

Synthesis of sodium β'' -alumina powder by sol–gel combustion

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Abstract

Magnesia stabilized sodium β'' -alumina powder was prepared by sol–gel combustion using metal nitrates and citric acid. The thermal decomposition of the nitrate–citrate gels and the crystallization behavior of β'' -alumina were studied. The nitrate–citrate gel exhibits self-propagating combustion behavior after ignition. β'' -alumina crystallizes gradually from the sodium aluminum oxide intermediate phase to form the major phase at 1100 °C. The synthesized β'' -alumina powder was formed into dense electrolyte tubes by slip casting and subsequent sintering. The non-conducting *c*-axis of the hexagonal β'' -alumina grains tends to be oriented in the radial direction in the cast tubes.

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1. Introduction

Sodium β - or β'' -alumina ceramics exhibit high sodium conductivity at relatively low temperatures (<300 °C).^{1–3} As a result, these materials have been used as the electrolyte or sodium-ion separator in various devices such as (a) sodium sulfur and sodium nickel chloride (ZEBRA) batteries for electric vehicles and load leveling systems,^{4,5} (b) the sodium heat engine or alkali metal thermoelectric converter (AMTEC) for direct thermoelectric energy conversion,⁶ (c) gas sensors^{7,8} and (d) galvanic cells for measurement of thermodynamic data.^{9,10}

Sodium β -alumina and β'' -alumina have the chemical composition $(\text{Na}_2\text{O})_{1+x}\cdot 11\text{Al}_2\text{O}_3$ where $x=0.25–0.55$ and $x=0.55–0.65$, respectively. The β'' -alumina has a considerably higher ionic conductivity than β -alumina. Therefore, β'' -alumina is the preferred electrolyte for most applications.¹¹

The fabrication of dense polycrystalline β'' -electrolyte involves three distinct stages; powder preparation, forming into shape and high temperature sintering, but at temperatures in excess of 1550 °C this material has a high vapor pressure which requires containment, and in addition tends to decompose unless stabilized with dopants such as lithia and magnesia.^{12,13}

The conventional method of synthesizing this material begins with mechanical mixing of the precursor components of β'' -alumina (containing Al, Na, Mg, and/or Li), followed by a calcination step to decompose the reactants and form the β'' -alumina phase. For instance, Sudworth reported a method based on the boehmite route.⁵ Boehmite ($\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O}$) is calcined at 800 °C and then mixed with sodium carbonate and lithium hydroxide followed by calcination at 1200 °C to form β'' -alumina. Typically, a significant amount of ball-milling is required subsequent to calcination to achieve fine powders suitable for sintering. The milling process generally yields non-homogeneous mixtures which require high temperatures to convert the reactants to β'' -alumina. This high temperature calcination stage usually leads to excessive grain growth resulting in poor mechanical strength.

In order to overcome these shortcomings various techniques such as chemical co-precipitation,¹⁴ solution spray-drying,¹⁵ solution spray-freezing¹⁶ and sol–gel¹⁷ have been developed. However, these methods are cost and energy intensive and a number of difficulties in obtaining high purity, ultra-fine and homogeneous particles of β'' -alumina with narrow size distribution have been pointed out by several investigators.

The synthesis of β'' -alumina powder by sol–gel combustion is the focus of the present work. Sol–gel combustion is a novel method, with a unique combination of the chemical sol–gel process and the combustion process, based on the gelling and subsequent combustion of an aqueous solution containing salts of the desired metals and some organic fuel, giving a voluminous

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and fluffy product with a large surface area.¹⁸ This process has the advantages of inexpensive precursors, a simple preparation method, and a resulting nano-sized powder. This work is aimed at investigating the phase evolution during combustion and the subsequent calcination of powders prepared by the sol–gel combustion method. An optimized procedure to fabricate the dense β'' -alumina electrolytes is also reported.

2. Materials and methods

2.1. Powder preparation

MgO-stabilized sodium β'' -alumina powder (SG- β'') consisting of 77.3 mol% Al_2O_3 , 12.7 mol% Na_2O and 10.0 mol% MgO was synthesized using the sol–gel combustion method. The starting materials were aluminum nitrate, magnesium nitrate, sodium nitrate and citric acid, all of analytical purity. Appropriate amounts of the above mentioned materials were dissolved in a minimum amount of distilled water. The molar ratio of metal nitrates to citric acid was 1:1. As water was evaporated by heating, the solution formed a very viscous brown gel. Increasing the temperature to about 220 °C led to ignition of the gel. The dried gel burned in a self-propagating combustion manner to form a loose powder. The as-burnt powder was calcined in air at 1100 °C and converted to β'' -alumina.

2.2. Slip casting and sintering

Dense electrolyte tubes were successfully produced using slip casting and subsequent high temperature sintering. Slip casting was carried out in plaster moulds and water was used as the dispersion medium. However, as reported by Johnson et al.,¹⁹ the β'' -alumina powders were difficult to disperse in water because excess alkali ions leach out from the powder and impart a high pH \approx 15 to the slurry, leading to a tendency towards gelation. The first issue arising from gelation is uneven wall thickness of the cast tubes and the second is binding the tube to the mould, resulting in difficulties in the tube removal process. The problem was obviated by washing the powders with distilled water before slip preparation.

The slip was prepared by mixing a 40:60 ratio by weight of powder and water and ball milling in a 250 mL wide-mouth Nalgene bottle for 72 h. The slip was cast into a plaster mould, allowing a residence time of 2 min to grow the wall thickness to 1 mm and the excess poured out.

The green electrolyte tube was sintered at 1650 °C for 30 min in a buffer of β -alumina powder with 2 wt% Na_2CO_3 to minimize the sodium loss and prevent the conversion of β'' -alumina to β -alumina, which was followed by annealing at 1475 °C for 45 min during cooling.

The MgO-stabilized powder was compared with Li_2O -stabilized β'' -alumina powder for the fabrication of electrolyte tubes. The Li_2O -stabilized powder was supplied by MES-DEA Inc. and identified as MES- β'' . The conventional

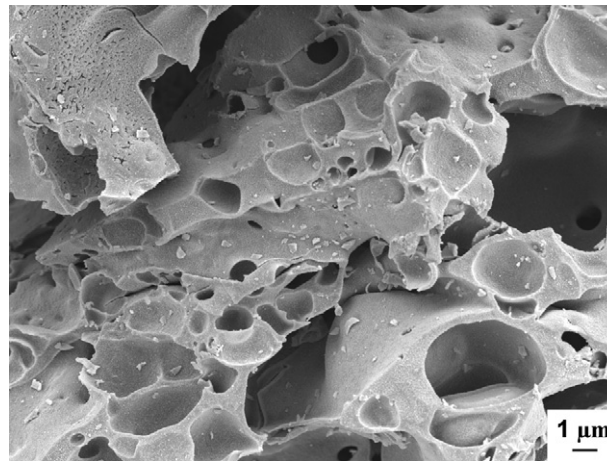


Fig. 1. SEM image of the gel after combustion of citric acid–nitrate solution.

production method for this powder has been outlined by Sudworth.⁵

2.3. Characterization methods

The phase identification of powders and fabricated electrolyte was performed by X-ray diffraction (XRD) using $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$). The powders and solid electrolyte microstructure were examined by scanning electron microscopy (SEM). A particle size analyzer was used to determine the particle size distribution of powders by liquid phase sedimentation. The ASTM standard test method (C373-88) was applied to determine the bulk density of the sintered products. The ultimate integrity of the β'' -alumina tubes was examined by means of a liquid penetrant test.

3. Results and discussion

The experimental observation showed that nitrate–citrate gel exhibits a self-propagating combustion behavior during heating. When the dried gels were ignited, the combustion propagated rapidly to form a loose powder (Fig. 1), which contained a large amount of microscopic pores due to the liberation of gaseous species such as CO , CO_2 or H_2O during combustion.

The combustion could be considered a thermally induced anionic, redox reaction of the gel wherein the citrate acts as reductant and nitrate acts as the oxidant.¹⁸ Fig. 2 shows the DTA/TGA traces for the nitrate–citrate dried gel. There is an endothermic peak along with two exothermic peaks at 222 °C, 540 °C, and 731 °C. The first sharp endothermic peak at 222 °C with a concurrent large weight loss of near 59.1% corresponds to the melting point of citric acid and could be explained by a competing reaction between vaporization and decomposition of the gel, as observed in other systems.^{18,20} For pure citric acid, the results of DTA and TGA showed that the exothermic reaction takes place near 500 °C accompanied by weight loss of about 1%, corresponding to the decomposition reaction of the carboxyl group.²¹ Another experiment showed that citrate gel without nitrate ions, washed with deionized water before gelation, did not exhibit auto-combustion behavior. Therefore, the

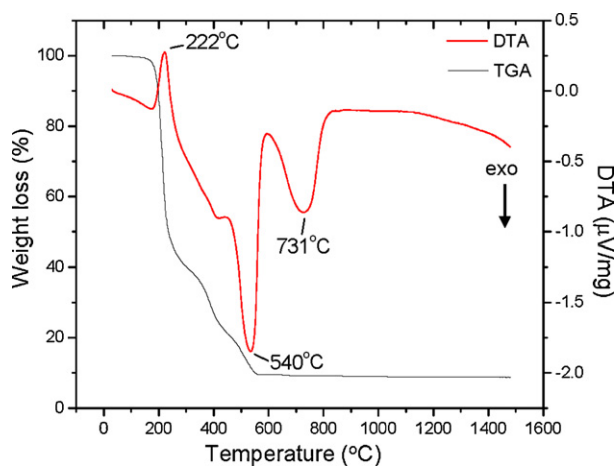


Fig. 2. DTA/TGA traces for the nitrate–citrate gel (heating rate: 10 °C/min).

lowering of the decomposition temperature may be attributed to the presence of nitrate ions in the gel. Hence, the first sharp endothermic peak could be described as an autocatalytic anionic oxidation–reduction reaction between the nitrates and citric acid in conjunction with moisture and citric acid evaporation. The decomposition of unreacted nitrates and citric acid remaining after combustion could be responsible for the second exothermic peak near 540 °C with a weight loss of 30.7%. The last broadened exothermic peak at 731 °C accompanied by a minor weight loss of 0.7% could be considered as a solid state reaction corresponding to the formation of crystalline sodium aluminum oxide.

Since the nitrate ions provide an in situ oxidizing environment for the decomposition of the organic component, the rate of oxidation reaction increases slightly. The combination of a lower reaction temperature and an increase in kinetics results in a self-propagating combustion of the nitrate–citrate gel.^{18,21}

To aid further interpretation of the reaction processes, the DTA/TGA was supplemented by XRD analysis (Fig. 3). The as-burnt powders exhibit an amorphous pattern; β'' -alumina is crystallized gradually from a sodium aluminum oxide intermediate phase and appears as a major phase coexisting with minor amounts of β -alumina and sodium aluminum oxide at 1100 °C. Sodium aluminum oxide with mullite structure requires little diffusion to transform to β /'-alumina; this leads to the absence of an extra exothermic peak in the DTA trace related to β -alumina formation at 1100 °C as reported by Yamaguchi et al.²² Eventually, at 1400 °C, sodium aluminum oxide is transformed to β'' -alumina with a small amount of β -alumina.

Fig. 4 shows the SEM images of SG- β'' samples calcined at 1100 °C (a) and 1400 °C (b) for 1 h. The sample calcined at 1100 °C consists of agglomerated β'' -alumina crystals with an average particle size of 0.4 μm . This fine structure at a relatively high temperature of 1100 °C could be explained by the presence of pores between the particles, which decreases the diffusion rate and thereby hinders grain growth. The β'' -alumina crystals with plate-like hexagonal shape along with needle-like particles could be identified at 1400 °C. The needle-like particles were identified by EDS to have a composition close to sodium aluminum oxide.

The average particle size of both SG- β'' and MES- β'' powders after milling was approximately 0.7 μm which is desirable for uniform slips (Fig. 5). The bulk density and shrinkage of SG- β'' sintered product were measured to be 3.01 g cm⁻³ (\approx 93% theoretical) and 20 \pm 1%, respectively. The liquid penetrant test showed that the fabricated electrolytes were fully leak tight and impervious. The bulk density of SG- β'' sintered tubes fabricated by slip casting here is close to those fabricated by isostatic pressing. Miller et al.²³ reported a bulk density of spray dried Li₂O-stabilized β'' -alumina powders formed by isostatic pressing to be between 3.0 and 3.2 g cm⁻³ depending on pressing pressure and sintering temperature. In contrast, the liquid penetrant test showed that our electrolytes fabricated by slip casting from MES- β'' were highly porous.

Fig. 6 shows the X-ray diffraction patterns of the SG- β'' and MES- β'' powders. A higher β'' phase fraction is found in the SG- β'' compared to the MES- β'' . The SEM images of the fracture surface of the tubes (Fig. 7) show that the one fabricated from SG- β'' is dense while the MES- β'' tube possesses a high level of porosity. The high level of densification observed for the SG- β'' tube can be explained by a higher β'' -alumina phase content compared to that of MES- β'' , promoting the liquid phase sintering. This is consistent with the results from the X-ray diffraction.

The average grain size after high temperature sintering for SG- β'' was calculated from the SEM micrograph of the interior surface of the tube (Fig. 8) to be near 4.5 μm . The non-conducting *c*-axis of the hexagonal β'' -alumina grains tends to be oriented in the radial direction. A comparison of the X-ray diffraction pattern of randomly oriented powder with those of the slip cast tube confirms this conjecture (Fig. 9). The observed texture in the slip cast tube causes higher relative intensity for the characteristic peaks, e.g. (1 0 7), of the casting compared to those for randomly oriented powders. Although such unfavorable

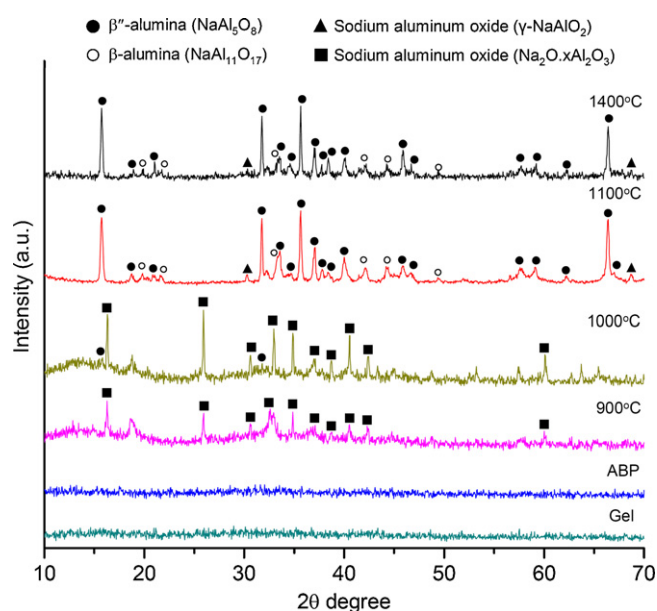


Fig. 3. X-ray diffraction patterns of the gel, as-burnt powder and powders calcined at various temperatures for 1 h.

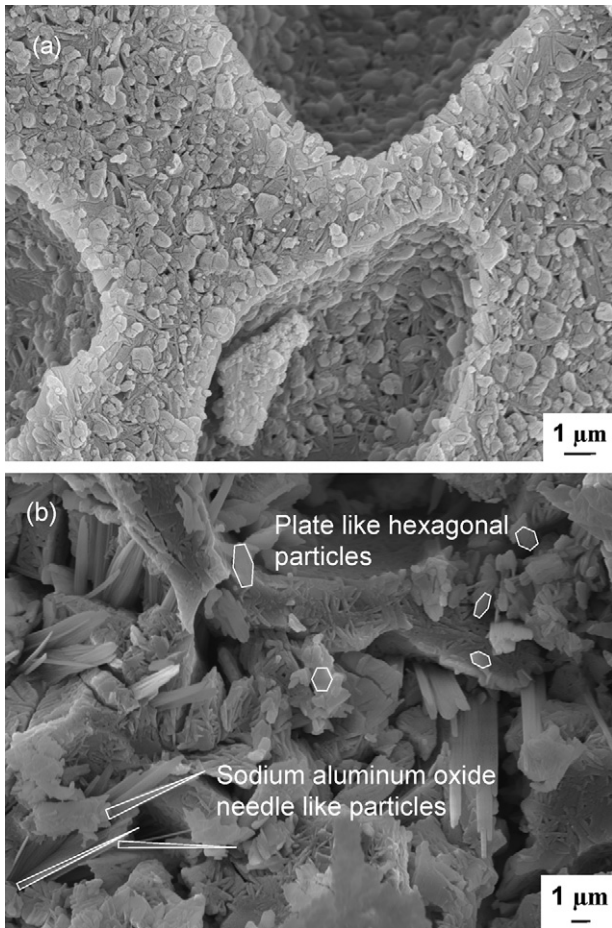


Fig. 4. SEM image of samples calcined at (a) 1100 °C and (b) 1400 °C for 1 h.

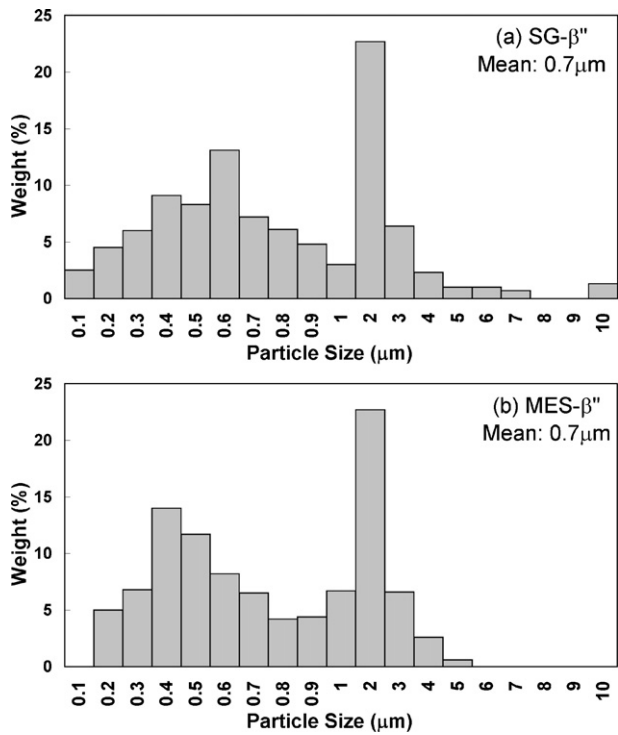


Fig. 5. Particle size distribution graphs for (a) SG-β'' and (b) MES-β'' powders (note change of scale at 1 μm).

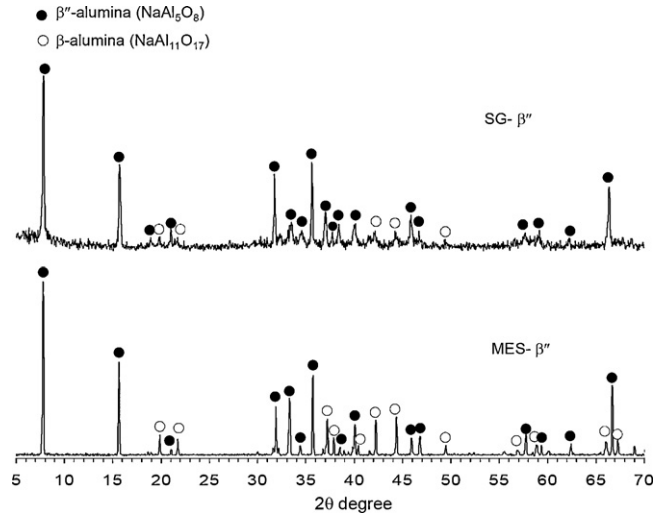


Fig. 6. X-ray diffraction patterns of SG-β'' and MES-β'' powders.

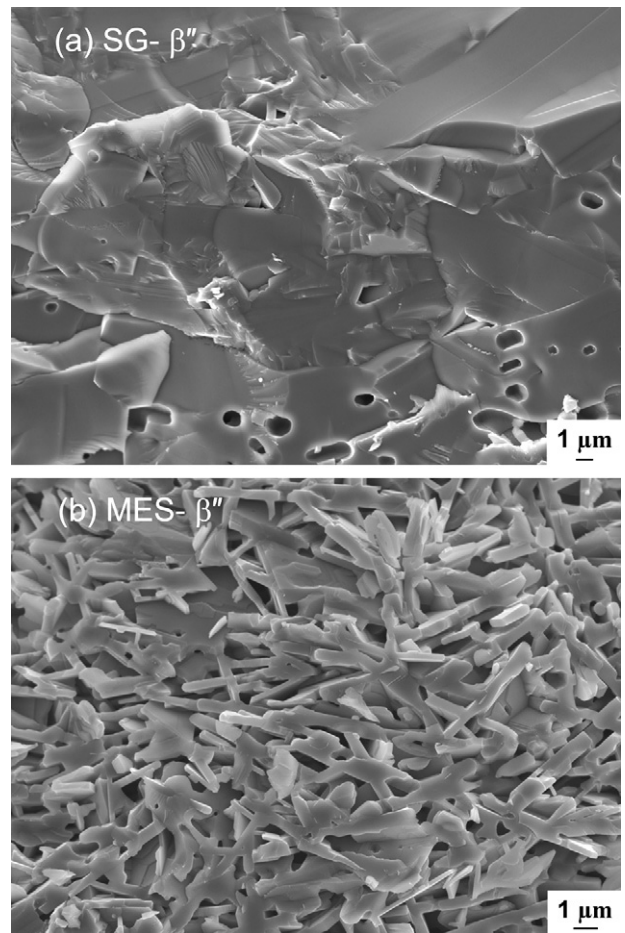


Fig. 7. SEM images of the fracture surface of cast tubes of (a) SG-β'' and (b) MES-β'' sintered in buffer at 1650 °C for 30 min.

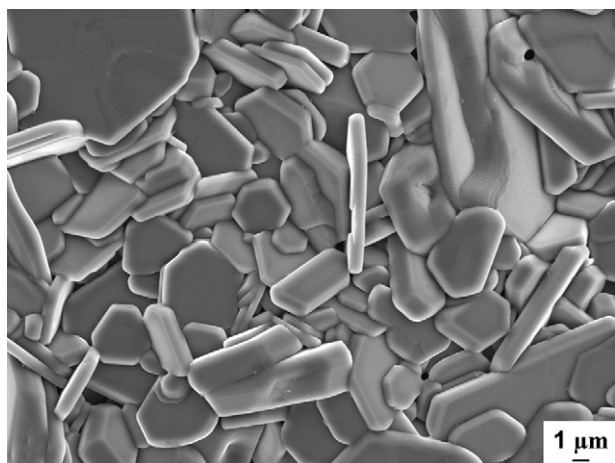


Fig. 8. SEM image of interior surface of SG- β'' cast tube sintered in buffer at 1650 °C for 30 min.

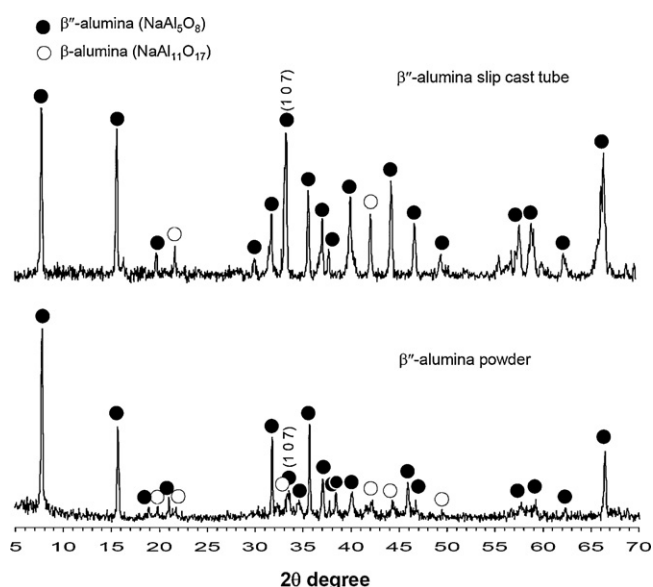


Fig. 9. Comparison between the X-ray diffraction patterns of SG- β'' -alumina from powder and from the sintered tube.

texture does occur during slip casting, the degree of orientation is negligible and does not degrade the electrolyte conductivity.^{11,24}

4. Conclusions

Magnesia stabilized β'' -alumina powder was synthesized at a relatively low temperature of 1100 °C by the sol–gel combustion method using a nitrate–citrate gel. The nitrate–citrate gel exhibits an auto-combustion behavior. The combustion can be considered as a thermally induced autocatalytic anionic redox reaction of the gel including citric acid as a fuel and metal nitrates as a reductant. β'' -alumina with fine microstructure is crystallized gradually from the sodium aluminum oxide intermediate phase and appears as a major phase along with β -alumina at 1100 °C.

Dense electrolyte tubes were fabricated from the synthesized powders by slip casting and subsequent sintering. The bulk

density of the sintered product was measured as 3.01 g cm⁻³ (\approx 93% theoretical). The electrolyte microstructure showed significant grain growth due to high temperature sintering. It was found that the non-conducting c -axis of the hexagonal β'' -alumina grains tends to be oriented in the radial direction in the cast tubes.

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