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Synthesis of lanthanum aluminate via the ethylenediaminetetraacetic acid gel route

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Abstract

$LaAlO_3$ was successfully synthesized by the ethylenediaminetetraacetic acid gel route. The precursors and the derived powders were characterized by differential thermal analysis, thermogravimetric analysis, Fourier transform infrared spectroscopy and X-ray diffraction. Well-crystallized $LaAlO_3$ phase was obtained at 800 °C for 2 h, without formation of any intermediate phase.

Keywords: EDTA; Powder; $LaAlO_3$; Synthesis

1. Introduction

Lanthanum aluminate ($LaAlO_3$) with a perovskite-type structure has excellent microwave dielectric properties and very low lattice constant mismatch with high temperature superconductor and barium strontium titanate ferroelectrics. It is widely used as a substrate for high temperature superconductor [1] and ferroelectric thin films [2]. $LaAlO_3$ has a negative temperature coefficient of resonant frequency ($\tau_f = -44 ppm/°C$), it can be mixed with other dielectrics with positive τ_f, such as $SrTiO_3$ [3] and $La_{2/3}TiO_3$ [4], to form a solid solution with τ_f close to 0.

Generally, $LaAlO_3$ can be prepared with solid-state reaction of aluminium oxide (Al_2O_3) and lanthanum oxide (La_2O_3) [5–8]. A number of wet chemical methods have been developed to synthesize $LaAlO_3$ at a lower temperature. Synthesis of $LaAlO_3$ from lanthanum nitrate and aluminium nitrate precursors via an aerosol-furnace technique was reported by Lux et al. and annealing at 1100 °C for 1 h was required to form pure $LaAlO_3$ [9]. Kumar et al. [10] prepared $LaAlO_3$ by the self-ignited combustion process of a corresponding nitrate–citrate precursor at 700 °C for 4 h. Taspinar and Tas [11] synthesized $LaAlO_3$ by homogeneous precipitation from aqueous solutions containing urea (CH_4N_2O) in the presence of nitrate salts and heating the precipitate at 850 °C. The self-propagating combustion synthesis of an aqueous solution containing CH_4N_2O and the respective nitrate salts of lanthanum and aluminum yielded phase pure $LaAlO_3$ after heating at 750 °C for 16 h. Shoup et al. [12] prepared well-crystallized $LaAlO_3$ powders at 800 °C from an all alkoxide sol-gel route. Adak et al. [13] obtained pure $LaAlO_3$ powder by heating a mixture of polyvinyl alcohol and a mixed metal nitrate solution at 675 °C for 2 h. Using the polymerized complex technique based upon in situ polyesterification between citric acid and ethylene glycol, Kakihana et al. [14] synthesized pure perovskite lanthanum aluminate by heating at 700 °C for 8 h or at 750 °C for 2 h. Mentruit et al. [15] prepared $LaAlO_3$ via an all alkoxide (aluminium isopropoxide and lanthanum ethoxide) sol-gel route, the powder obtained at 600 °C for 6 h have 50 $m^2\ g^{-1}$ specific surface area. Iketani et al. [16] prepared $LaAlO_3$ at 900 °C for 1 h starting with a hydrazine monohydrate solution.

The ethylenediaminetetraacetic acid (EDTA) gel method has been used to synthesize superconductor oxides [17] and microwave dielectrics [18]. The main advantage of the method stems from the large stability constant of most EDTA complexes and the large number of elements with which EDTA forms complexes. In this paper we synthesized $LaAlO_3$ powder by the EDTA gel route.

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2. Experimental

The procedure used to prepare $LaAlO_3$ by the EDTA gel route is shown in Fig. 1. EDTA was dissolved in ammonium hydroxide solution, followed by the addition of $La(NO_3)_3$ solution (La_2O_3 powder dissolved in nitric acid) and aluminium nitrate nonahydrate ($Al(NO_3)_3$ $9H_2O$). With the addition of $La(NO_3)_3$ solution and $Al(NO_3)_3$ $9H_2O$, the solution pH decreased. If the solution pH was less than 5, EDTA would precipitate. Therefore, it was necessary to add ammonium hydroxide solution. During the process, the molar ratio of EDTA to total metal cations concentration EDTA/M was 1 and the cation ratio of La:Al = 1:1.

After achieving complete dissolution, the resultant colourless solution was heated at about 80 °C with continuous stirring on a hot plate to evaporate superfluous water for 1–2 h, and then nitric acid was added to decrease the solution pH to about 0.5. With the addition of nitric acid, an unidentified white precipitation occurred. Adding nitric acid continuously at 80 °C, the solution became transparent again. If the temperature of solution is less than 80 °C, the formed precipitation would not dissolve. On the other hand, if enough nitric acid was rapidly added to adjust the solution pH to about 0.5, the formation of intermediate precipitation can be avoided. The solution, while stirred with a magnetic stirrer, was heated for several hours at 140 °C. The solution became highly viscous and it finally gelled to a transparent brown resin. Throughout the process, no signs of precipitation or turbidity were observed. Porous resin intermediates, i.e. precursor powders, were obtained by charring the resin at 250 °C for 2 h. This solid resin precursor was pulverized and then calcined at 750–1000 °C for 2 h to obtain $LaAlO_3$.

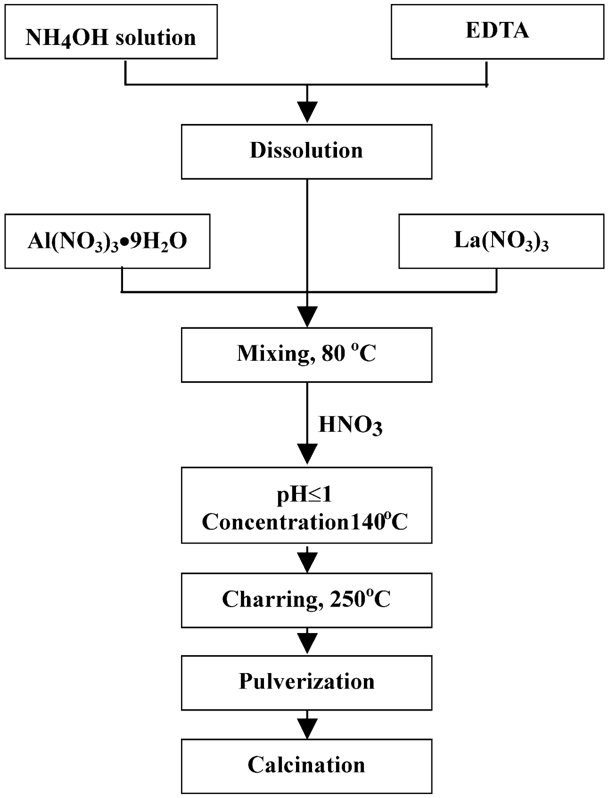

Fig. 1. Flow chart for the preparation of $LaAlO_3$ ceramic powders.

Differential thermal analysis (DTA) and thermogravimetric (TG) analysis were employed to analyse the decomposition and oxidation process of the precursor at a heating rate of 20 °C/min under static air. Fourier transform infrared spectroscopy (FT-IR) was used to determine the chemical bonding of the $LaAlO_3$ precursor and $LaAlO_3$ precursor calcined at 800 °C for 2 h. The spectrometer (Nexus model, Thermo Nicolet Corporation) was controlled by a computer system and software package called OMNIC (Version 6.0a). X-ray diffraction (XRD) analysis using a Rigaku D/Max-IIIB diffractometer with monochromatic CuK_α radiation was used to identify the phases of the samples. The operating condition was 30 kV and 30 mA. Scans were conducted at 8°/min at a sampling interval of 0.02.

3. Results and discussions

In this procedure, the solution pH plays an important role in the formation of gel. When the solution pH is greater than 5, the solution is stable at both room temperature and high temperature ($\geqslant 80$ °C), but a transparent gel cannot be formed. If the solution pH is greater than 1, white, silky clusters will first form during the concentration process and then the clusters rapidly increase in quantity; finally the solution becomes an opaque, white mass. Therefore it is very important to adjust the solution pH to about 0.5 in this experiment.

Fig. 2 shows the results of differential thermal analysis (DTA) and thermogravimetric (TG) analysis for the $LaAlO_3$ precursor. The first weight loss in the TG curve

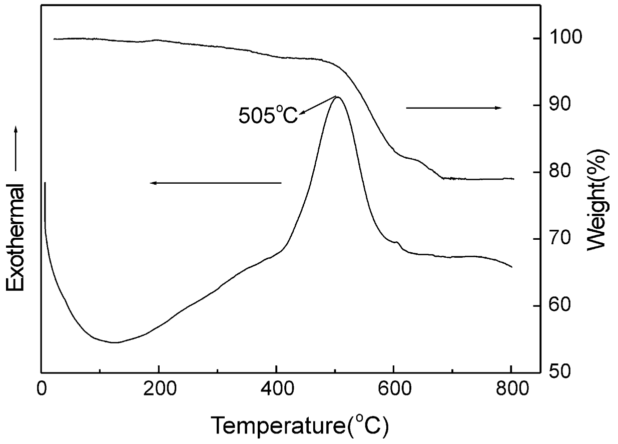

Fig. 2. TG and DTA curves for $LaAlO_3$ precursor heated: air at 20 °C/min.

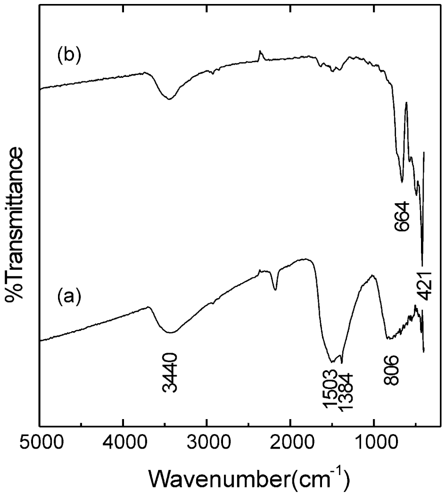

Fig. 3. FT-IR spectra of $LaAlO_3$ prepared by EDTA gel route. (a) precursor powder, (b) after calcination of precursor powder at 800 °C for 2 h.

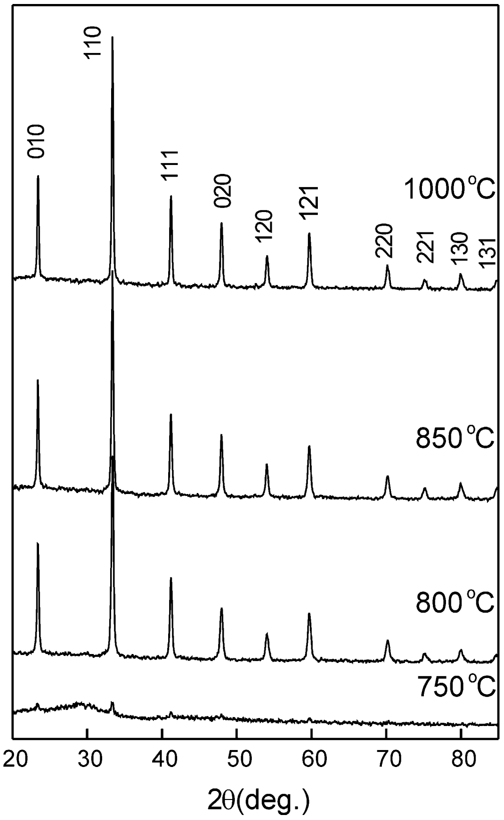

Fig. 4. XRD patterns of the $LaAlO_3$ powder calcined at various temperatures for 2 h.

is due to the dehydration of the precursor. The endothermic peak around 505 °C in the DTA curve, accompanied by the sharp weight loss, is due to the breakup of EDTA compounds into carbonates and nitrates, volatilization of NH_4NO_3 and the elimination of residual CO_3^{2-} and NO_3^-. During this period, the polymer network broke down into smaller organic moieties [17,19], and some of them containing no metal ion volatilized. The weight loss around 640 °C in the TG curves is associated with further oxidation of the sample. TG shows that the decomposition of the precursor has almost no weight change after 700 °C.

Fig. 3 shows the FT-IR spectra of $LaAlO_3$ precursor and calcined powder at 800 °C for 2 h. The strong and sharp absorption bands at 1384 and 1503 cm^{-1} can be attributed to the vibrational modes of carboxylate ions. The broad absorption band at 3440 cm^{-1} is associated with the O–H stretch of intermolecular hydrogen bonds or molecular water. The band at 806 cm^{-1} corresponds to nitrate ions. After calcining the $LaAlO_3$ precursor at 800 °C for 2 h, the bands corresponding to carboxylate ions and nitrate ions disappear and new bands at 421 and 664 cm^{-1} are observed. These bands are assigned to AlO_6 octahedra in $LaAlO_3$, which is the only crystalline phase in accordance with the XRD analysis. Our results are similar to that reported by Adak et al. [13].

Fig. 4 shows the XRD patterns of the precursor calcined in static air at 750–1000 °C for 2 h. After being heated at 750 °C in air for 2 h, the powder is almost amorphous, as is characterized by the broad continuum, but some weak XRD peaks show up in addition to the continuum, which correspond to reflections from rhombohedral $LaAlO_3$. Heating the precursors to 800 °C yields pure rhombohedral $LaAlO_3$ with a perovskite structure, and the XRD patterns are in excellent accord with JCPDS card 85-848. With increasing heating to 850 and 1000 °C, the diffraction peaks become stronger and sharper, reflecting greater crystallization. No other significant changes are observed and all diffraction lines could be indexed in a pseudo-cubic system. Furthermore, no peaks are observed for any other phases.

4. Conclusion

$LaAlO_3$ was synthesized via an EDTA gel route. The solution pH affected the formation of gel. XRD analysis showed that a pure perovskite $LaAlO_3$ formed directly from the precursors at 800 °C for 2 h, without the formation of any intermediate phase.

Acknowledgements

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