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Ceramics International 39 (2013) 5667–5674

CERAMICS INTERNATIONAL

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Low-temperature synthesis of lanthanum monoaluminate powders using the co-precipitation–calcination technique

Tomasz Brylewski*, Mirosław M. Bućko

AGH University of Science and Technology, Faculty of Materials Science and Ceramics, al. Mickiewicza 30, 30-059 Krakow, Poland

Received 30 October 2012; received in revised form 20 December 2012; accepted 25 December 2012
Available online 2 January 2013

Abstract

Using the co-precipitation–calcination technique, lanthanum aluminate ($LaAlO_3$) powders were successfully synthesized from ammonia and metal chloride aqueous solutions as starting materials. The thermal decomposition and crystallization behavior of the gel precursors were characterized by means of DTA/TGA analyses. The phase evolution of the powders obtained after gel calcination in the temperature range of 600–900 °C was studied using X-ray diffraction analysis. The crystallization temperature of $LaAlO_3$ depends on the concentration of the starting solutions and on the presence or absence of ammonia chloride. The gel was precipitated from the high-concentration starting solution and then washed—this procedure guaranteed its homogeneity and led to the direct formation of phase-pure $LaAlO_3$ at temperatures as low as 835 °C. On the other hand, failure to remove co-precipitated ammonia chloride from either the high-concentration or low-concentration starting solution prior to calcination results in an increase in the crystallization temperature of $LaAlO_3$ (up to 903 °C), and to the deterioration in gel homogeneity—aluminum and lanthanum oxides are formed aside from lanthanum aluminate. TEM investigations show that the best $LaAlO_3$ powder, obtained after calcination at 900 °C for 2 h in air, consists of isometric particles no larger than 15 nm in diameter. The obtained powder may be used to produce single-phase bulk samples with excellent microstructure.

Keywords: Lanthanum monoaluminate; Co-precipitation–calcination technique; Powder technology; Sintering

1. Introduction

Lanthanum monoaluminate, $LaAlO_3$, which belongs to the rare-earth aluminate family with a perovskite-type structure, has been extensively investigated for a number of years as a material with many potential applications due to its excellent dielectric properties [1–17]. This compound coexists in the La_2O_3–Al_2O_3 system as an intermediate stable phase with $La_2O_{3x}11Al_2O_3$ with a hexagonal structure of the β-Al_2O_3 type and melts congruently at temperature of about 2107 ± 20 °C[1,18–20].

Recently, many efforts have been undertaken in order to apply $LaAlO_3$ in the nuclear industry as a material that would absorb neutrons [2], as well as a dielectric resonator and microwave device substrate, due to their high quality factor (Q_f=68 GHz), high relative permittivity (ε_r=23) and relative low temperature coefficient of resonant frequency ($\tau_f = -44$ ppm/°C) [3]. Lanthanum monoaluminate is also an important ceramic material as a single-crystal substrate for depositing high-temperature superconducting Y–Ba–Cu–O and Bi–Sr–Ca–Cu–O thin and thick films, on account of the advantages it offers in comparison with other substrate materials (e.g., $SrTiO_3$, MgO) [4–6]. The desirable microwave properties of $LaAlO_3$ are a consequence of its substantially lower dielectric constant (ε=23) and a suitably low loss tangent ($\tan\delta < 10^{-5}$ at 10^9 Hz) in comparison to other perovskite materials, such as $SrTiO_3$ (ε=277) [7,8]. In addition, the thermal expansion coefficient of $LaAlO_3$ is very similar to that of high temperature superconductor material, for example of $YBa_2Cu_3O_{7-x}$ ($11–12 \times 10^{-6}$ vs. $11–13 \times 10^{-6}$ 1/K, respectively) [9,10], and, furthermore, this material exhibits long-term reliability under specific operating conditions at the temperature of liquid nitrogen. In addition, due to its high surface area and catalytic selectivity, $LaAlO_3$ has been applied as a

*Corresponding author. Tel.: +48 12 6175229; fax: +48 12 6172493.
E-mail address: brylew@agh.edu.pl (T. Brylewski).

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http://dx.doi.org/10.1016/j.ceramint.2012.12.083

catalytic material for oxidative coupling of methane and hydrogenation and hydrogenolysis of hydrocarbons [11].

In general, $LaAlO_3$ perovskite ceramics might be applied in the form of single crystals readily grown by means of the Czochralski technique [21], as an electrically insulating buffer layer deposited, for instance, on SiO_2 [3], and in the form of a dense polycrystalline material with fine-grained microstructure [22].

Due to low homogeneity related to incomplete oxide reactions and difficulties in obtaining fine-grained samples at the required high temperatures of synthesis, polycrystalline lanthanum aluminate prepared thus far using the solid state reaction method of directly mixing binary pure oxides La_2O_3 and Al_2O_3 and sintering them at temperatures as high as 1600 °C and higher [4,10] has had limited application in practice. In many cases the application of low-temperature (750–900 °C) chemical methods such as sol–gel [23,24], co-precipitation [25–30], organic metal precursor [15,22,31–38], polyvinyl alcohol evaporation [39], aerosol-furnace technique [40] or molten salt [41,42] made it possible to obtain $LaAlO_3$ samples of higher homogeneity (both chemical and morphological) at lower temperatures in comparison with the materials prepared via solid state reaction [4,43], owing to the formation of homogeneous and fine powders, which facilitates synthesis during the calcination and sintering reactions. However, many literature references on a variety of soft chemical methods point out that the most important issue is the overly high calcination temperature of the precursor powders, which is responsible for the full conversion of $LaAlO_3$ phase, and subsequently makes it impossible to obtain a dense polycrystalline sample with the desirable narrow particle-size distribution. The aqueous co-precipitation method with the use of ammonium carbonate solution as a precipitating agent yields micropowders with limited $LaAlO_3$ formation occurring at 900 °C; after further sintering at over 1300 °C $LaAlO_3$ becomes completely converted to the desired phase [25]. Similar results were reported by Vidsayagar et al. [26] and Krylov et al. [27] for incomplete $LaAlO_3$ formation in the temperature range of 1100–1350 °C from a co-precipitate obtained by adding ammonium hydroxide to a solution containing lanthanum and aluminum salts. Recently, Li et al. [29] and Kuo et al. [30] have used this method to synthesize pure $LaAlO_3$ in a range of low calcination temperatures, i.e., 700–800 °C.

Furthermore, when using the aerosol-furnace technique [40] utilizing water-soluble La and Al salts, the prepared fine and spherical powders heated at 1200–1500 °C still contain La_2O_3 and Al_2O_3. Complete conversion to $LaAlO_3$ has only been observed after additional thermal treatment at 1100 °C. Taspinar et al. [22]. have shown that by utilizing both homogeneous precipitation from nitrates of lanthanum and aluminum and self-propagating combustion synthesis using an aqueous solution containing urea, the obtained sphere-like particles of the precursors were completely converted to pure $LaAlO_3$ at 850 °C. It is worth to notice that the prepared pelletized samples of the above powders exhibit a significant degree of densification, $>99\%$ of the theoretical density after sintering at 1500 °C for 6 h, and the final grain-size of this sample does not exceed the micrometer level. Kakihana and Okubo [32] obtained a pure $LaAlO_3$ powder by calcinating the precursor at 700 °C using a polymerized complex technique based on in-situ polyesterification between citric acid and ethylene glycol. Iketani et al. [37] prepared a pure lanthanum aluminate powder at 900 °C starting with a hydrazine monohydrate solution. Adak et al. [39] obtained a pure $LaAlO_3$ powder by thermally treating a mixture of polyvinyl alcohol and a mixed metal nitrate solution at 675 °C.

The aim of the present work was to study the preparation of lanthanum monoaluminate nanometric powder using the co-precipitation–calcination method. The influence of the co-precipitation procedure and the calcination temperature of the precursor gels on their thermal behavior, structure and microstructure was discussed.

2. Experimental

An aluminum and lanthanum chlorides water solution of about 0.9 M (M–molar concentration mol/dm^3) was used. The molar ratio of the components was 1:1 as recalculated to aluminum and lanthanum oxides. A part of the solution was diluted tenfold in distilled water to obtain a ca. 0.09 M solution. The high-concentration and low-concentration solutions were both introduced into a vigorously stirred ammonium solution precipitation agent. The amount of ammonia exceeded the stoichiometric proportion by 10%. In the case of the high-concentration solution of the chlorides, the concentration of ammonia was extremely high and equal to about 13 M. In the second case the solution of the precipitation agents was diluted tenfold ($\sim$1.3 M). The obtained gels were filtered and a part of each was washed with distilled water to fully remove precipitation by-products. All gels were dried at room temperature for 24 h, and then for 2 h at 100 °C. Altogether, four precursor were prepared: two samples from the high-concentration solutions: washed (HW) and unwashed (HU), and, likewise, two samples from the low-concentration solutions: washed (LW) and unwashed (LU). The dried gels were calcinated for 1 h in air in the temperature range of 600–900 °C, with a 6 °C/min temperature increase rate.

On the basis of the obtained results, the conditions required for the preparation of a larger amount of pure lanthanum aluminate phase powder were determined. The gel precipitated from the high-concentration solutions was washed, dried, and calcinated for 2 h at 900 °C in air. The obtained powder was ground for 12 h using a rotary–vibratory mill and zirconia grinding media in dry ethanol. The powder was dried at 70 °C, isostatically pressed under 350 MPa, and then sintered in air at 1300, 1400 and 1500 °C for 2 h with a heating rate of 10 °C/min.

The thermal decomposition of the gels was studied by means of simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) using an STA 449 F3 Jupiter Thermal Analyzer (Netzsch). The heating rate of 10 °C/min and a final temperature of 1000 °C was used. The phase compositions of the powders were characterized using X-ray diffraction analysis. An X'Pert Pro diffractometer (Panalytical) with CuK_α radiation was used. The transmission electron microscope (TEM) EM420 (Philips) was used to characterize the morphology of the powders. The obtained powder was dispersed in dry ethanol by means of an ultrasonic disintegrator, and the suspension was deposited on a carbon film spread out on a standard copper mesh. The morphology and microstructure of the bulk samples were observed with the scanning electron microscope FEI Nova NanoSEM 200. For morphological observations the samples were polished and then thermally etched at 1200 °C for 30 min. Such a procedure allowed grain boundaries to be revealed and was useful for grain size and shape determination. In order to evaluate the grain size distribution and the corresponding average grain size of sintered pellets, SEM images after binarization were processed using the Image *J* 3.14 program. Pore size distributions in green bodies were determined by means of mercury porosimetry using the Porosimeter 2000 (Carlo Erba Instruments). Green bodies from unmilled and milled powder, obtained during uniaxial pressing under a pressure of 50 MPa, were examined using porosimetric analysis; the maximum pressure of mercury in the porosimeter, equal to 202.7 MPa, corresponds to pore penetration within a radius of up to 3.7 nm. The apparent density of the sintered samples was measured with the Archimedes' method.

3. Results and discussion

To evaluate the mechanism of the thermal decomposition of the gel precursors and to simultaneously determine the optimal conditions for their thermal decomposition via calcination, which makes it possible to obtain fully reacted powders with the desired phase and chemical composition that maintain their fine-crystalline structure, differential thermal analysis (DTA) coupled with thermogravimetric analysis (TG) were applied. Fig. 1 shows the DTA and TG curves for the afore-mentioned four types of precursor gels obtained using different co-precipitation procedures and designated as LU, LW, HU and HW. Ammonium chloride by-products were removed from the dried LU and HU gels by 30 min of heating at 200 °C prior to the TG/DTA analysis. The presence of ammonium chloride in the samples undergoing the thermal analysis caused significant weight loss of up to 80% or more, and a strong heat effect at about 230 °C related to decomposition of the salt (see insets in Fig. 1a and c). The heat effects related to the decomposition of the aluminium–lanthanum hydroxide gel and the crystallisation of the respective phases are weak and difficult to analyze.

The DTA curves of the unwashed gels (LU and HU) show three distinct endothermic peaks, accompanied by the total weight loss of 40%, as indicated by the TG curves (Fig. 1a and c). On the other hand, for the washed precursor gels (LW and HW) one broad endothermic peak

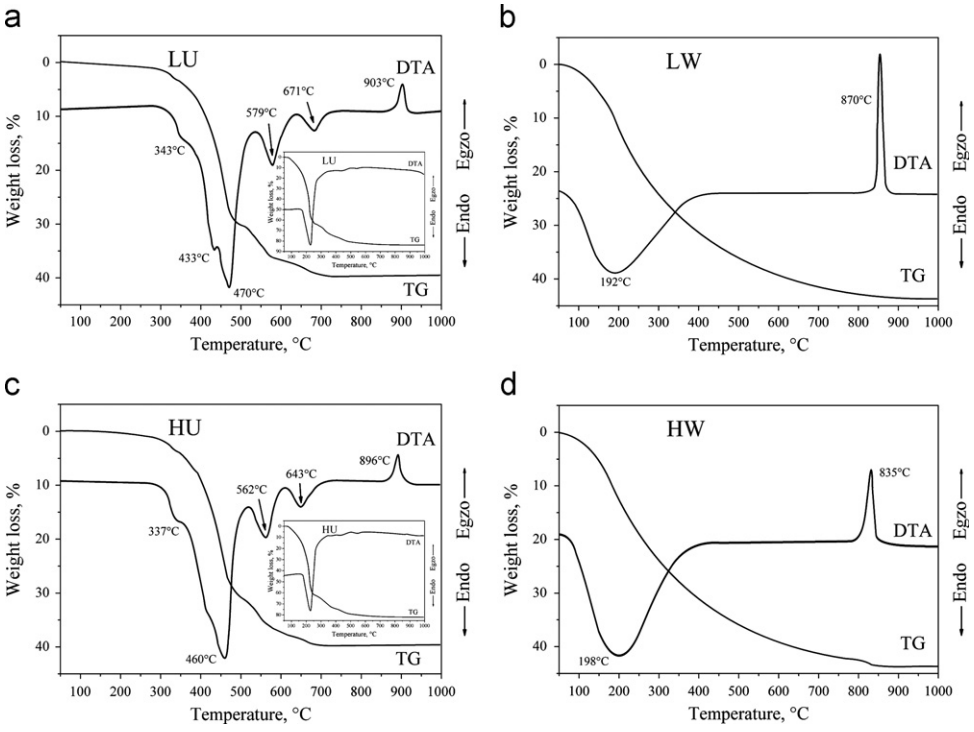

Fig. 1. DTA and TG curves for the LU (a), LW (b) HU (c) and HW (d) precursor gels. Inset: TG/DTA analysis for non-pre-heated samples of LU (a) and HU (c).

around 200 °C is visible on the DTA curves, followed by a total weight loss of 42% up to ~850 °C (Fig. 1b and d). The DTA curves indicate that for all studied precursor gels only single, sharp exothermic peaks appeared in the temperatures from 835 to 903 °C, the occurrence of which depends on both solution concentration and the washing procedure. It was found during DTA/TG analyses of individual unwashed hydroxide gels of La and Al, the results of which are shown in Fig. 2a and b, that $Al(OH)_3$ decomposition takes place in a four-step process, with individual steps at 430, 564, 725 and 843 °C, after which Al_2O_3 is formed; on the other hand, $La(OH)_3$ decomposition takes place at 285 °C, with the subsequent formation of La_2O_3. The first endothermic peaks appearing at about 130–160 °C for both studied hydroxide gels correspond to the elimination of residual water.

It may be assumed that the overlapping endothermic effects at ca. 450 °C, seen in the DTA curves (Fig. 1a and c) for the LU and HU gels, may be ascribed to the dehydroxylation of $La(OH)_3$ that starts during the initial stage of $Al(OH)_3$ decomposition. The other endothermic peaks at 562 and 643 °C (HU) as well as at 579 and 671 °C (LU) are probably indicative of the subsequent stages of Al hydroxide decomposition.

The washed gels (LW and HW) were free from chlorides and contained completely homogeneous mixtures of La and Al hydroxides, which decreased the temperature of their decomposition; this is reflected by the broad endothermic peak observed at ca. 200 °C, seen in Fig. 1b and d. Moreover, the presence of the sharp exothermic peak detected for all studied precursor gels indicates that the decomposition of the washed precursor gels lead to the formation of the $LaAlO_3$ compound at a crystallization temperature lower than in the case of the unwashed precursor gels. These results show that the concentration of the applied solutions also affected the temperature of synthesis. The lowest temperature of $LaAlO_3$ crystallization, 835 °C, was observed for the washed gel precipitated from the high-concentration solutions (HW). Kuo et al. [30] reported a crystallization temperature of 810 °C for lanthanum monoaluminate gels precipitated at pH 9, while Taspinar and Tas [22] observed that precursor gels prepared by means of the precipitation process exhibited the $LaAlO_3$ crystallization temperature of 992 °C. On the other hand, Adak et al. [39] identified the presence of the $LaAlO_3$ pure phase in the powders obtained after thermally treating a mixture of polyvinyl alcohol and a mixed metal nitrate solution at 675 °C. Kakihana and Okubo [32], who applied polymerization, found no clear exothermic peaks corresponding to $LaAlO_3$ crystallization. This discussion shows that the discrepancy between the present report and the previous ones [22,30,32,39] may probably be attributed to different procedures of precursor gel preparation.

Fig. 3 shows the XRD patterns of the powders heated at various temperatures for 1 h. These powders were produced from the four types of gels obtained using different co-precipitation procedures and designated as LU (Fig. 3a), LW (Fig. 3b), HU (Fig. 3c) and HW (Fig. 3d). Calcination of the unwashed precursor gels, which were precipitated from the low- and high-concentration starting solutions (LU and HU, respectively), lead to the simultaneous crystallization of an impurity phase, such as the La_2O_3 (ICDD database code no. 01-083-1349) and θ-Al_2O_3 phases (ICDD database code no. 01-079-1559), as illustrated by the X-ray diffraction patterns in Fig. 3b and d. In the case of the afore-mentioned precursor gels, peaks corresponding to the lanthanum aluminate phase, $LaAlO_3$ (ICDD database code no. 01-070-4120) were observed only at the calcination temperature of 800 °C. On the other hand, the powders obtained from the washed precursor gels precipitated in both low- and high-concentration solutions (designated as LW and HW) through calcination at 600 and 700 °C for 1 h were primarily amorphous, and were characterized by a rise in the background at about 20° to 35° (Fig. 3b and d).

Nevertheless, in the precursor gels co-precipitated from the low-concentration solution (LW) and calcinated at over 700 °C, La_2O_3 and θ-Al_2O_3 were observed along with the $LaAlO_3$ phase (Fig. 3b). Fig. 3d reveals that after calcinating the samples designated as HW at 800–900 °C for 1 h the amorphous part of XRD pattern disappeared; this implies the complete transformation of the washed precursor gels precipitated in the high-concentration

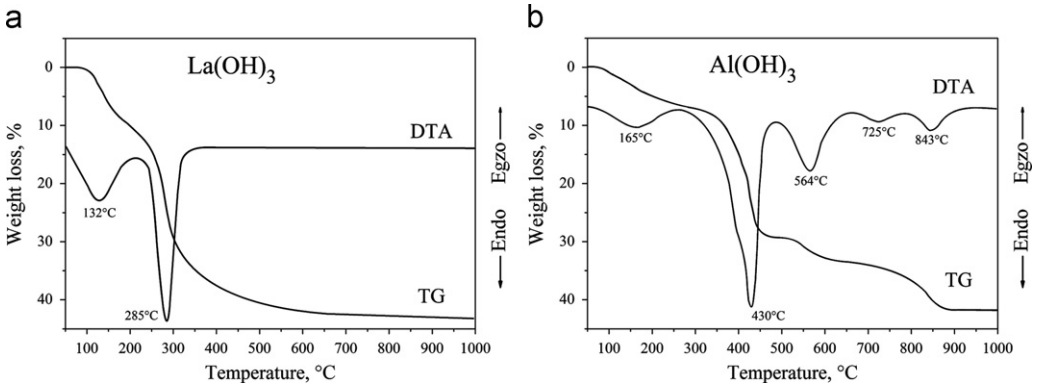

Fig. 2. DTA and TG curves for the unwashed lanthanum (a) and aluminum (b) hydroxide gels.

solution into a single-phase $LaAlO_3$ structure, as reflected in its sharp peaks. Furthermore, the absence of peaks for either La_2O_3 or Al_2O_3 suggests that the stoichiometry of metal ions is maintained in our chemical synthesis procedure. It is not unlikely that $LaAlO_3$ does not form through a solid-state reaction between the afore-mentioned isolated La and Al oxide fine particles, but directly from the amorphous precursor powder containing $La(OH)_3$ and $Al(OH)_3$ without significant segregation of individual material. The absence of any intermediate crystalline substances in the studied precursor gels designated as HW strongly supports this conclusion. The reaction process leading to $LaAlO_3$ formation may be expressed using the following equations:

$$LaCl_3 + AlCl_3 + 6NH_3 \cdot H_2O \rightarrow La(OH)_3 + Al(OH)_3 + 6NH_4Cl \quad (1)$$

$$La(OH)_3 + Al(OH)_3 \rightarrow LaAlO_3 + 3H_2O \quad (2)$$

$$La_2O_3 + Al_2O_3 \rightarrow 2LaAlO_3 \quad (3)$$

It should be noted that the washed gels precipitated in the high-concentration solution (HW) significantly lower the crystallization temperature of $LaAlO_3$ to about 800 °C, which is unattainable using either the classical solid-state reaction method or the other soft chemical techniques.

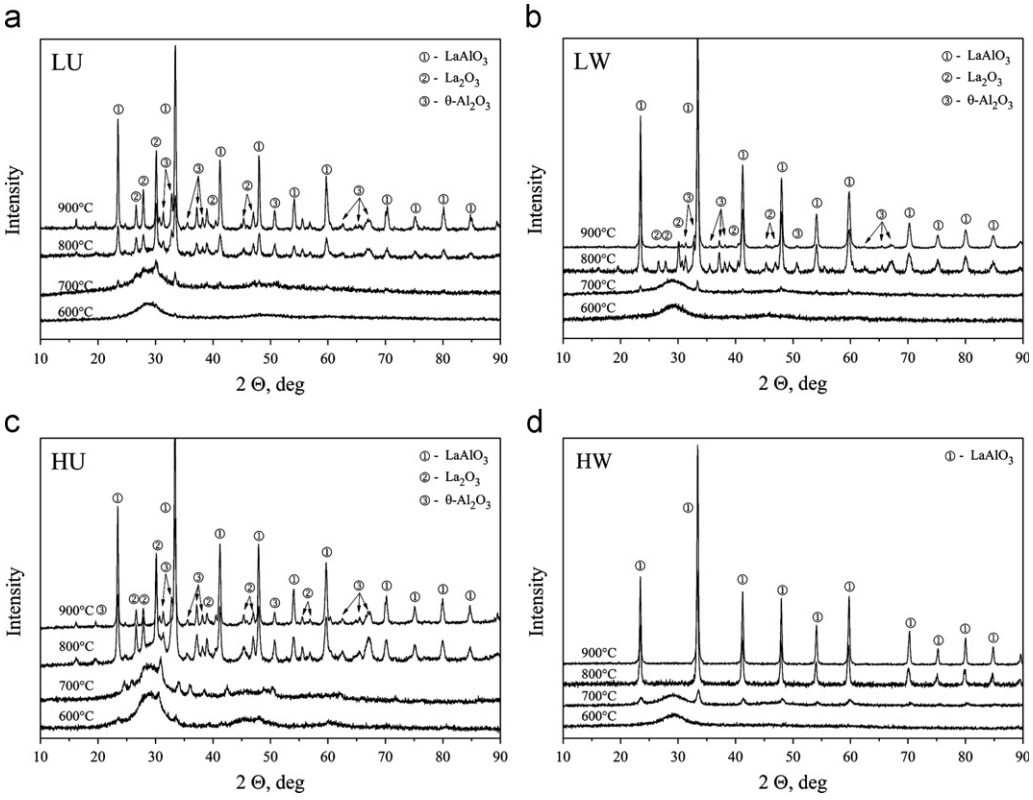

Fig. 3. XRD patterns for the LU (a), LW (b), HU (c) and HW (d) powders heated at various temperatures for 1 h.

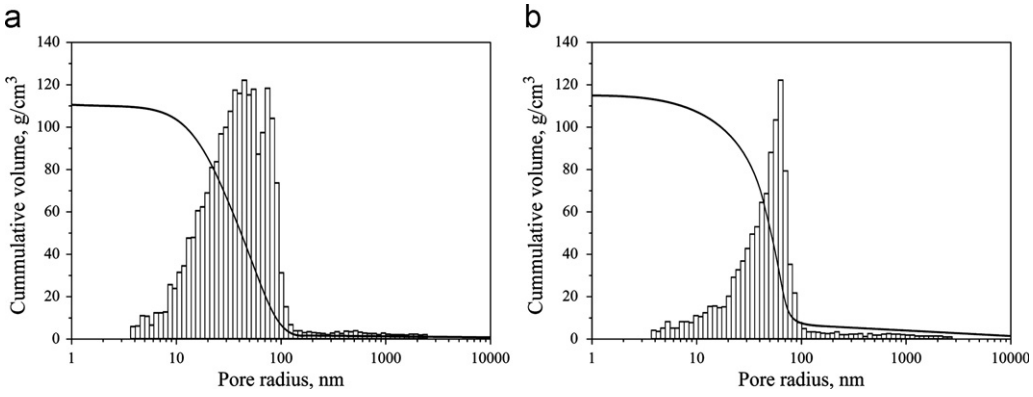

Fig. 4. Pore size distributions of green bodies obtained from raw (a) and ground (b) $LaAlO_3$ powders. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Based on the conducted studies the optimal conditions for the production of lanthanum aluminate powders were determined. More significant amounts of this powder were obtained by starting with high-concentration solutions (0.9 M mixture of aluminum and lanthanum chlorides and 13 M ammonia hydroxide) and washing the precipitated gel. The optimal conditions for calcination were found to be 900 °C and 2 h. Based on the X-ray analysis of the $LaAlO_3$ phase composition it may be concluded that the powders obtained in the afore-mentioned conditions have a single-phase structure. The Rietveld analysis of the obtained diffraction pattern indicates the presence of a perovskite phase in the powders; this phase appears to crystallize as a rhombohedral structure with the *R*-3*c* space group. The established values of lattice parameters, $a=0.53556(1)$ nm and $c=1.31518(2)$ nm, are consistent with reference data [44]. These results prove that using the co-precipitation–calcination technique it is possible to obtain a fully reacted $LaAlO_3$ perovskite at the relatively low temperature of 900 °C.

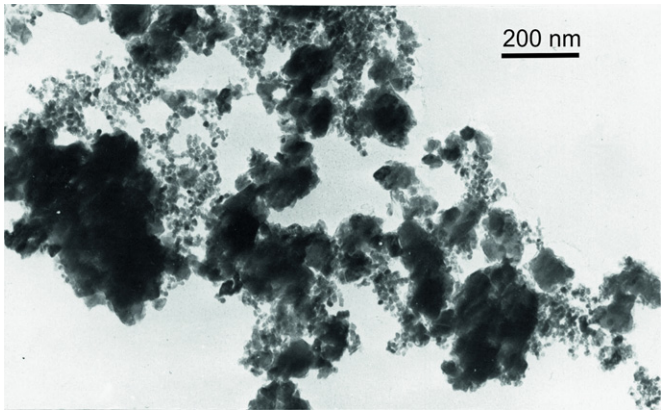

Fig. 5. TEM image of the $LaAlO_3$ powder calcinated for 2 h in air at 900 °C.

Fig. 4 shows the pore size distributions of green bodies obtained from the raw (Fig. 4a) and ground (Fig. 4b) $LaAlO_3$ powders. The results of porosimetric measurements for the green body from unmilled powder suggest that it exhibits a two-modal particle size distribution, which indicates its aggregation and agglomeration. The populations of pores with smaller and larger mean size correspond to the inter- and intra-aggregate (agglomerate) porosities, respectively. In order to decrease aggregation the powder was milled for 12 h in dry ethanol using zirconia grinding media and a rotary–vibratory mill. As can be seen in Fig. 4b, the green body from milled powder has a single-modal pore size distribution. The $LaAlO_3$

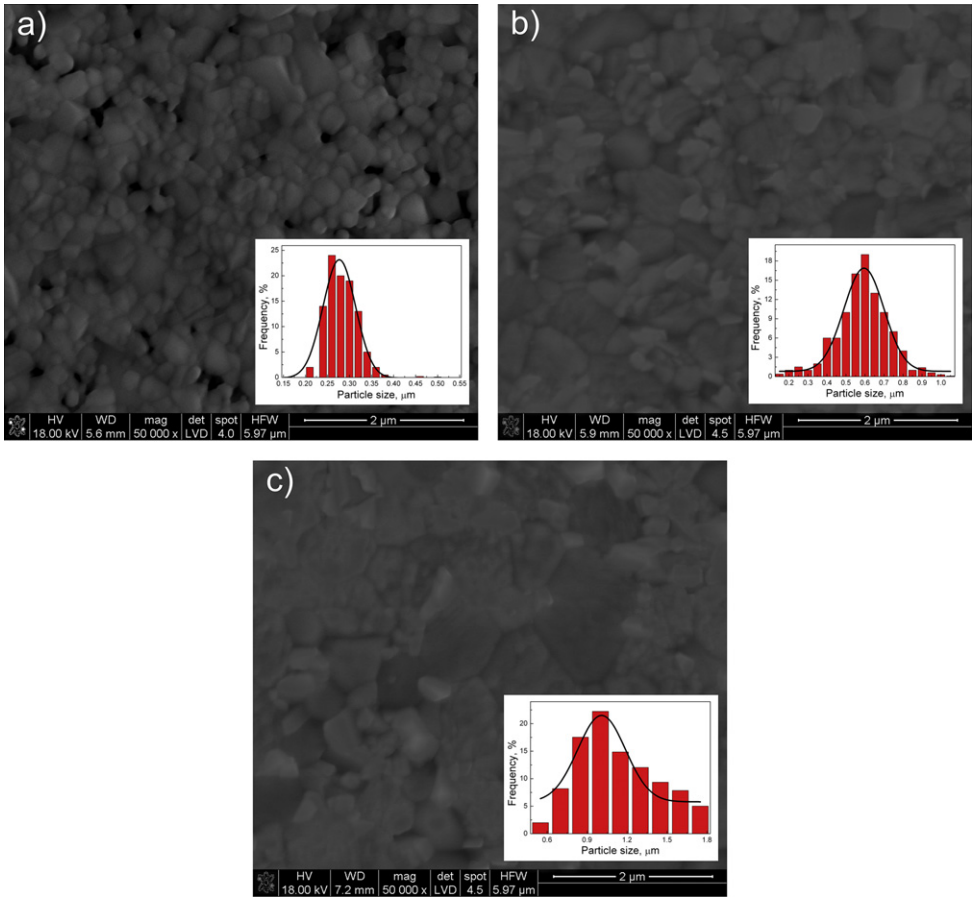

Fig. 6. SEM images of the polished and thermally etched surfaces of the $LaAlO_3$ samples sintered for 2 h in air at 1300 (a), 1400 (b) and 1500 °C (c). The inset shows the grain size distribution.

powder prepared by calcinating the washed precursor gel precipitated in the high-concentration solution (HW) is very fine. The TEM image of the powders calcinated in air at 900 °C for 2 h (Fig. 5) shows that the powder is composed of regular, isometric particles up to 15 nm in size. Small amounts of agglomerates formed during the calcination process may also be seen; they reach a size of up to 0.1 μm.

Fig. 6 shows SEM images of the polished and thermally etched surfaces of $LaAlO_3$ samples sintered for 2 h at 1300, 1400 and 1500 °C. Different conditions of sintering result in materials with different microstructures. The sample sintered at the lowest temperature, i.e., 1300 °C (Fig. 6a), is characterized by fine microstructure and isometric grains. Grain size showed a Gaussian distribution with an average grain size of 0.3 μm (inset of Fig. 6a). The porosity of this sample was considerable, up to about 7%. The microstructure of the sample sintered at 1400 °C (Fig. 6b) is characterized by lower porosity (3%) when compared with the sample described above. Its grains also exhibit isometric and partly irregular shape. The size of the grains ranged from about 0.2 up to 1 μm, with an average of 0.6 μm (inset of Fig. 6b). A similar microstructure was observed in the SEM microphotograph taken for the sample sintered at 1500 °C (Fig. 6c), but in this case some grains grew to 0.5–1.8 μm, and average grain size was 1 μm (inset of Fig. 6c). The porosity of this ceramic material is lower than 1%.

4. Conclusions

The co-precipitation–calcination technique utilizing metal chloride aqueous solutions as starting materials and ammonia hydroxide as a precipitating agent proved to be a useful tool for the synthesis of single-phase, nanosize, and homogeneous $LaAlO_3$ powders. High-concentration starting solutions and washing the precursor gel guarantee sufficient homogeneity of the gel and the subsequent direct synthesis of lanthanum monoaluminate. If the co-precipitated ammonia chloride is not removed prior to calcination, aluminum and lanthanum oxides are formed aside from lanthanum aluminate and the homogeneity of the gel deteriorates. The lanthanum aluminate powder obtained after 2 h of calcination of the washed precursor gel in air at 900 °C consists of isometric particles up to 15 nm in size. After 12 h of milling in a dry ethanol medium, its grain size distribution becomes single-modal, which implies a lower degree of aggregation. The developed powder may be used to obtain single-phase, dense, homogeneous bulk samples with excellent microstructures.

Acknowledgements

The present work was carried out under the statutory activities of the Department of Technology of Ceramics and Refractories, Faculty of Materials Science and Ceramics, AGH University of Science and Technology (contract No. 11.11.160.603).

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