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Ceramics International 34 (2008) 1703–1707
CERAMICS INTERNATIONAL
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Synthesis of lanthanum beta-alumina powders by the polymeric precursor technique

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Received 10 March 2007; received in revised form 21 March 2007; accepted 10 May 2007
Available online 10 August 2007

Abstract

La-β-Al_2O_3 ($LaAl_{11}O_{18}$) powders were synthesized by the polymeric precursor technique using lanthanum nitrate and aluminum nitrate. The transformations during thermal treatment of the precursor solution with ethylene glycol and citric acid were evaluated by thermal analysis. Fourier transform infrared spectroscopy analysis was performed after calcinations of the polymeric resin for determination of residual carbon. The specific surface area was evaluated by the BET method. Fine powders with ~121 m^2/g specific surface area and 20 nm average particle size were obtained and observed by scanning and transmission electron microscopy. Nearly single phase $LaAl_{11}O_{18}$ was obtained after pressing and sintering these powders at 1600 °C with small additions of MgO. The sintered pellets were characterized by X-ray diffraction and scanning electron microscopy. Impedance spectroscopy measurements carried out in the 1000–1200 °C range show the electrolytic behavior of the La-β-Al_2O_3 pellets, suggesting their application as solid electrolytes in high temperature potentiometric oxygen sensors.

Keywords: A. Powders: chemical preparation; C. Electrical conductivity; D. β-Al_2O_3; E. Sensors

1. Introduction

One of the most important applications of ceramic solid electrolytes is for monitoring oxygen levels at high temperatures, e.g. in steelmaking processes [1]. The monitoring is essential for the required quality of the final product [2]. High temperature oxygen sensors are assembled with high melting point ceramic materials to withstand the high temperature of molten steels in the 1500–1700 °C range, and to have a lifetime large enough to enable data to be collected before disruption of the sensor at these harsh conditions. Zirconia based solid electrolytes are widely used in commercial sensors to control the oxygen content in molten steels due to their high oxide ion conductivity and thermal shock resistance [3]. However, these solid electrolytes are not suitable for measuring low oxygen potentials (<200 ppm [2]) because at these oxygen levels they show a significant n-type electronic conductivity at high temperatures, short-circuiting the signal [2]. Another solid electrolyte, La-β-Al_2O_3 (also known as lanthanum hexaluminate, La_2O_3–$11Al_2O_3$ or $LaAl_{11}O_{18}$ [4,5]), has been proposed to be used in devices for determining low oxygen levels in molten steels [5]. La-β-Al_2O_3 has been synthesized by several techniques: sol–gel [6,7], solid state reaction [8], coprecipitation of lanthanum and aluminum nitrates [9], and by mixing La_2O_3, α-Al_2O_3 and $4MgCO_3{\cdot}Mg(OH)_2{\cdot}6H_2O$ followed by grinding, calcining, pressing and sintering [10]. It has also been reported that the densification and the electrical properties of La-β-Al_2O_3 can be improved by addition of MgO [11,12]. La-β-Al_2O_3 was used as an ionic conductor to determine the standard molar Gibbs energy of lanthanum zirconate formation, a thermodynamic application for electromotive force measurements on a galvanic cell [13]. La-β-Al_2O_3 solid electrolyte has also been proposed for the measurement of sulfur content in steel with less than ~50 ppm of oxygen using La_2O_2S + La_2O_3 as an auxiliary electrode [10].

In this work La-β-Al_2O_3 was prepared by the polymeric precursor method (Pechini technique). Among other chemical preparation techniques, the Pechini technique is a simple way to prepare ceramic powders and gives higher yield than that obtained by solid state reaction of elemental oxides. It is based on the ability of certain alpha-hydroxycarboxylic acids to form polybasic acid chelates with a large number of cations. After

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0272-8842/$34.00
doi:10.1016/j.ceramint.2007.05.009

chelation between the complex cation and citric acid, the polyesterification of an excess of hydroxycarboxylic acid with glycol occurs by heating the solution to form a viscous resin [14–17]. The ceramic powders are obtained after calcination of the polymeric resin.

In this work, an experimental sequence for the synthesis of single-phase La-β-Al_2O_3 ceramic powders by the polymeric precursor technique was established. The powders were sintered and the high temperature electrical response of sintered pellets was evaluated by impedance spectroscopy, taking into account the possibility of using these pellets in sensing devices for monitoring oxygen content at high temperatures.

2. Experimental

Commercial $Al(NO_3)_3{\cdot}9H_2O$ (Vetec), $La(NO_3)_3{\cdot}6H_2O$ (Vetec) and MgO (Baker Analyzed) were used. The precursor solutions of aluminum, lanthanum and magnesium were prepared by adding aluminum nitrate, lanthanum nitrate and magnesium oxide to ethylene glycol and citric acid and heating at 90 °C under continuous stirring. The precursor solutions were mixed in the molar ratios 1La:11Al:xMg (x = 0.015, 0.08 and 1.2) and calcined at 120 °C to promote the polyesterification reaction. The polymeric solutions were calcined at 350 °C for 4 h and the resultant black powder was then heated at 800 °C for 4 h. This material was milled in an attritor with zirconia grinding media and isopropyl alcohol at 1200 rpm during 1 h.

For evaluating the decomposition stages of the La-β-Al_2O_3 polymeric resin, thermogravimetry and differential thermal analyses were performed under the following conditions: from 25 to 1400 °C with 10 °C/min heating and cooling rates, under synthetic air (50 cm^3/min), with α-Al_2O_3 powder as reference, in a model STA409 Netzsch thermal analyzer.

The La-β-Al_2O_3 ceramic powders were characterized by laser scattering (CILAS 1064) for evaluation of the particle size distribution, by diffuse reflectance FTIR (Magna IR 560 Nicolet) in the 400–4000 cm^{-1} range for searching residual carbon species, by BET analysis (Micromeritics-ASAP 2000) for determination of specific surface area, and by electron microscopy (SJEM-200C) for observation of the powder morphology.

After characterization, the powders were pressed into cylinders (10 mm diameter × 1 mm thickness) by uniaxial (100 MPa) followed by isostatic (200 MPa) compaction. The pellets were sintered at 1200, 1300, 1400, 1500 and 1600 °C for 2 h with a 10 °C/min heating rate. Sintering was performed with the pellets positioned inside an alumina crucible with a powder bed of the same composition of the pellets to maintain the initial stoichiometry. The density of the sintered pellets did not show appreciable dependence on the MgO content (x = 0.015, 0.08 and 1.2 mol). Results shown hereafter are for La-β-Al_2O_3 prepared with 1.2 mol% MgO. The specimens were analyzed by X-ray diffraction (Bruker-AXS, D8 Advance) with Cu Kα radiation, 40 kV–40 mA, 30–80 2θ range, 0.05 step size and 5 s counting time per step, and by scanning electron microscopy (Philips-XL 30).

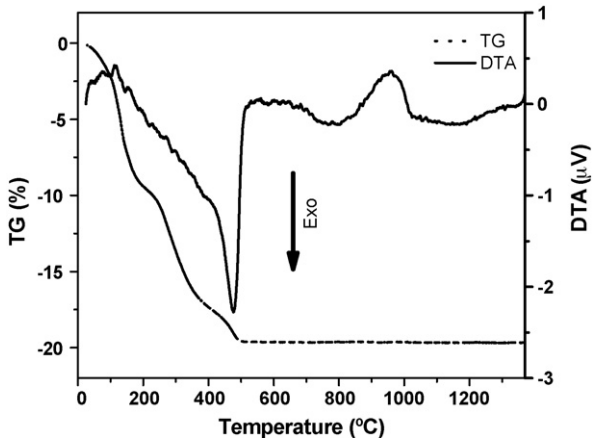

Fig. 1. Thermogravimetric and differential thermal analysis of La-β-Al_2O_3 prepared by the polymeric precursor technique.

For electrical measurements, platinum paste was applied to the parallel surfaces of the sintered specimens and cured at 800 °C. The electrical properties were studied by impedance spectroscopy in the 1 kHz–10 MHz frequency range in the 1000–1200 °C range with a Hewlett-Packard 4192A LF impedance analyzer. An alumina sample holder with a S-type thermocouple, with its junction close to the specimen, and platinum leads were used inside a resistive furnace.

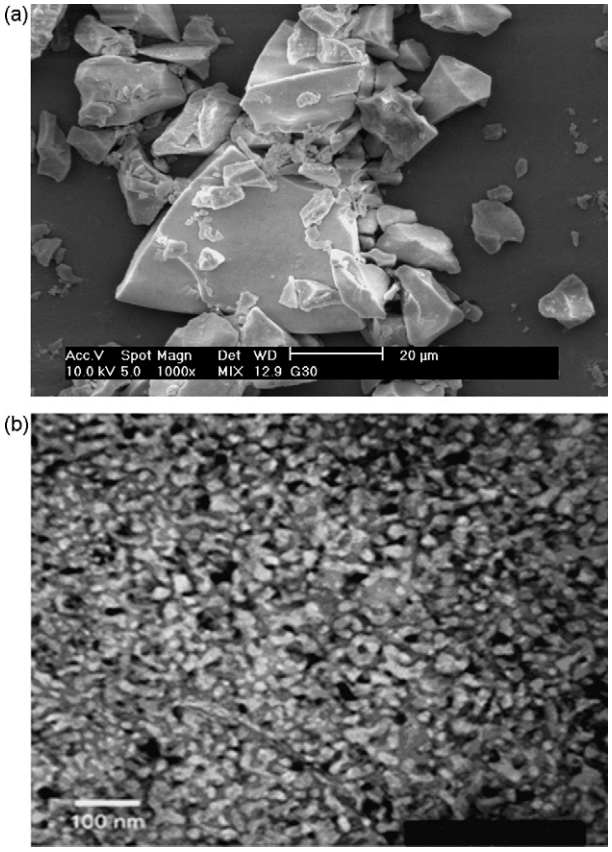

Fig. 2. Scanning electron microscopy (a) and transmission electron microscopy (b) micrographs of a powder dispersion of La-β-Al_2O_3 prepared by the polymeric precursor technique.

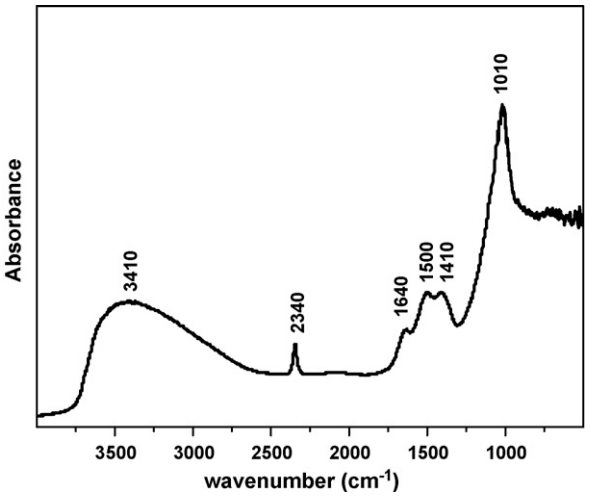

Fig. 3. Diffuse reflectance infrared Fourier transform spectroscopy analysis of La-β-Al_2O_3 prepared by the polymeric precursor technique.

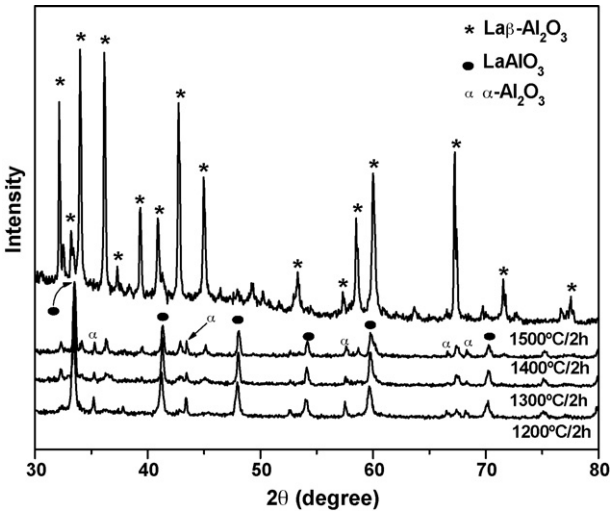

Fig. 4. X-ray diffraction patterns of La-β-Al_2O_3 sintered pellets for different sintering temperatures.

3. Results and discussion

Fig. 1 shows the results of thermal analysis of La-β-Al_2O_3 ceramic powders prepared by the polymeric precursor technique. The differential thermal analysis curve shows an endothermic reaction that starts at approximately 100 °C with a sharp peak at 500 °C, related to a 20% mass loss without further loss of mass up to approximately 1400 °C. The loss of mass upon heating at 10 °C/min proceeds by at least three steps: the first, for increasing temperature from room temperature to approximately 250 °C is due to water removal; the second, from that temperature to approximately 350 °C is probably related to pyrolysis of organic materials; the last one, associated to the sharp endothermic peak in the DTA curve, may be assigned to the decomposition of $La_2(CO_3)_3$. The endothermic process occurring from 1160 to 1400 °C is associated to the formation of the main desired phase, La $Al_{11}O_{18}$, via the formation of the $LaAlO_3$ precursor [18]. The

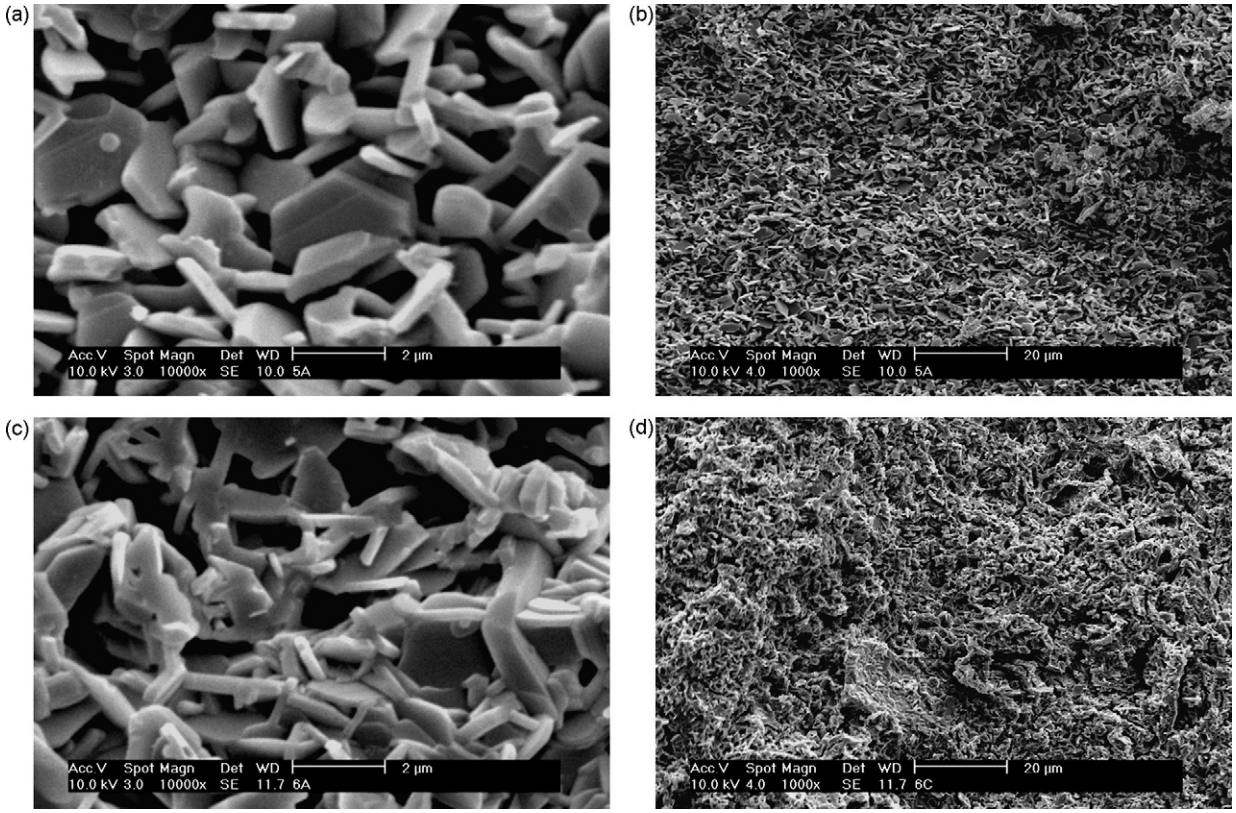

Fig. 5. Scanning electron microscopy micrographs (a and b) of fracture surfaces of La-β-Al_2O_3 sintered pellets; (c and d) for pellets sintered after attrition milling the powders.

endothermic peak at ~960 °C is assigned to the decomposition of $La_2(CO_3)_3$ [19].

The powders prepared by the polymeric precursor technique were calcined at several temperatures in the 600–800 °C range with and without flowing oxygen gas for removal of carbon species. The specific surface area of the powders after calcination in air at 800 °C/4 h was determined by the BET method as 115 m^2/g, with a corresponding average particle size in the nanosize region (~20 nm). Fig. 2a shows a micrograph obtained by scanning electron microscopy of this powder. The distribution of particle size, in agreement with the laser scattering results, is in the range 1–20 μm, showing that the powders are agglomerated, confirmed by the transmission electron microscopy results (Fig. 2b). The TEM micrograph is composed of tiny particles with a sharp size distribution with an average size of approximately 20 nm.

The calcination procedure in the polymeric precursor technique is an important step for the synthesis of electroceramics because remaining carbon species are often undesirable. Diffuse reflectance infrared Fourier transform absorption spectroscopy experiments have been performed to look for carbon species in the powders. Fig. 3 shows the results. The powders prepared by the polymeric precursor technique present absorption bands close to 3400 cm^{-1} due to water (O–H stretching) and at approximately 1410 and 1500 cm^{-1} due to asymmetric and symmetric stretching modes of carbonate groups; the one at 2340 cm^{-1} is assigned to two angular deformation modes and the intense absorption at 1010 cm^{-1} is probably due to the fundamental vibration mode of La–O combined to the O–H angular deformation mode (1640 cm^{-1}) of the aluminum hydroxide [19,20].

Fig. 4 shows X-ray diffraction patterns of La-β-Al_2O_3 pellets sintered at 1200, 1300, 1400 and 1500 °C for 2 h. The higher is the sintering temperature, the larger is the La-β-Al_2O_3 phase content. Below 1400 °C three are the phases: $LaAlO_3$, α-alumina and La-β-Al_2O_3. As the temperature is increased, $LaAlO_3$ and α-alumina reacts for forming La-β-Al_2O_3. At 1500 °C the material is near single-phase La-β-Al_2O_3 (ICDD file # 34-0467).

Fig. 5 shows micrographs with 1000× and 10,000× magnifications obtained by scanning electron microscopy of fracture surfaces of La-β-Al_2O_3 pellets sintered at 1600 °C, before (Fig. 5a and b) and after (Fig. 5c and d) comminuting the powders in an attritor. The grains are evenly distributed, are similar and present hexagonal platelet-like shape with an average size of 2 μm. The specimen shows closed pores and interconnected open pores in a dense network structure. Attrition milling the powders before sintering improved the sintered density (cf. Figs. 5b and d).

The sintered pellets were analyzed by the impedance spectroscopy technique. The $[-Z''(\omega) \times Z'(\omega)]$ impedance spectroscopy diagrams of La-β-Al_2O_3 sintered pellets are composed of two semicircles: one well resolved at high frequencies, due to the intragranular component of the electrical resistivity, and other at lower frequencies due to the intergranular component [21,22]. Fig. 6a shows these diagrams measured at several temperatures: 895, 988, 1083, 1175 and 1268 °C. The inset in Fig. 6a shows details of the high temperature impedance diagrams in the high frequencies region. As expected in thermally activated processes, the higher is the temperature the lower is the intergranular and intragranular electrical resistivities. Fig. 6b shows the corresponding Bode diagrams, depicting the scattered values of the impedance Z as a function of the frequency in the low frequency region, known to occur at the interface electrolyte–platinum electrodes. A detailed analysis of the electrical behavior at different temperatures and under different partial pressure of oxygen of La-β-Al_2O_3 sintered pellets, using powders prepared by the polymeric precursor technique, is under way and will be reported elsewhere [23].

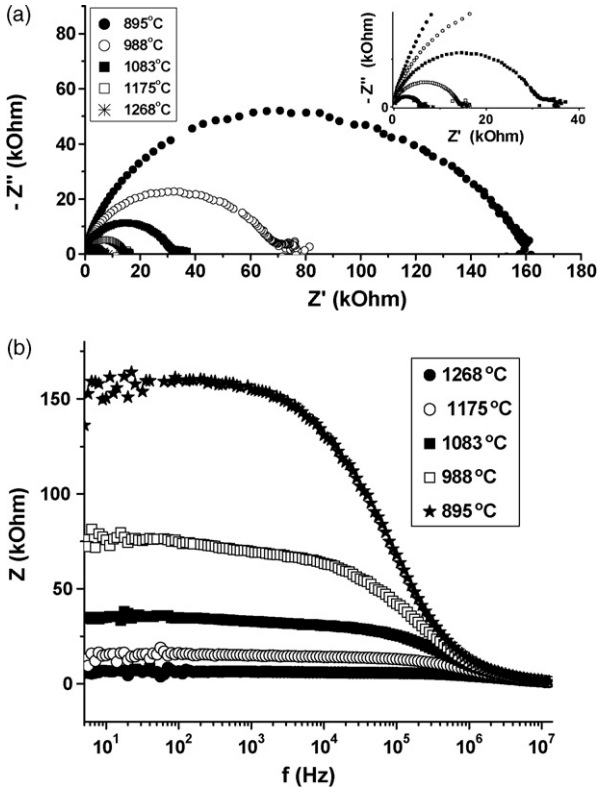

Fig. 6. (a) Impedance spectroscopy diagrams of La-β-Al_2O_3 sintered pellets. Measurement temperatures: 895, 988, 1083, 1175 and 1268 °C. The inset shows the high temperature diagrams. The numbers substituting for the experimental points stand for the logarithm of the frequency; (b) corresponding Bode diagrams.

4. Conclusions

La-β-Al_2O_3 powders have been successfully prepared by the polymeric precursor technique. Particles with average grain size in the submicron range (20 nm) were obtained. Nearly single phase $LaAl_{11}O_{18}$ pellets have been obtained by pressing and sintering at 1500 °C for 2 h. The impedance spectroscopy results in the 1000–1200 °C range show a thermally activated process for electrical conduction. The polymeric precursor technique is suitable for producing sinteractive powders for the preparation of solid electrolytes to be used in high temperature oxygen sensors.

Acknowledgments

The authors thank CNEN, FAPESP (99/10798-0 and 05/53241-9) and CNPq (306496/88) for financial support. Thanks are also due to Dr. D. Gouvêa for DRIFT measurements, to C.V. Moraes for SEM analysis and to N.M. Ferreira for TEM analysis.

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