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Synthesis of nanocrystalline 8 mol% yttria stabilized zirconia powder from sucrose derived organic precursors

K. Prabhakaran [*], Anand Melkeri, N.M. Gokhale, S.C. Sharma

Naval Materials Research Laboratory, Shil-Badlapur Road, Anandnagar P.O. Addl., Ambernath, Thane 421 506, India

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Abstract

An organic precursor synthesis of 8 mol% yttria stabilized zirconia (YSZ) powder from Zr–Y composite nitrate solution and sucrose has been studied. Oxidation of sucrose in Zr–Y composite nitrate solution containing excess nitric acid *in situ* generates hydroxy carboxylic acids that forms a white sol which showed peaks at 1640 cm^{-1} and 1363 cm^{-1} in IR spectrum corresponding to hydroxy carboxylic acid complexes of Zr and Y. Precursor mass obtained by drying the sol on calcinations at 600 °C produced loosely agglomerated particles of cubic YSZ. Deagglomerated YSZ contain submicron particles with D_{50} value of 0.5 μm and the particles are aggregates of nanocrystallites of nearly 10 nm size. Compacts prepared by pressing the YSZ powder sintered to 96.7% TD at 1450 °C. The sintered YSZ ceramic showed an average grain size of 2.2 μm.

Keywords: A. Sintering; Yttria stabilized zirconia; Sucrose; Oxidation; Organic precursors; Nanocrystalline powder

1. Introduction

8 mole % yttria stabilized zirconia (YSZ) is well known as electrolyte material in electrochemical devices such as sensors, oxygen pumps and solid oxide fuel cells (SOFC) owing to its oxide ion conductivity at high temperature and relatively low cost [1–5]. YSZ powder is also used for preparation of Ni–YSZ cermet anode for SOFC [6–9]. The YSZ ceramic material for the electrochemical devices has to be dense and impervious to gases. Further, mechanical strength and toughness of the YSZ material must be sufficiently high to prevent breakdown of the device during use at elevated temperature and thermal cycling. Dense YSZ ceramics with superior properties for electrolyte applications have been prepared from fine and non-agglomerated powders. Wet chemical methods have been used for preparation of homogeneous fine powders, which are sinterable at low temperatures. A number of wet chemical processes such as sol–gel method, co-precipitation, hydrothermal process, spray drying, spray pyrolysis, freeze drying, combustion synthesis, auto ignition, polymer precursor synthesis and oxalate precipitation route have been reported for preparation of yttria doped zirconia powders [10–22]. However, most of the above reports focus on tetragonal (3–5 mol% yttria stabilized zirconia) phase for structural applications.

Sucrose has been used as complexing agent and fuel for combustion for preparation of a number of ceramic fine powders by various authors [23–30]. Bose and Wu explained the chemistry of sucrose synthesis by proposing the formation of gluconic acid complexes during the synthesis of Al_2O_3–CeO_2 mixed oxide nano powders [28]. The present work reports synthesis of nanocrystalline 8 mol% yttria doped zirconia powder from Zr–Y composite nitrate solution and sucrose. In this work, organic precursors such as hydroxy carboxylic acid complexes of Zr–Y has been prepared by oxidation of sucrose *in situ* by nitric acid. Nanocrystalline YSZ powder prepared from the organic precursors has been characterized.

2. Experimental

$ZrOCl_2 \cdot 8H_2O$ (99%) and Y_2O_3 (99.9%) used were procured from Indian Rare Earth Ltd. Sucrose (Merck, India) and nitric acid (Merck, India) used for this study were of AR grade. Deionised water was used for preparation of solutions. Flow chart of the process for preparation of YSZ powder by sucrose synthesis is shown in Fig. 1. One mole of $ZrOCl_2 \cdot 8H_2O$ was dissolved in 500 ml (approximately 8 mol) of concentrated

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[*] Corresponding author. Tel.: +91 251 681950; fax: +91 251 680604.
E-mail address: kp2952002@yahoo.co.uk (K. Prabhakaran).

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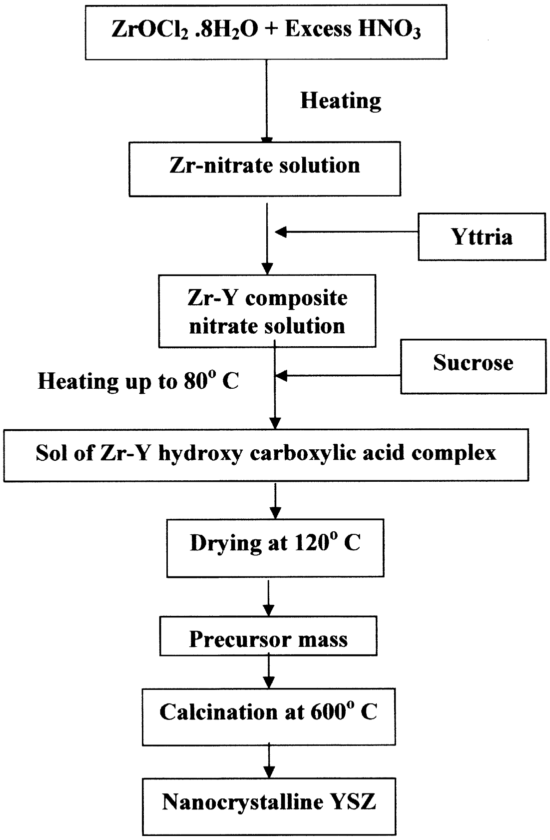

Fig. 1. Flowchart for the synthesis of nanocrystalline YSZ.

nitric acid and the solution was heated on a hot plate to eliminate chloride [14]. Absence of chloride in the solution was confirmed using silver nitrate solution. The resulting solution was diluted with water and filtered to remove any insoluble materials. The solution was analyzed for zirconium content using mandelic acid method [32]. About 0.087 mol of yttria was dissolved in the solution to get 8 mol% YSZ composition.

Total concentration of zirconium and yttrium in the final Zr–Y composite nitrate solution was 0.75 mol/l. Three moles of sucrose per mole of zirconium and yttrium ion was dissolved in the Zr–Y composite nitrate solution and then heated on a hot plate till a vigorous evolution of gas bubbles were observed due to oxidation reactions. As soon as the oxidation reaction initiate the solution was removed from the hot plate and left to stand for half an hour to ensure completion of the reaction resulting in the formation of a white sol. The sol was dried in an oven at 120 °C to form a black precursor mass.

Infrared spectrum of the sol was recorded using an infrared spectrophotometer (Perkins-Elmer 1600 series FTIR). Viscosity of the sol was measured using Brookfield viscometer (RVT model). TGA–DTA analysis of the sol dried at 120 °C was carried out at a heating rate of 10 °C/min in air atmosphere in a thermal analyzer (Setsys 16/18, Setaram Scientific and Industrial Equipment, France). The precursor mass was heated at 600 °C in a muffle furnace to remove the organic mater. Calcined powder was deagglomerated by attrition milling in isopropanol medium for 24 h.

XRD (Philips analytical PW 1710) analysis of the calcined powder was carried out using Cu Kα radiations. Particle size distribution (Malvern Master Size Analyzer 2000) and surface area (Sorptomatic 1990, Thermo Finnigan) of the deagglomerated powder was measured. Crystallite size in powder particles was measured from TEM.

Green compacts were prepared by pressing the powder at 50 MPa in a hydraulic press using a steel die set. The pressed samples were sintered at temperature in the range 1300–1500 °C for 2 h at a heating rate of 5 °C/min. Density of the sintered samples was measured by Archimedes principle. Microstructure of the powder and fractured surface of sintered sample were observed under scanning electron microscope (LEO 1455).

3. Results and discussion

One mole of the $ZrOCl_2 \cdot 8H_2O$ reacts with 2 mol of nitric acid to form zirconyl nitrate and 0.087 mol of Y_2O_3 took 0.522 mol of nitric acid to form yttrium nitrate. Therefore, the amount of remaining nitric acid in the Zr–Y composite nitrate solution was approximately 5.4 mol per mole of zirconium and yttrium ions. This solution when heated with sucrose caused vigorous evolution of gas bubbles to be observed at about 80 °C. Further external heating of the solution was not required because heat released due to an exothermic reactions took place was sufficient to boil the solution. The solution boiled with vigorous evolution of brown nitrous fumes. These exothermic reactions sustained for nearly half an hour and finally turned the solution in to a viscous white sol. It is well known that sucrose undergoes hydrolysis in aqueous acidic medium in to glucose and fructose [33]. Nitric acid oxidizes the glucose thus formed in to saccharic acid and a small amount of oxalic acid. The fructose produced from sucrose is oxidized to a mixture of trihydroxy glutaric acid, tartaric acid and glycolic acid [33]. These hydroxy carboxylic acids forms complex with zirconium and yttrium ions resulted in a white sol. IR spectrum of the sol is shown in Fig. 2. Peak observed at wave numbers 1640 cm^{-1} and 1363 cm^{-1} in the IR spectrum are attributed to carboxyl group complexed with the Zr and Y ions. Formation of Zr–Y hydroxyl complexes was further confirmed by synthesizing an analogous complex from Zr–Y composite nitrate solution and analytical reagent grade tartaric acid. A white precipitate obtained by mixing Zr–Y composite nitrate solution and tartaric acid solution showed similar peaks in the IR spectrum as the white sol.

Viscosity of the sol measured in a Brookfield viscometer was 1600 mPa s at shear rate of 10 s^{-1}. The hydroxyl carboxylic acid complexes of Zr and Y in the sol are expected to be in the nanometer size range. This was evidenced from the fact that the sol did not show any sedimentation during aging for a period of more than 1 month. The high stability of the sol particles against sedimentation would also be due to its hydrophilic nature. The sol on drying in an oven at 120 °C formed a black precursor mass. The black colour of the precursor mass is due to charring of un-reacted hydroxy carboxylic acids and carbohydrates in presence of nitric acid during drying at 120 °C. The precursor mass could be a uniform dispersion of Zr–Y hydroxy

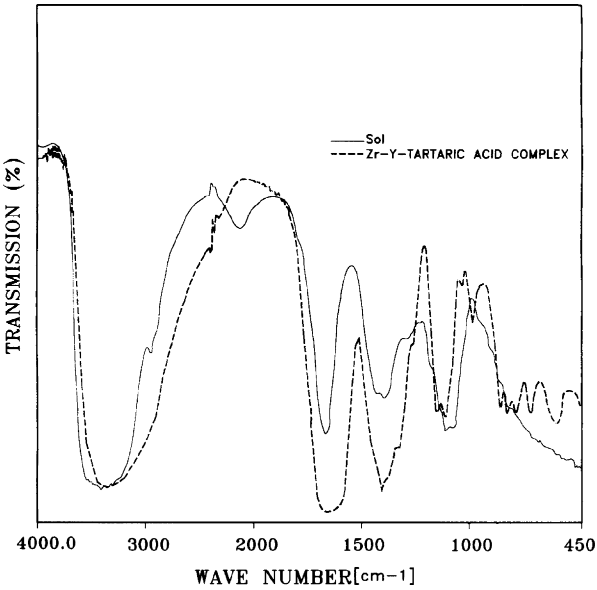

Fig. 2. IR spectrum of the sol showing formation of Zr–Y hydroxy carboxylic acid complex.

carboxylic acid complexes in the charred organic matrix. In our previous work [29,30] for preparation of lanthanum strontium manganite (LSM) and lanthanum strontium chromite (LSC) materials by sucrose synthesis a dark viscous polymeric resin was obtained when aqueous acidic (pH 1) metal nitrate solution heated with sucrose instead of the white sol obtained in the present work. In the earlier case, polymerization of sucrose through condensation of hydroxyl groups took place and the metal ions were attached to the polymer structure by co-ordination through the –OH group [29–31]. These resins on drying produced foams with interconnected macro porous structure, which facilitated their easy combustion. Instead of the foam precursor obtained in sucrose synthesis of LSM and LSC a relatively dense mass was obtained in the present case.

Fig. 3 shows TGA–DTA plot of the precursor sample. Weight loss of nearly 2.5% observed up to 200 °C is due to moisture present in the sample. Above 200 °C, the precursor mass decomposes in two stages. Weight loss of nearly 37% observed in the temperature range 200–350 °C is attributed to dehydration and decarboxylation of hydroxyl carboxylic acids complexes and un-reacted hydroxy carboxylic acids. Nearly 40 wt.% loss observed in the temperature range 350–740 °C is due to burnout of the carbon. A broad exothermic peak from 200 °C to 740 °C was observed in the DTA corresponding to the dehydration, decarboxylation and burn out of carbon from the precursor mass.

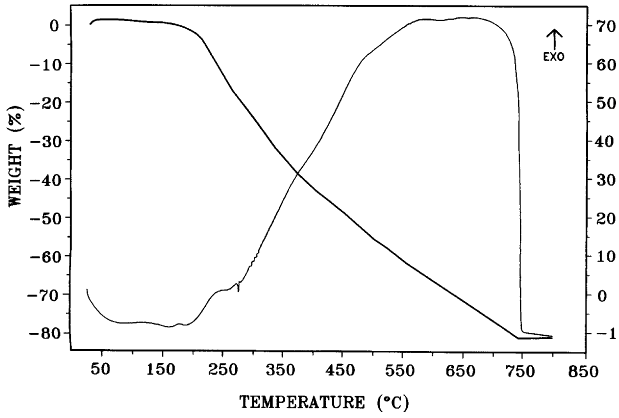

Fig. 3. TGA–DTA plot of the precursor mass sample.

It is well known that the strength of powder particle aggregates increases with increase in calcination temperatures, which make the deagglomeration process laborious. Therefore, it was decided to remove the organics from the precursor mass at low temperature. Though TGA showed weight loss up to 740 °C complete burnout of organics from the precursor mass was possible by heating at 600 °C for a period of nearly 8 h in a muffle furnace. The powder obtained after calcinations at 600 °C showed peaks corresponding to cubic YSZ phase. Broad XRD peaks indicate nanocrystalline nature of the YSZ material. However, YSZ sample calcined at 1200 °C showed sharp peaks of cubic phase in XRD spectrum indicating considerable grain growth during calcination. The crystallite size calculated using Scherer equation was 9.4 nm and 32.8 nm for the YSZ powder calcined at 600 °C and 1200 °C, respectively. Fig. 4A and B shows the XRD spectrum of YSZ as prepared (after removal of organic matter by calcinations at 600 °C) and calcined at 1200 °C for 1 h, respectively.

The YSZ obtained by calcination of the organic precursors at 600 °C comprised a soft agglomerate of fine particles. These agglomerates were broken down in to fine particles by planetary

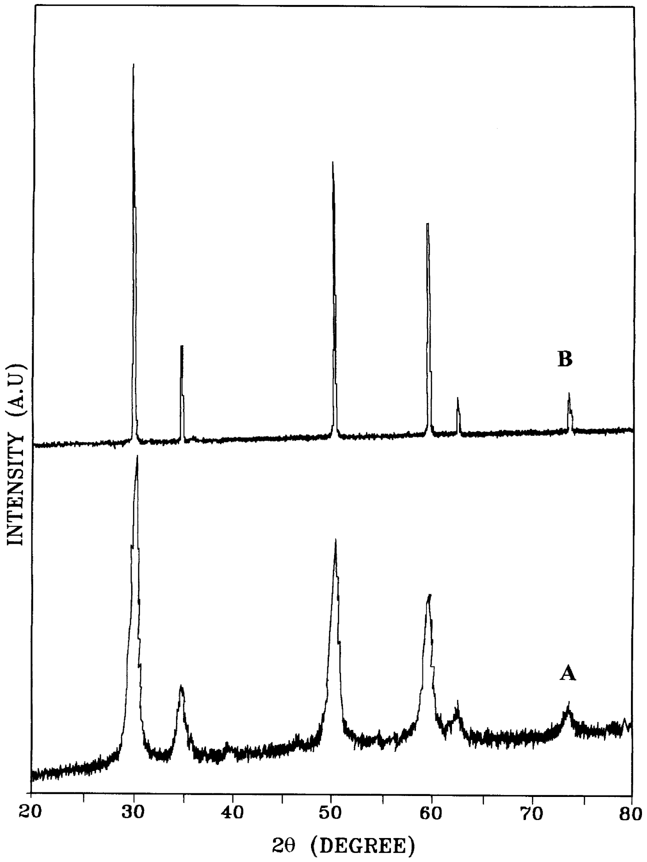

Fig. 4. XRD spectrum of the YSZ (A) after removal of organic matter by calcinations at 600 °C and (B) after calcinations at 1200 °C for 1 h.

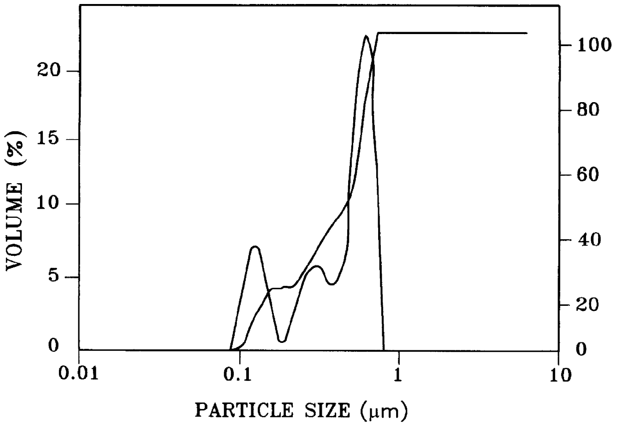

Fig. 5. Particle size distribution of the YSZ powder.

milling in iso-propanol medium for 24 h. Fig. 5 shows particle size distribution of the YSZ powder obtained after planetary milling. The powder contains all submicron particles with size in the range of 0.1–0.8 μm. D_{50} value of the YSZ powder was 0.5 μm. Surface area of the YSZ powder was 36.4 m^2/g. SEM photomicrograph of the YSZ powder is shown in Fig. 6. Fine particles and their agglomerates are clearly seen in the micrograph. It is well known that fine particles have a high tendency to agglomerate during drying of their suspensions. Agglomerates observed in the SEM photograph are formed during drying of the YSZ powder after ball milling in iso-propanol medium. Fig. 7 shows TEM photograph of the YSZ powder. The individual powder particles were aggregates of nanocrystallites. The crystallite size observed in TEM is nearly 10 nm. The crystallite size observed in TEM is in agreement with the crystallite size (9.3 nm) calculated from XRD data.

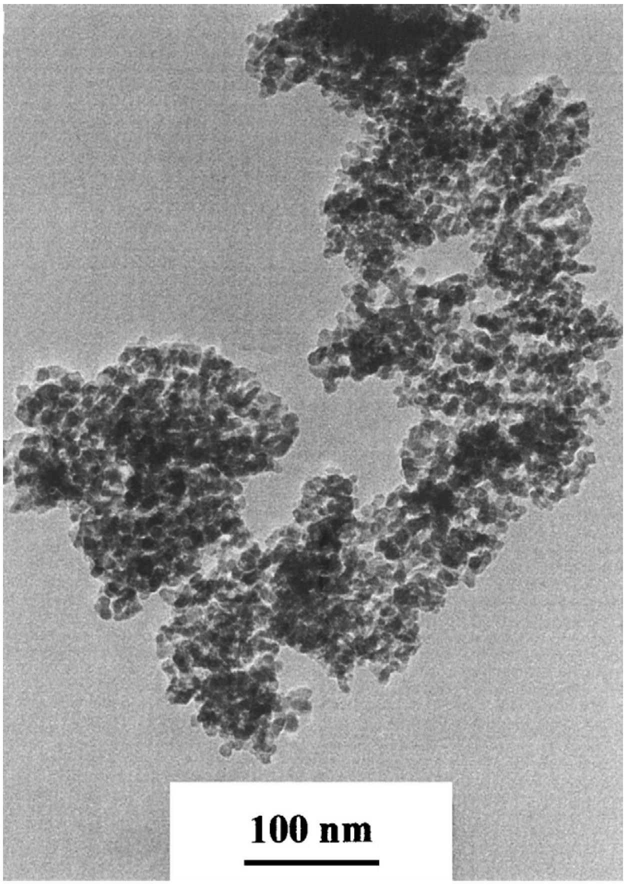

Fig. 7. TEM photomicrograph of the YSZ powder.

The deagglomerated YSZ powder pressed at 50 MPa pressure in a 10 mm diameter cylindrical steel die showed a green density of 54% TD. Fig. 8 shows sintered density versus sintering temperature of the YSZ powder compacts. The YSZ powder compact sintered at 1300 °C showed density of 93.6% TD. The density of the YSZ samples increased with sintering temperature up to 1450 °C and thereafter remains more or less constant. The maximum sintered density observed was 96.7% TD. The sintered YSZ sample showed grain size in the range of 1.2–3.5 μm. Average grain size calculated from the fractured surface microstructure, by linear intercept method, was 2.2 μm. Few isolated micro pores were observed in the grain boundaries. SEM photomicrograph of fractured surface of the YSZ sample sintered at 1450 °C is shown in Fig. 9.

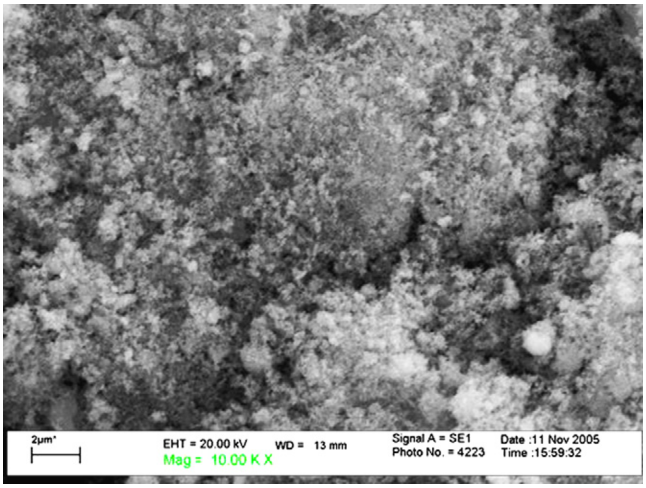

Fig. 6. SEM photomicrograph of the YSZ powder.

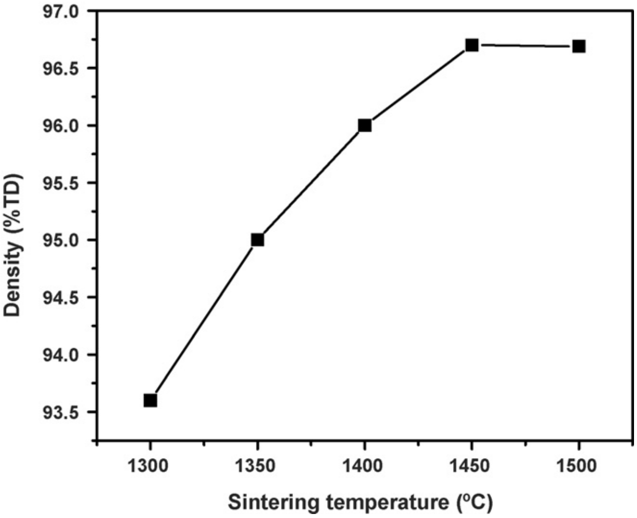

Fig. 8. Sintered density vs. sintering temperature of the YSZ powder compacts.

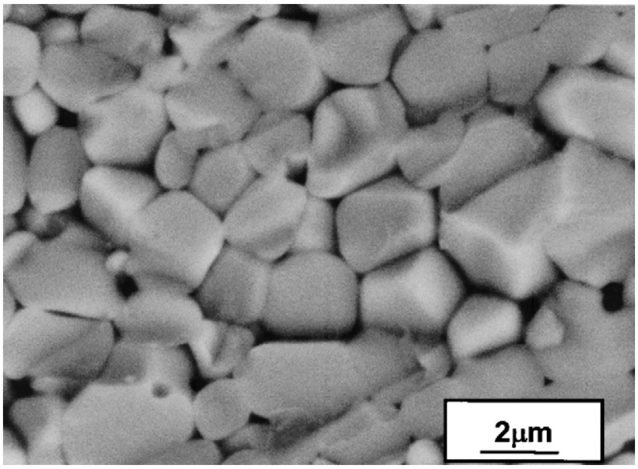

Fig. 9. SEM photomicrograph of fractured surface of the YSZ sintered at 1450 °C.

4. Summary and conclusions

Zr–Y composite nitrate solution containing excess nitric acid when heated with sucrose formed a stable white sol. IR spectral study revealed the sol contain hydroxyl carboxylic acid complexes of Zr and Y. Hydroxy carboxylic acids were formed *in situ* from sucrose by oxidation with nitric acid. Calcination of the Zr–Y hydroxy carboxylic acid complexes at 600 °C produced loosely agglomerated particles of cubic YSZ. The YSZ deagglomerated by planetary milling contain submicron particles with D_{50} value of 0.5 μm. The powder particles were aggregates of nanocrystallites of nearly 10 nm size. YSZ ceramic with density 96.7% TD and average grain size 2.2 μm could be prepared by cold compaction of the powder and sintering at 1450 °C.

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