candidates for use in wireless communication applications, which require a combination of high permittivity (ε), near zero temperature coefficient of the resonant frequency (τ_f), and high quality factor (Q). $Ba(Mg_{1/3}Ta_{2/3})O_3$ and $Ba(Mg_{1/3}Ta_{2/3})O_3$ were found to have superior microwave dielectric properties suited to temperature-stable microwave resonators [1,2]. On the other hand, complex perovskites $A(B'_{1/2}B''_{1/2})O_3$ ($A = Me^{2+}$, Me^{3+}, $B' = Me^{2+}$, Me^{3+}; $B'' = Me^{4+}$, Me^{5+}, Me^{6+}) feature moderate permittivities of 20–35 combined with small negative τ_f values and high quality factors [3–8]. The $A(B'_{1/2}B''_{1/2})O_3$ compounds can be combined with the materials having positive τ_f to form the solid solution with zero τ_f [9–11].

In $A(B'_{1/2}B''_{1/2})O_3$ family, $La(Mg_{1/2}Ti_{1/2})O_3$ has been reported to be a promising microwave dielectrics having ε ~25–29 and $Q \times f = 75{,}500$ GHz [7,8]. It is suitable substrate for $YBa_2Cu_3O_x$ thin film used in microwave applications. Generally, the preparation of $La(Mg_{1/2}Ti_{1/2})O_3$ ceramics are performed by a conventional solid-state reaction of mechanically mixed powders. The inevitable inhomogeneity that is inherent to this technique inhibits the required compositional and microstructural homogeneity of sintered products. To date, very few literatures reported the low temperature synthesis of single phase $La(Mg_{1/2}Ti_{1/2})O_3$. As a wet chemical method, ethylenediaminetetraacetic acid gel route [12–15] has been widely used to prepare superconductors, microwave dielectrics and $BaTi_2O_5$, but the synthesis of $La(Mg_{1/2}Ti_{1/2})O_3$ via this route has not been reported.

In this paper, the low temperature synthesis of $La(Mg_{1/2}Ti_{1/2})O_3$ powder through auto-ignition of the ethylenediaminetetraacetic acid gel is reported. The $La(Mg_{1/2}Ti_{1/2})O_3$ powders obtained through this technique were characterized by XRD, FTIR, SEM and laser particle size analysis.

2. Experimental procedure

2.1. Preparation of specimens

Butyl titanate ($Ti(OC_4H_9)_4$), La_2O_3, $Mg(NO_3)_2{\cdot}6H_2O$, 65–68% nitric acid, EDTA and ammonium hydroxide

---

* Corresponding author. Tel.: +86 27 87543755; fax: +86 27 87543755.
E-mail address: xuyebin@yahoo.com (Y. Xu).

0272-8842/$30.00 © 2005 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2005.01.002

solution were used as the starting materials. EDTA was dissolved in ammonium hydroxide solution (NH_3 25% by weight in water), to which butyl titanate was added gradually with continuous stirring. The solution was heated at 80 °C on a hot plate and nitric acid was added to the stirred solution to adjust the pH of the solution to 4. When the opaque, white solution became a clear, light yellow color, then $La(NO_3)_3$ (La_2O_3 dissolved in nitric acid) and $Mg(NO_3)_2{\cdot}6H_2O$ was added slowly to the EDTA-Ti solution. The molar ratio of EDTA to total metal cations concentration EDTA/M was important and chosen to be unity. With the dissolution of $Mg(NO_3)_2{\cdot}6H_2O$, the solution became clear, and then nitric acid was added to adjust the pH of solution to about 0.5. Thermal dehydration of the pH adjusted solutions to evaporate the excess solvent (at 80 °C on a hot plate), resulted in the highly viscous yellowish gel. The gel was heated further at 140 °C until it became a deep brown resin with high viscosity. Throughout the process, no signs of precipitation were observed. The sample beaker was removed from the hot plate and placed into an oven immediately to char the resin at 250 °C for 30 min. The resin swelled and ignited with an evolution of a large volume of gaseous products. The auto-ignition resulted in a voluminous $La(Mg_{1/2}Ti_{1/2})O_3$ powder with traces of carbonaceous material. Finally, the as prepared powder was calcined at 500–1000 °C for 2 h in static air.

For the purpose of comparison, LMT was also prepared by the conventional solid-state reaction. The powders La_2O_3, MgO and TiO_2 were mixed in the stoichiometric proportion and ball-milled for 6 h in planetary mills. The as-dried material was calcined at 1200 °C for 2 h in static air.

2.2. Analysis of specimens

The phases were identified by powder X-ray diffraction (XRD) analysis using a Rigaku D/Max-IIIB diffractometer with Cu Kα radiation. Fourier transform infrared spectroscopy (FT-IR) was used to determine the chemical bonding of the $La(Mg_{1/2}Ti_{1/2})O_3$. Scanning electron microscopy (SEM) was used to observe the morphology of powders. The particle size distribution of $La(Mg_{1/2}Ti_{1/2})O_3$ powder was determined by laser scattering particle size analyzer.

3. Results and discussions

In this EDTA gel combustion method, the pH of solution plays an important role. In the process of forming EDTA-Ti solution, nitric acid has to add to adjust the pH of solution to 4, otherwise precipitation will occur [13,14]. In the process of forming gel, If the pH of solution is larger than 5, the solution is stable, but the solution cannot form gel. It was necessary to decrease the pH of the solution to about 0.5. With the addition of nitric acid, white precipitation occurred. Adding nitric acid continuously at 80 °C to decrease the pH of solution to about 0.5, the solution became transparent again. The solution is stable at 80 °C and the gel can be obtained, although the precipitation will develop at room temperature [15].

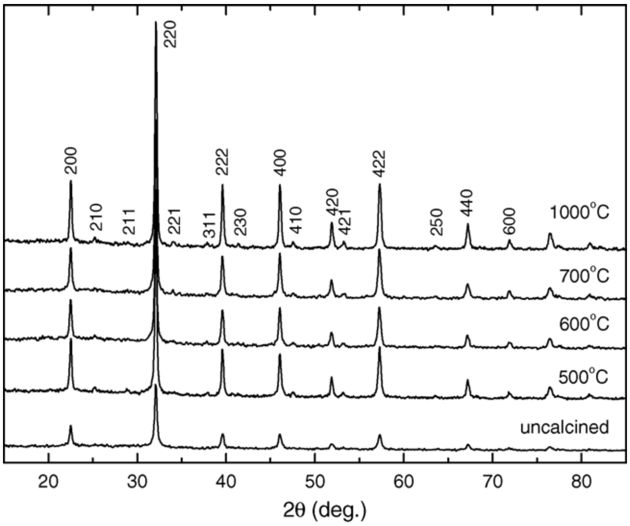

Fig. 1. XRD patterns of the $La(Mg_{1/2}Ti_{1/2})O_3$ powders: uncalcined and after calcination at various temperatures for 2 h.

Fig. 1 shows the XRD patterns of $La(Mg_{1/2}Ti_{1/2})O_3$ powders. The XRD pattern of the $La(Mg_{1/2}Ti_{1/2})O_3$ powder obtained after combustion shows the characteristic peaks of well crystalline $La(Mg_{1/2}Ti_{1/2})O_3$. Crystallinity of the powders drastically increases with an increase in the post-synthesis calcination temperature and no other significant changes in the XRD patterns are observed. The XRD patterns are in excellent accord with JCPDS card 49–242 and all diffraction lines could be indexed in a cubic system.

Fig. 2 shows the FT-IR spectra of $La(Mg_{1/2}Ti_{1/2})O_3$ powders. The strong and sharp absorption bands at 1382 and 1494 cm^{-1} can be attributed to the vibrational modes of carboxylate ions. Broadened absorption band at 3440 cm^{-1} associate with the O–H stretch of intermolecular hydrogen

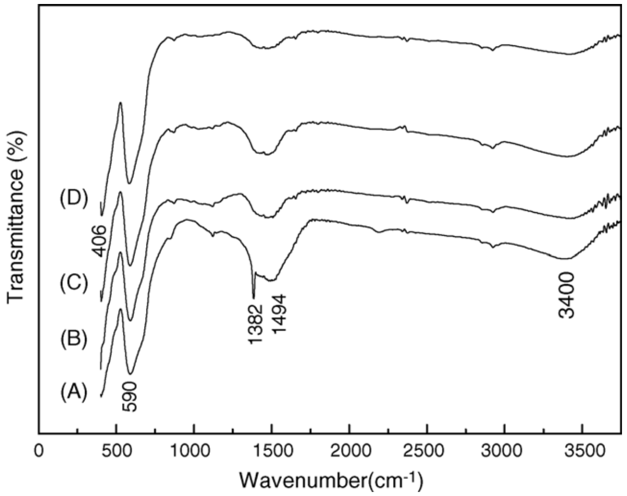

Fig. 2. FTIR spectra of the $La(Mg_{1/2}Ti_{1/2})O_3$ powders: (A) uncalcined and after calcination at (B) 500 °C; (C) 600 °C; (D) 1000 °C for 2 h.

bonds or molecular water. The band at 590 and 406 cm^{-1} correspond to metal–oxygen stretching vibration and metal–oxygen bending vibration, respectively [16]. The spectrum of crystalline $\mathrm{La(Mg_{1/2}Ti_{1/2})O_3}$ is similar to that of pervoskite titanates and niobates.

The SEM photographs of the $\mathrm{La(Mg_{1/2}Ti_{1/2})O_3}$ powders shown in Fig. 3, reflect the foamy and agglomerate particle nature of the powder. The surfaces of the powders show a lot of pores, which may be formed by the evolved gases during combustion. Fig. 4 shows the particle size distribution curves of the $\mathrm{La(Mg_{1/2}Ti_{1/2})O_3}$ powders after calcination at 700 and 1000 °C for 2 h. Increasing the calcination temperature from 700 to 1000 °C, the average agglomerate particle size of $\mathrm{La(Mg_{1/2}Ti_{1/2})O_3}$ powders remain unchanged almost except particles with size greater than 60 μm disappear. Therefore, the higher calcination temperature breaks more agglomeration and narrow the particle size distribution of $\mathrm{La(Mg_{1/2}Ti_{1/2})O_3}$ powder.

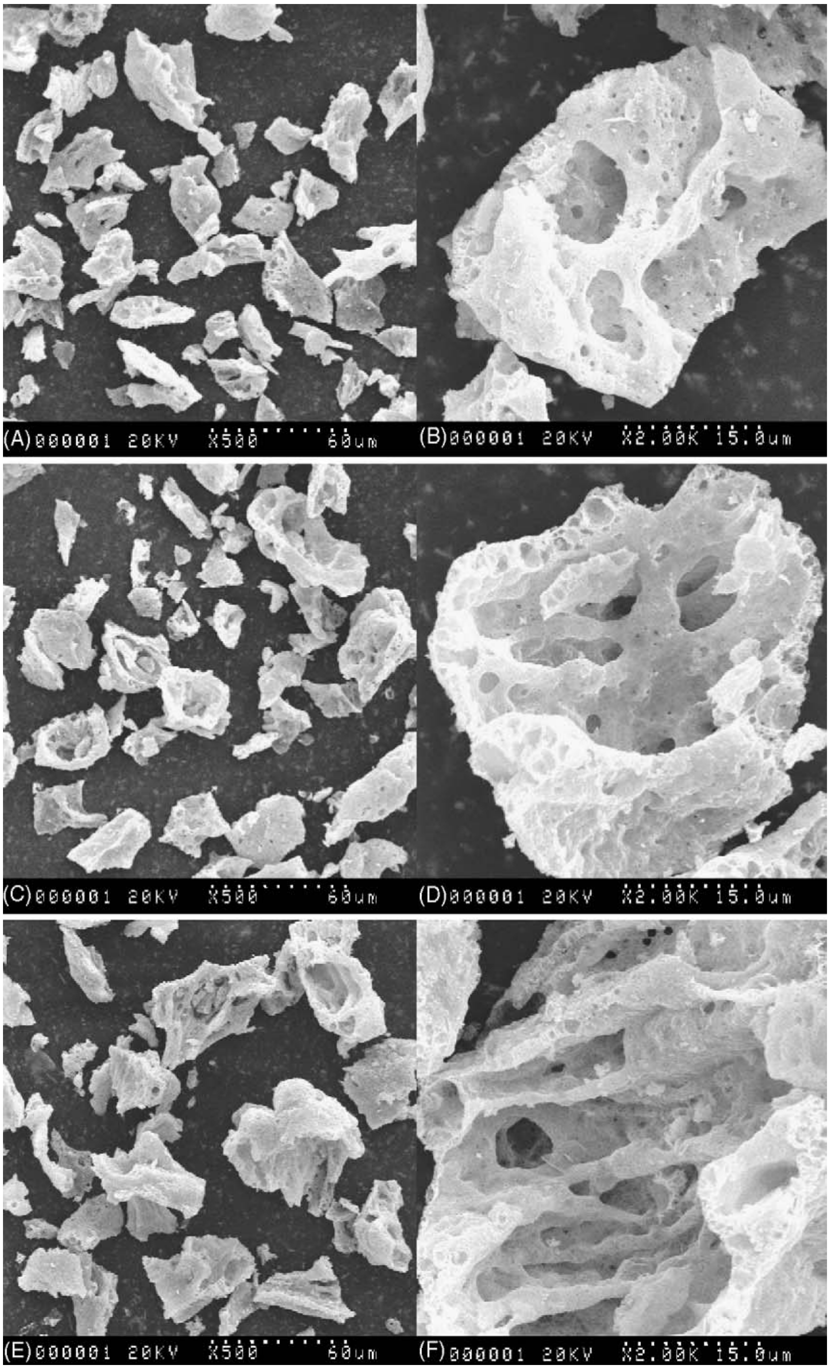

Fig. 3. SEM photographs of the $\mathrm{La(Mg_{1/2}Ti_{1/2})O_3}$ powders after calcination at different temperatures for 2 h: (A and B) 500 °C; (C and D) 700 °C; and (E and F) 1000 °C.

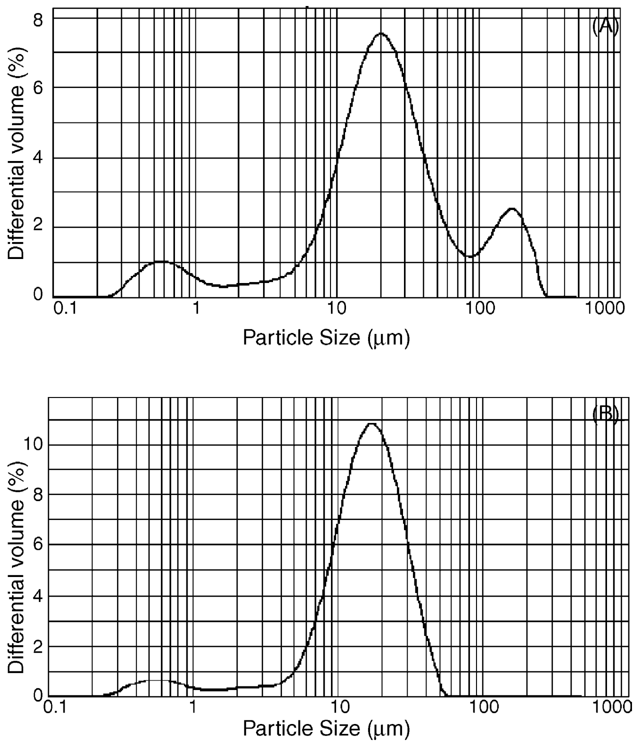

Fig. 4. Grain size distribution of the $La(Mg_{1/2}Ti_{1/2})O_3$ powders after calcination at: (A) 700 °C and (B) 1000 °C for 2 h.

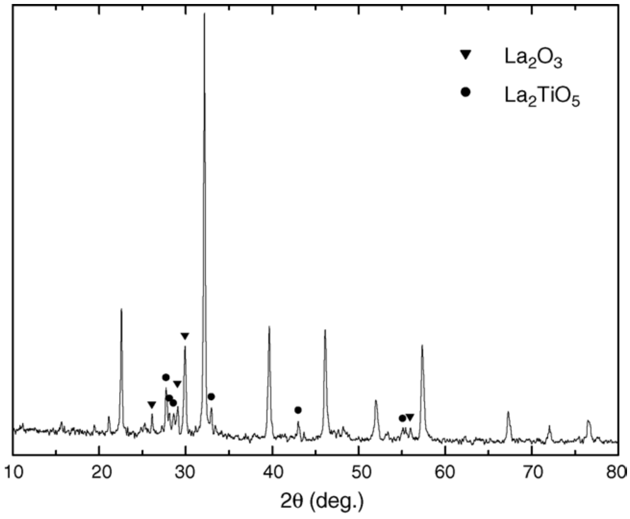

Fig. 5. XRD pattern of the products obtained by solid-state reactions at 1200 °C for 2 h.

Fig. 5 shows XRD pattern of the products obtained after calcining an intimate mixture of La_2O_3, MgO and TiO_2 in static air at 1200 °C for 2 h. $La(Mg_{1/2}Ti_{1/2})O_3$ phase forms as a major phase, but the reflections from La_2O_3 and La_2TiO_5 can still be found clearly. Therefore, the EDTA gel combustion technique can lower the crystallization temperature of $La(Mg_{1/2}Ti_{1/2})O_3$ by at least 700 °C.

4. Conclusions

$La(Mg_{1/2}Ti_{1/2})O_3$ powders were successfully synthesized through ethylenediaminetetraacetic acid gel (EDTA) combustion route. The auto-ignition of the EDTA gel directly resulted in voluminous $La(Mg_{1/2}Ti_{1/2})O_3$ powder with traces of carbonaceous material. The pH of solution was found to have a significant influence on the gel formation.

Acknowledgment

X. Yuan is grateful for the support of National Natural Science Foundation of China under grant number 60171034.

References

[1] S. Kawashima, M. Nishida, I. Ueda, H. Ouchi, $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics with low dielectric loss at microwave frequencies, J. Am. Ceram. Soc. 66 (1983) 421–423.

[2] S. Nomura, K. Toyama, K. Kaneta, $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics with temperature-stable high dielectric constant and low microwave loss, Jpn. J. Appl. Phys. 21 (1982) 624–626.

[3] M. Takata, K. Kageyama, Microwave characteristics of $A(B_{1/2}^{3+}B_{1/2}^{5+})O_3$ ceramics (A = Ba, Ca, Sr; B^{3+} = La, Nd, Sm, Yb; B^{5+} = Nb, Ta), J. Am. Ceram. Soc. 72 (1989) 1955–1959.

[4] H. Kagata, J. Kato, Dielectric properties of Ca-based complex perovskite at microwave frequencies, Jpn. J. Appl. Phys. 33 (1994) 5463–5465.

[5] J. Takahashi, K. Kageyama, T. Fujii, T. Yamada, K. Kodaira, Formation and microwave dielectric properties of $Sr(Ga_{0.5}Ta_{0.5})O_3$-based complex perovskites, J. Mater. Sci. Mater. Electron. 8 (1997) 79–84.

[6] S. Kucheiko, H.J. Kim, D.H. Yeo, H.J. Jung, Microwave dielectric properties of $LaZn_{0.5}Ti_{0.5}O_3$ ceramics prepared by sol–gel process, Jpn. J. Appl. Phys. 35 (1996) 668–672.

[7] S.Y. Cho, C.H. Kim, D.W. Kim, K.S. Hong, J.H. Kim, Dielectric properties of $Ln(Mg_{1/2}Ti_{1/2})O_3$ as substrates for high-T_c superconductor thin films, J. Mater. Res. 14 (1999) 2484–2487.

[8] G. Harshe, A.S. Bhalla, L.E. Cross, Synthesis and dielectric properties of a cubic perovskite: $La(Mg_{1/2}Ti_{1/2})O_3$, Mater. Lett. 18 (1994) 173–175.

[9] D.H. Yeo, J.B. Kim, J.H. Moon, S.J. Yoon, H.J. Kim, Dielectric properties of $(1-x)CaTiO_{3-x}La(Zn_{1/2}Ti_{1/2})O_3$ ceramics at microwave frequencies, Jpn. J. Appl. Phys. 35 (1996) 663–667.

[10] M.P. Seabra, M. Avdeev, V.M. Ferreira, R.C. Pullarb, N.McN. Alford, Structure and microwave dielectric properties of $La(Mg_{0.5}Ti_{0.5})O_3$–$CaTiO_3$ system, J. Eur. Ceram. Soc. 23 (2003) 2403–2408.

[11] I. Levin, J.Y. Chan, J.E. Maslar, T.A. Vanderah, Phase transitions and microwave dielectric properties in the perovskite-like $Ca(Al_{0.5}Nb_{0.5})O_3$–$CaTiO_3$ system, J. Appl. Phys. 90 (2001) 904–914.

[12] J. Fransaer, J.R. Roos, L. Delaey, O. Van Der Biest, O. Arkens, J.P. Celis, Sol–gel preparation of high-Tc Bi–Ca–Sr–Cu–O and Y–Ba–Ca–O superconductors, J. Appl. Phys. 65 (1989) 3277–3279.

[13] Y.B. Xu, X.M. Chen, L.B. Wang, Sol–gel preparation of $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$, J. Am. Ceram. Soc. 84 (2001) 669–671.

[14] Y.B. Xu, G.H. Huang, H. Long, Sol–gel synthesis of $BaTi_2O_5$, Mater. Lett. 57 (2003) 3570–3573.

[15] Y.B. Xu, G.H. Huang, H. Long, Synthesis of lanthanum aluminate via the ethylenediaminetetraacetic acid gel route, Ceram. Int. 29 (2003) 837–840.

[16] J.T. Last, Infrared-absorption studies on barium titanate and related materials, Phys. Rev. 105 (1957) 1740–1750.