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Powder synthesis and sintering of high density thoria–yttria ceramics

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Abstract

ThO_2–n mol% Y_2O_3 ceramic powders with submicron average particle size were prepared by the citrate technique using thorium oxalate, yttrium nitrate, citric acid and ethylene glycol. For $n = 3$, 6, 9 and 12, reactive thoria–yttria solid solution powders with surface areas of 17.3, 11.1, 9.4 and 8.7 m^2/g, respectively, were obtained. X-ray diffraction, scanning electron microscopy and transmission electron microscopy were carried out for characterization of the powders. Pressing and sintering at 1550 °C/2 h produced pellets with densities higher than 90% of the theoretical density. The pellets were also characterized by XRD and SEM.

1. Introduction

Thorium oxide is one of the structurally stable oxides. Its structure is the cubic CaF_2-type up to its melting point at ≈3300 °C. Yttrium oxide crystallizes in the Tl_2O_3-type structure, common to the majority of the rare earth oxides [1]. Extensive solid solutions up to 45–50 mol% Y_2O_3 are reported for the ThO_2–Y_2O_3 system, the most important thoria-based electrolyte [1], and for several rare earth–thorium oxide systems [2].

Thorium oxide, like other oxides of tetravalent cations (zirconium oxide, cerium oxide) is a material with predominant electrical conduction via O^{2-} ions [1,3]. The technological applications of these oxygen ion-conducting solid electrolytes are manifold, after forming solid solutions with oxides of lower valence cations [4]. Zirconia-based solid electrolytes, for example, are widely used in the steel industry to determine the oxygen content during the fabrication of steel, i.e., for process control in the industry. They are also widely used as a manufactured component in the automotive industry, to determine the relative amount of oxygen-containing chemicals that are by-products of the engine combustion (CO, CO_2, NO_x, etc.) during vehicle operation.

Another promising technological application is in the electrical energy production industry. Much effort has been put in the development of appropriate components for environmental clean energy production using solid oxide fuel cells (SOFCs) [5]. The most studied solid electrolyte for SOFCs is yttria-doped zirconia but research work is being pursued on the search for new solid electrolytes with improved ionic conductivity.

The role played by the dopants with lower valence (2+ and 3+) than the tetravalent (Zr^{4+} or Th^{4+}) oxide host is the introduction of oxygen vacancies in the lattice, required for charge neutrality. These vacancies are known to be responsible for the observed high ionic conductivity in these systems. The ionic conductivity of fluorite-type oxides, e.g., doped thoria and doped zirconia, depends on the nature of dopant and its concentration.

Zirconia-based solid electrolytes find applications in several commercial devices, but not thoria-based solid electrolytes. This is due to several reasons: first, for the same dopant, yttria for example, the ionic conductivity

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of zirconia is larger than that of thoria electrolytes. Second, even though its specific activity is very low, thoria is predominantly an alpha emitter, preventing its unrestricted use in commercial applications. Third, due to its high melting point, very high temperatures are required for sintering thoria compacts obtained using the conventional methods to densities higher than 90% of the theoretical density. Back in 1973, Ca^{2+}-doped thorium oxide pellets were prepared by solid state synthesis and pre-sintering at 1400 °C and sintered at a temperature as high as 2000 °C to get dense samples [6]. Later, preparation of high density thoria pellets sintered at 1150 °C was reported using niobia as additive [7]. Microwave heating thorium nitrate in the presence of polyvinyl alcohol was used to produce thorium oxide powders, which after pressing, were sintered at 1300 °C to densities higher than 90% of the theoretical density [8].

In this paper, we deal with the preparation of thoria–yttria solid electrolytes by a wet chemical route, based on Pechini's method [9], to produce surface active powders which could be sintered at relatively low temperatures. Moreover, radio-toxicity problems are minimized since the preparation is in wet environment [8] and the natural radiation is restricted to the container. We have studied this oxide because of its wide availability in Brazil (it is produced on a large scale in a pilot plant at this Institute as thorium nitrate to be deposited in mantles for candles to brighten their lights). Moreover, wet chemical methods such as precipitation, polymeric precursor, sol–gel, etc., usually produce powders that can be sintered to high densities at temperatures lower than the ones required for powders prepared via solid state synthesis.

2. Experimental

Thorium oxalate, $Th(C_2O_4)_2$, and thorium nitrate, $Th(NO_3)_4$, were produced in a pilot plant of this Institute. Thorium oxide powders were obtained by calcination of thorium oxalate. Yttrium nitrate was obtained by adding commercial yttrium oxide to nitric acid at 60 °C under stirring for several hours. After dissolution, distilled water was added and the standardization of the solution was done by precipitation with ammonia, calcination of the precipitate at 800 °C/1 h and weighing of the resulting oxide powder. The experimental sequence for preparing ThO_2–n mol% Y_2O_3 ($n = 3$, 6, 9 and 12) ceramic powders was the following: citric acid and ethylene glycol (60:40 wt% ratio) were added to a mixture of thorium nitrate and yttrium nitrate for the desired stoichiometry (n value) of thoria–yttria; the temperature of the bath, kept at 60 °C was raised to 110 °C for NO_2 elimination producing a brownish resin; the resin-to-oxide transformation was carried out in two steps: calcination at 400 °C/6 h in air yielding a black powder, followed by annealing at 800 °C/24 h under flowing oxygen for carbon removal and solid solution formation, yielding a light brown powder [10,11]. The carbon content in the powders was determined using a LECO CS244 carbon analyzer. Fig. 1 shows a flowchart of the main experimental steps for the preparation of the thoria–yttria powders.

The distribution of the particle size was determined by particle size analyses carried out on the powders with a 5100 Micromeritics Sedigraph Analyzer. This analysis allows size determinations in the 0.18–300 μm range assuming the detected particles to be spherical. The solution was prepared under ultrasound homogenization (for 6 min) with 1 g of the powder, 50 ml of distilled water and sodium hexametaphosphate as deffloculant.

The specific surface was determined by the BET method using a Strohlein Instruments Area-meter II equipment.

Powder suspensions were prepared for observation in a JEOL JEM200C transmission electron microscope. The specimens were prepared by dispersing the powder under ultrasound in a dilute solution of distilled water and sodium hexametaphosphate. The dispersion was sprayed over the TEM sample holder and coated with gold by sputtering in an argon gas plasma.

Specimens for X-ray diffraction analysis were prepared by adding the thoria–yttria powders to a 200 mesh silicon powder ($\simeq 80/20$ volume ratio), mixing in an agate mortar and inserting in a glass sample holder using isopropanol as medium for obtaining a flat surface to be positioned in the Bragg diffraction surface of the X-ray diffractometer in a θ–2θ Bragg–Brentano configuration.

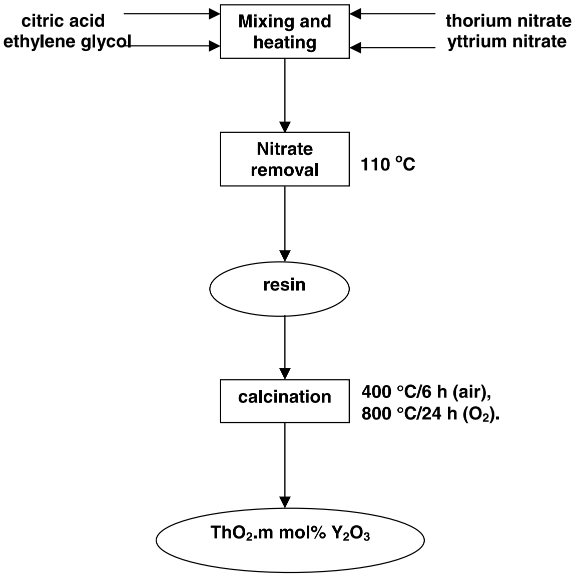

Fig. 1. Experimental sequence followed for preparing thoria–yttria powders by the citrate technique.

Measurements were performed in a Bruker-AXS D8 Advance X-ray diffractometer with CuKα radiation at 40 kV – 40 mA in the 25–95° 2θ range.

Ceramic pellets were prepared as 10 mm diameter by 2 mm thickness discs by uniaxially cold pressing the powders at 147 MPa followed by sintering at 1550 °C/2 h in air. The apparent densities of the sintered pellets were evaluated by the Archimedes method (immersion in water). The theoretical density of each composition was evaluated taking into account the lattice parameter determined by X-ray diffraction in polished surfaces of the sintered pellets.

For SEM observations, the surfaces of the pellets were polished with silicon carbide powder, followed by diamond paste (15, 9, 6 and 1 μm sequence). Afterwards, they were chemically etched with boiling orthophosphoric acid for ≈20 min, followed by 1500 °C/30 min thermal etching, to study morphological aspects of the grains in the JEOL JXA6400 scanning electron microscope.

3. Results and discussion

3.1. Powder characterization

The amount of carbon in the powder, after calcination of the polymeric resin at 400 °C/6 h was determined to be in the 7–22 wt% range. A second calcination at 800 °C/24 h under flowing oxygen produced powders with ≈0.3 wt% of residual carbon.

Table 1 shows values of the specific surface determined by the BET method and the corresponding average particle size of ThO_2–n mol% Y_2O_3 ($n = 3$, 6, 9 and 12) powders prepared by the citrate technique. The specific surface (8.7–17.3 m^2/g) is close to the values reported for thoria powders obtained by microwave heating a mixture of thorium nitrate and polyvinyl alcohol (10–15 m^2/g) [8]. Reported results for thoria obtained using the gel combustion synthesis technique yielded also similar values (9.9–15.8 m^2/g) [12]. Recently [13] a value of 13 m^2/g for the surface area of thoria powders obtained by the gel combustion technique was reported. The equation $D = 6/(F\rho S)$ was used to give an indication of the order of magnitude of the average particle size D; F, S and ρ stand for the packing factor [14], the specific surface and the theoretical density, respectively. The packing factor was assumed as unity to determine the order of magnitude of D values. The calculated D values are in the 36–71 nm range, showing that the citrate technique is suitable for preparing submicron thoria–yttria powders.

Table 1
Values of specific surface (S) and the corresponding average particle diameter (D) for all thoria–yttria compositions prepared by the citrate technique

Composition	S (m^2/g)	D (nm)
ThO_2–3 mol% Y_2O_3	17.3	36
ThO_2–6 mol% Y_2O_3	11.1	56
ThO_2–9 mol% Y_2O_3	9.4	66
ThO_2–12 mol% Y_2O_3	8.7	71

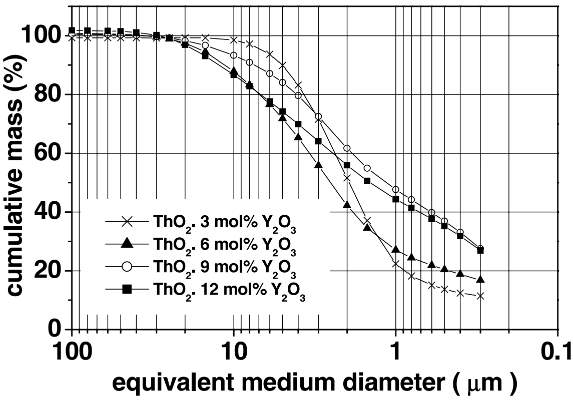

Fig. 2. Curve of distribution of particle size of ThO_2–n mol% Y_2O_3 ($n = 3$, 6, 9 and 12) ceramic powders prepared by the citrate technique.

The agglomerated particle size distribution, measured by X-ray sedigraphic analysis, is shown in Fig. 2. The median equivalent diameters of the agglomerates (far from the real solid powders, the technique assumes spheroidal particles) are in the 1.5–2.5 μm range. Comparing these values with those determined by the BET method (see Table 1), one may conclude that the sedigraphic results are indeed related to agglomerated powders. In order to be sure of the average particle size of the thoria–yttria powders prepared by the citrate technique, suspensions were prepared for observation in a transmission electron microscope.

Fig. 3 shows a typical micrograph obtained by TEM analysis of the ThO_2–9 mol% Y_2O_3 powders prepared by the citrate technique. The powders are very fine, with an evaluated average particle size of tens of nanometers, of the same order of magnitude of the particle size determination by the BET method.

X-ray diffraction measurements on ThO_2–n mol% Y_2O_3 powders prepared by the citrate technique were carried out. Only the X-ray reflections due to thorium oxide are detected. Within the detection limits of this technique no reflections due to yttria were detected, which could be taken as a preliminary evidence of solid solution formation. Solid solution formation for all compositions were carefully studied by the determination of the variation of the lattice parameters with yttria content. The results were published elsewhere [15]. Analysis of the lattice parameter showed that it decreases for increasing yttria addition, a further evidence of solid solution formation [16].

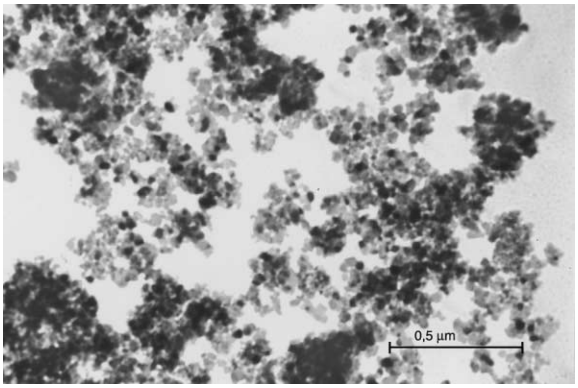

Fig. 3. TEM micrograph of ThO_2–9 mol% Y_2O_3 powders prepared by the citrate technique shown in Fig. 1.

3.2. Characterization of the sintered ceramics

The results of the apparent densities are shown in Table 2. The density values are in the 88–95% TD range. The density increases with yttria content up to 9 mol% Y_2O_3 and decreases for larger content, even though the limit for solid solution of yttria in thoria was reported as 15 mol% at 1400 °C [17]. A higher value was obtained for the ThO_2–9 mol% Y_2O_3 specimen which was prepared by mixing the stoichiometric compositions of the individual oxides. After sintering in the same conditions as the specimen prepared using powders obtained by the citrate technique, 75% TD was determined. This result was expected. It is already known that powders prepared by wet chemical methods are more sinteractive than powders prepared by physical mixing of the starting oxides.

The X-ray diffraction results on the sintered pellets with different yttria content are shown in Fig. 4. A decrease of the half-width of the main diffraction lines due to an increase of the crystallite size after sintering at 1550 °C is observed.

The SEM micrograph of the polished and etched surface of the ThO_2–9 mol% Y_2O_3 sintered ceramic pellet is shown in Fig. 5 for the specimen prepared from powders obtained by the citrate technique. It was found that the larger the yttria content, the lower is the porosity. An increase in the average grain size was also noticed. Moreover the grain sizes are homogeneously distributed and the grain shape is approximately spherical. Fig. 6 shows a SEM micrograph for a ThO_2–9 mol% Y_2O_3 sintered specimen prepared from powders obtained by the powder mixing technique. Small grain

Table 2
Hydrostatic density of the ThO_2–*n* mol% Y_2O_3 ($n = 3, 6, 9, 12$) sintered pellets

Composition (nominal)	TD (%)
ThO_2–3 mol% Y_2O_3	93.6
ThO_2–6 mol% Y_2O_3	94.5
ThO_2–9 mol% Y_2O_3	95.0
ThO_2–9 mol% Y_2O_3 (mp)	75.2
ThO_2–12 mol% Y_2O_3	90.6

The powders were prepared by the citrate technique. The density of a ThO_2–9 mol% Y_2O_3 sintered pellet prepared using mixed oxide powders (mp) is also shown for comparison purposes.

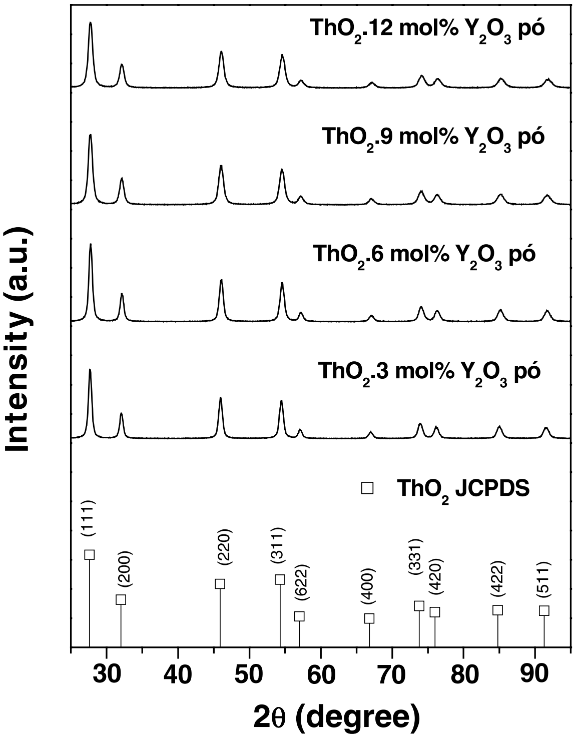

Fig. 4. X-ray diffraction patterns of ThO_2–*n* mol% Y_2O_3 ($n = 3, 6, 9, 12$) sintered pellets.

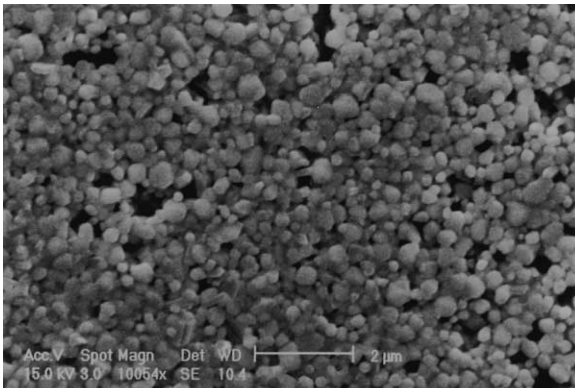

Fig. 5. SEM micrographs of polished and (thermally and chemically) etched ThO_2–9 mol% Y_2O_3 surfaces of sintered pellets. Powders prepared by the citrate technique. Sintering conditions: 1550 °C/2 h.

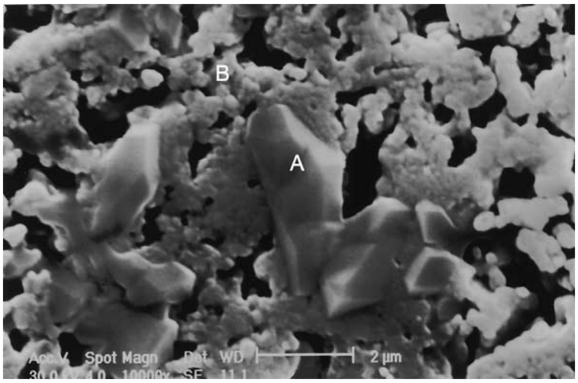

Fig. 6. SEM micrograph of polished and (thermally and chemically) etched ThO_2–9 mol% Y_2O_3 surface of sintered pellet. Powders prepared by the powder mixing technique. Sintering conditions: 1550 °C/2 h.

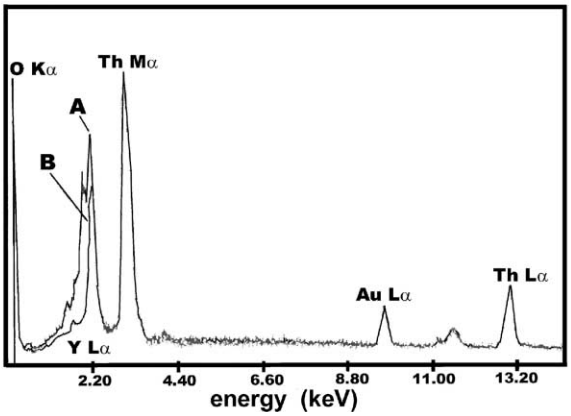

Fig. 7. EDS analysis of the large (A) and small grains (B) shown in Fig. 6. The Th Mα lines (2.996 and 2.986 keV) overlap the Th Mβ line (3.145 keV). The line at 11.5 eV corresponds to Au Lβ.

sizes (≈0.2 µm) as well as large grain sizes (≈2.0 µm) are easily identified. The analysis of this micrograph by EDS (Fig. 7) shows that the large grains present a higher yttria content. That means that a relationship holds between grain growth and yttria content, the yttrium ions being heterogeneously distributed over the specimens. These SEM results are an evidence that the preparation of ceramic powders by wet chemical techniques, here the citrate technique, results not only in sinteractive and homogeneous powders, but also in sintered ceramic bodies with grain sizes homogeneously distributed with an even chemical composition.

4. Conclusions

Reactive thoria–yttria powders with average particle sizes in the submicron range have been obtained following a polymeric precursor route. Thoria–yttria pellets prepared by pressing and sintering these powders at 1550 °C (less than 50% of the thoria melting point) have densities higher than 90% TD, homogeneous chemical composition, and homogeneous grain morphology in comparison with pellets obtained by pressing and sintering physically blended thorium and yttrium oxides.

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