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Novel approach for the bulk synthesis of nanocrystalline yttria doped thoria powders via polymeric precursor routes

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Abstract

Three different polymeric precursor routes viz., (i) amorphous citrate process, (ii) Pechini process and (iii) polyethylene glycol assisted process were compared for synthesising nanocrystalline powders of 7.5 mol% yttria doped thoria (YDT). In each of the processes, parameters such as metal-to-fuel ratio or composition of fuel were varied and the effects were analysed. TG/DTA studies were conducted to identify the ignition temperatures of the precursors. Also, a novel experimental procedure with controlled combustion was devised for the preparation of powders based on the thermal analysis data. All the processes result in phase pure and nanocrystalline powders. The average crystallite size of the powders ranged between 9 and 18 nm. The powder samples were analysed for their carbon content and studied for their sinterability. Densities as high as 99% th.d. could be achieved by sintering the compacts of powders obtained from (i) amorphous citrate process with CA/M ratios 2.0 and 3.0, (ii) Pechini processes (independent of fuel composition) and (iii) PEG-assisted process using PEG 4000 at a relatively low temperature of 1500 °C for 2 h.

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1. Introduction

Zirconia and thoria based solid electrolytes are well known oxide ion conductors. They are used in oxygen sensors and in thermochemical and kinetic experiments [1–3]. These materials exhibit high oxide ion conductivity with ionic transport number $\geqslant 0.99$ over a wide range of temperatures and oxygen partial pressures. While zirconia electrolytes can be used at relatively high oxygen partial pressures ($\approx 10^5$–10^{-18} bar at 1000 °C), thoria based electrolytes can be used at lower oxygen partial pressures ($\approx 10^{-6}$–10^{-25} bar at 1000 °C) [2]. The ionic conductivity of yttria doped thoria (YDT) attains a maximum at 7.5 mol% concentration of Y_2O_3 while in case of calcia stabilized zirconia (CSZ) this maximum is at 12–13 mol% concentration of CaO [1]. The 7.5 mol% Y_2O_3–ThO_2 has been identified as the most suitable electrolyte for monitoring oxygen concentration in liquid sodium coolant of fast reactors [4–9]. A solid electrolyte for this application is required as a ceramic body with high density ($\geqslant$ 99% th.d.) and fine-grained microstructure. The conventional method of preparing ceramic bodies requires very high sintering temperatures of the order of 1850–2200 °C [10–14] resulting in larger grain size and poor mechanical strength. Many soft chemistry routes are therefore investigated to prepare homogeneous and fine crystalline ceramic powders that could be sintered at relatively low temperatures. In recent years, combustion synthesis has attracted a good deal of attention as it is a simple and cost effective low temperature method for producing nanocrystalline powders [15–18]. While citric acid (CA) is used as the fuel in the amorphous citrate process [17], a mixture of

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citric acid and ethylene glycol (EG) is used in the Pechini process [18]. Polyalcohol such as polyvinyl alcohol (PVA) along with citric acid has also been used as fuel [17].

Syntheses of nanocrystalline powders of pure thoria by the combustion method have been carried out extensively in our laboratory using urea and /or citric acid as fuels [19–21]. Purohit et al. [22] have also prepared nanocrystalline pure ThO_2 powders by the combustion method using glycine as fuel. Limited reports are available in the literature regarding preparation of fine powders of YDT by the combustion method [23–25]. Table 1 compares the experimental conditions and the results reported in those works. Cosentino and Mucillo [23,25] had prepared fine powders of n mol% Y_2O_3–ThO_2 ($n = 3$, 6, 9 and 12) by the combustion method using 3:2 ratio by mass of citric acid and ethylene glycol as fuel. Pellet compacts of these powders achieved ≈90–95% th.d. when sintered at 1550 °C for 2 h in air. Arul Antony et al. [24] used equimolar quantities of citric acid and ethylene glycol as fuel and prepared 7.5 mol% Y_2O_3–ThO_2 fine powders. The authors reported that the pellet compacts could be sintered at 1350 °C for 20 h in purified argon atmosphere to yield products with >99% th.d.

In this work, we have carried out a systematic study of three different processes for the preparation of 7.5 mol% Y_2O_3–ThO_2 powders, namely (i) amorphous citrate process, (ii) Pechini process and (iii) polyethylene glycol (PEG) assisted process. Since the combustion techniques involve autocombustion of the polymeric precursor powders on heating, the processes sometimes become very violent. Hence, only small-scale batch preparations (typically in tens of gram quantities) are generally employed and scaling them up is difficult. With a view to overcome this problem, a novel approach was devised and adopted in this work, so that controlled combustion is achieved and the violent reactions can be avoided.

2. Experimental

2.1. Chemicals

Yttrium nitrate (99.9%, M/s. Indian Rare Earths, India), thorium nitrate (AR grade, M/s. Fisons, USA) and polyethylene glycol of average molecular weights of 400, 600, 4000 and 6000 (AR grade, M/s. Fluka, Switzerland) were employed in this work. AR grade nitric acid was further distilled in quartz apparatus and used.

2.2. Experimental procedure

As thorium and yttrium nitrates are highly hygroscopic, stock solutions of thorium and yttrium nitrates were first prepared in distilled water. The concentrations of thorium and yttrium in the stock solutions were estimated gravimetrically as their respective oxides after precipitating them first as oxalate followed by conversion to oxide by heating in air at 850 °C for 2 h. The concentrations were also estimated by evaporating a known quantity of the stock solution to dryness and decomposing the nitrate to give oxide by heating at 850 °C for 2 h.

The general procedure adopted for the preparation of oxide solid solution is schematically shown in Fig. 1. In the amorphous citrate process, the required stoichiometric quantities of metal nitrate solutions were mixed with the citric acid solution. On heating at 90–95 °C, the solution containing thorium and yttrium nitrates first turned white (indicating a precipitation of thorium citrate [26]) and then gradually became colourless when gel formation set in ensuring homogeneity of the

Table 1
Literature work on YDT preparation by combustion synthesis: experimental conditions and properties of sintered bodies

S. no.	Reference	YDT composition	Fuel	Powder characteristics		Pellet characteristics		
				Average particle size (μm)	Specific surface area (m^2/g)	Pelletising conditions	Sintering conditions	Rel. density
1	Cosentino and Muccillo [23]	ThO_2-9 mol% Y_2O_3	CA:EG in wt% ratio of 60:40	1.1[a]	–	10 mm dia, 2 mm thick, 150 MPa	1550 °C/2 h in air	91.2%TD
2	Arul Antony et al. [24]	ThO_2-7.5 mol% Y_2O_3	CA:EG in mol% ratio of 50:50	–	–	15 mm dia, 5 mm thick, 180 MPa	1350 °C/20 h in purified argon	>99%TD
3	Cosentino and Muccillo [25]	ThO_2-n mol% Y_2O_3 (n: 3, 6, 9, 12)	CA:EG in wt% ratio of 60:40	1.5–2.5[a]	8.7–17.3	10 mm dia, 2 mm thick, 147 MPa	1550 °C/2 h in air	90.6–95.0%TD

CA: citric acid; EG: ethylene glycol.

[a] From sedigraph analysis.

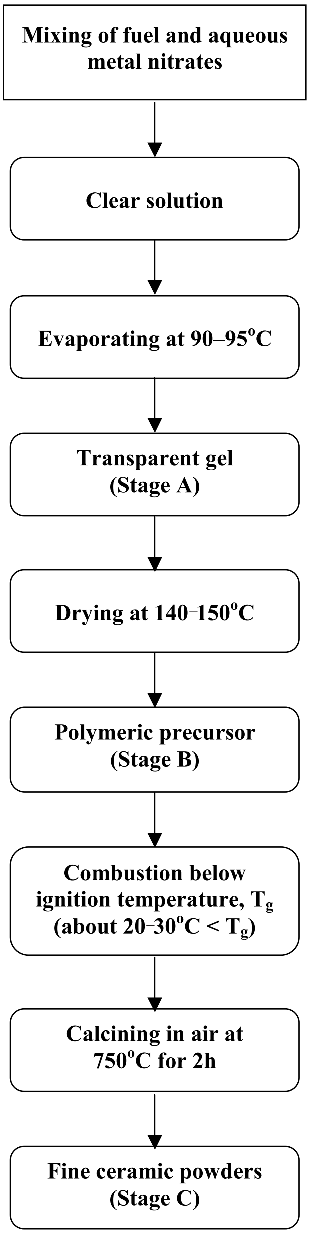

Fig. 1. Flow chart of the synthesis procedure for the amorphous citrate process, Pechini process and PEG-assisted process.

composition (stage A). The gel formation took place in 4–5 h. These gels were later dried in an electric oven at 140–150 °C for 10–15 h during which they expanded three or four times of their original volume resulting in the formation of bread like material (stage B). The products (termed henceforth as precursor) were ground and used for further studies. Precursors with citric acid-to-total metal ion ratios of 0.5, 1.0, 2.0 and 3.0 were prepared and the corresponding processes are denoted as ACP-0.5, ACP-1.0, ACP-2.0 and ACP-3.0, respectively.

In the Pechini process, the molar ratio of citric acid-to-total metal ion was maintained as 1.0 in the starting solution. The adequate amount of ethylene glycol was added to it so that the molar ratio of citric acid to ethylene glycol was 1:1 (denoted as PP 1:1). This was then converted into precursor by adopting the same procedure as in the case of the amorphous citrate process. Precursors were also prepared with 1:2 and 1:4 molar ratios of citric acid and ethylene glycol and the processes are represented as PP 1:2 and PP 1:4, respectively.

In the PEG-assisted process, the ratio of citric acid-to-total metal ion was again maintained as 1.0 in the starting solution. Polyethylene glycol was added to this solution such that the molar ratio of the total metal ion to PEG monomer was 1.0. Polyethylene glycols with molecular weights of 400, 600, 4000 and 6000 were used for this purpose and the respective processes are denoted as PEG 400, PEG 600, PEG 4000 and PEG 6000, respectively. Processing conditions to produce the precursor from this were identical as in the above two processes.

Thermal decomposition and mass loss characteristics of the polymeric precursors were studied by thermogravimetric and differential thermal analysis techniques. A simultaneous TG/DTA system of M/s. Rheometric Scientific Co., UK was used for this purpose. Approximately 15 mg of precursors were used as samples. The studies were carried out up to 1000 °C at a heating rate of 10 °C/min under flowing oxygen condition (flow rate = 50 ml/min). Ignition temperatures of the precursors were determined from the TG/DTA patterns.

The precursors (≈10–20 g) taken in an alumina crucible and placed in a quartz tube were first heated under flowing air for about 30 min at 20–30 °C lower than their ignition temperatures (obtained from the TG/DTA results) to effect the controlled combustion. The temperature of the sample was then increased by 10 °C and maintained at that level for another 30 min. This was continued up to 30 °C above the ignition temperature. This procedure consistently avoided the combustion reaction from occurring in a violent manner. The resulting powder was then calcined at 750 °C for 2 h under flowing air for elimination of any residual carbon.

The powders obtained after calcinations (stage C) were characterised by X-ray diffraction for phase identification and determination of crystallite size. A Siemens D500 X-ray powder diffractometer with Cu Kα radiation and graphite monochromator was used for this purpose. The average sizes of the crystallites in the samples were determined by measuring the broadening of the (1 1 1) peak profiles of the YDT phase and employing Scherrer's formula [27]. NBS silicon was used as internal standard for estimation of the instrumental broadening. The distribution of particle size in the calcined powders was estimated using Malvern Zeta Sizer-3. The specific surface area of the calcined powders was determined using a surface area analyser supplied by M/s. Quanta Chrome Inc. USA. Measurements were carried out on duplicate samples and the average of these results was taken as specific surface area. The amount of carbon present in the calcined powder was determined using a carbon analyser where the sample was oxidized in a stream of oxygen using an induction furnace and the evolved carbon dioxide gas was measured using an infrared detector. Again these measurements were made with duplicate samples and the average of the results was taken as the residual carbon content of the sample of each process.

The sinterability of the calcined powders were determined by compacting the calcined powders into 10 mm diameter and ≈1 mm thick pellets at 60 MPa for a duration of 15 min. Preliminary experiments were carried out to choose appropriate temperature for sintering. Temperatures ranging from 1100 to 1600 °C with soak times varying between 1 and 8 h were employed in these studies. Based on the results, a program of sintering at 1500 °C for 2 h was chosen. The heating/cooling rate adopted during the sintering process was 10 °C/min. The XRD pattern of the sintered pellets were taken and lattice parameters were derived. The densities of the sintered pellets were measured by pycnometry using dibutyl phthalate as the immersion liquid. Average of densities of two pellets from each process was taken as the density achievable by that process. The surface morphology of sintered pellets was studied by scanning electron microscopy (M/s. Philips, Netherlands, Model No. XL30).

3. Results and discussion

The colour of the precursors obtained during YDT syntheses varied from white, yellow to brown. No systematic trend or gradation in colour could be observed. The typical TG/DTA curves of the YDT precursors of three different processes are shown in Fig. 2. The TG/DTA curve of the precursor of the amorphous citrate process with citric acid to metal (CA/M) ratio of 0.5, shown in Fig. 2(a), indicates a gradual mass loss of ≈20% below ≈200 °C. This is followed by a major mass loss of ≈70% occurring in a very narrow temperature range of 208–215 °C which is accompanied by a sharp exothermic DTA peak indicating an ignition process. Further heating does not result in any major mass loss and thermal effects. The ignition temperature of the sample derived from the DTA peak is listed in Table 2.

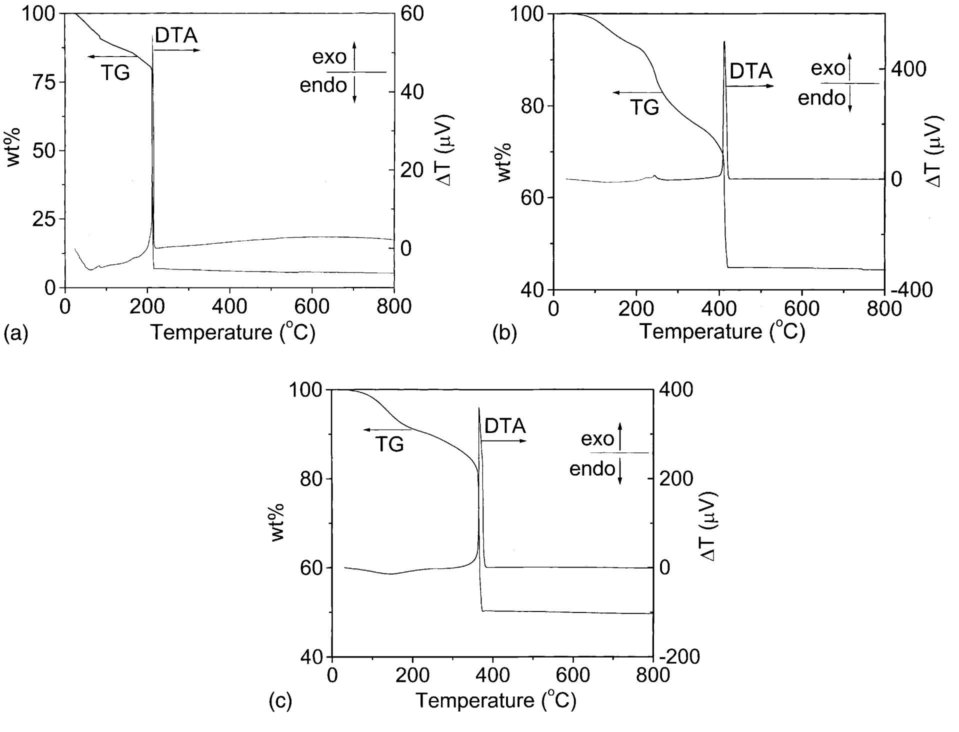

Fig. 2. TG/DTA trace of YDT-precursor synthesised by (a) the amorphous citrate process with CA/M = 0.5, (b) the Pechini process with CA:EG = 1:1 and (c) the PEG-assisted process using PEG400. Heating rate = 10 °C/min; gas ambient = flowing oxygen (50 ml/min).

Table 2
Properties of precursors, calcined powders and sintered pellets of YDT

Process	Ignition temperature of polymeric precursor (°C)	Calcined powder				Relative density of sintered pellet[a] (%TD)
		Particle size (μm)	Specific surface area (m^2/g)	Crystallite size (nm)[b]	Carbon content (wt%)[b]	
Amorphous citrate process						
ACP-0.5[c]	210	77	12.7	10	0.248	96
ACP-1.0	175	44	19.0	10	0.173	98
ACP-2.0	370	25	6.4	10	0.169	99
ACP-3.0	415	48	9.8	11	0.137	99
Pechini process						
PP-1:1[d]	380	29	2.2	12	0.145	99
PP-1:2	325	58	9.6	11	0.169	99
PP-1:4	260	62	29.0	10	0.248	99
PEG-assisted process						
PEG-400[e]	330	23	13.1	9	0.205	98
PEG-600	360	38	2.3	10	0.157	98
PEG-4000	365	36	4.8	18	0.191	99
PEG-6000	340	27	6.4	10	0.163	98

[a] After sintering the pellets at 1500 °C for 2 h in air.
[b] After calcining the precursors at 750 °C for 2 h in flowing air.
[c] ACP-0.5: amorphous citrate process with citric acid-to-total metal ions molar ratio of 0.5.
[d] PP-1:1: Pechini process with 1:1 molar ratio of citric acid and ethylene glycol.
[e] PEG-400: poly ethylene glycol assisted process using polyethylene glycol with average molecular weight of 400.

A similar behaviour was observed with other precursors having different CA/M ratios though their ignition temperatures varied. As seen from the table, the ignition temperature of the precursors was generally high when the fraction of citric acid was increased.

The TG/DTA curve of the YDT precursor prepared by the Pechini process with citric acid-to-ethylene glycol ratio (CA:EG) of 1:1 is shown in Fig. 2(b). The figure shows that the decomposition involved a multi-step process. After a cumulative mass loss of ≈25% below 350 °C, a major mass loss of ≈30% occurred in the temperature range of 350–420 °C. This was also accompanied by a sharp exothermic DTA peak. Further heating did not involve any major mass loss and heat effects indicating the conversion to oxide during the ignition process. The thermal behaviour of samples with CA:EG a ratio of 1:2 and 1:4 was also similar. It is seen from Table 2 that the ignition temperatures of the precursors were distinctly high when ethylene glycol was a constituent of the fuel and the ignition temperature decreased with the increase in CA/EG ratio.

Fig. 2(c) shows a typical TG/DTA curve of the YDT precursor prepared by the PEG-assisted process (PEG 400). The thermal decomposition behaviour of these precursors was similar to those from the Pechini process. The ignition temperatures were consistently above 330 °C for all compositions (between 330 and 365 °C). No systematics in these temperatures were observed with molecular weight of PEG used.

The typical XRD pattern of calcined YDT powders obtained by the amorphous citrate process with a CA/M ratio of 0.5 is shown in Fig. 3(a). Using the XRD pattern, the average crystallite size of the powders was calculated using the Scherrer equation and the sizes were generally in the range of 10–12 nm (except when PEG-4000 was used) and the data are shown in the Table 2. The XRD pattern of the sintered pellets from all processes were obtained with a view to determine the lattice parameters. The typical XRD pattern of the sintered pellet obtained by the amorphous citrate process with a CA/M ratio of 0.5 is shown in Fig. 3(b). Using X'Pert Plus software (M/s. Philips Analytical) all the diffracted lines from pellets of each processes were indexed and the structure was identified as fcc. The lattice parameter of YDT prepared by all the processes ranged between 557.72 ± 0.10 and 557.76 ± 0.10 pm. Comparison of this value with that of pure thoria ($a = 559.7$ pm) reported in JCPDS files [Index No. 42-1462] clearly indicates the solid solution formation. Also these values of the lattice parameter are in excellent agreement with the value of 557.8 pm reported in JCPDS files [Index No. 31-1390] for 7.5 mol% yttria doped thoria.

The particle sizes of the calcined powders were in the range of ≈20–80 μm. Specific surface area and the

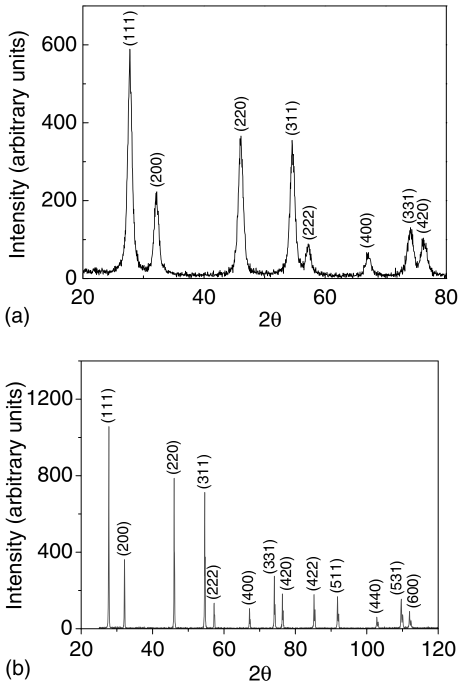

Fig. 3. X-ray diffraction pattern of (a) YDT powder after calcining at 750 °C for 2 h in air, (b) YDT pellet after sintering in air at 1500 °C for 2 h obtained by the amorphous citrate process with CA/M = 0.5. In (b), the split in the peaks is due to diffraction by copper Kα_1 and Kα_2 radiations.

residual carbon contents of the calcined powders are also shown in Table 2. Data on the specific surface area did not show any systematic trend, except in case of the Pechini process where an increase in the values was seen with an increase in ethylene glycol fraction in the fuel. The carbon content of samples prepared by the amorphous citrate process tended to decrease with increase in the CA/M ratio whereas in the Pechini process it was found to increase with increase in the ethylene glycol fraction in the fuel. No such systematic trend was observed in the PEG-assisted process. The carbon contents were distinctly high in samples from the amorphous citrate process with CA/M ratio of 0.5 and from the Pechini process with CA:EG ratio of 1:4.

The densities of pellets from each process after sintering at 1500 °C for 2 h in air are shown in Table 2. It is seen that the densities of the sintered pellets are generally high ($\geqslant 96\%$ th.d.) and densities as high as 99% th.d. could be achieved from the calcined powders. In the Pechini process, the densities of the sintered pellets were always ≈99% th.d. irrespective of residual carbon contents in the calcined powders while in the amorphous citrate process the densities tended to decrease with increase in residual carbon content and particle size of the calcined powders. Sintered densities of pellets obtained from the PEG-assisted process were generally lower than those obtained from the other two methods. Our experimental results show that Pechini processes have an edge over other methods since the density of the sintered products was independent of the fuel composition.

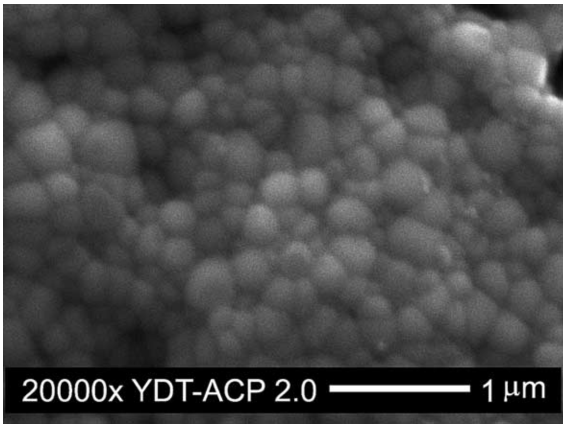

Fig. 4. Scanning electron micrograph of YDT pellet sintered at 1500 °C for 2 h in air using powders synthesised by the amorphous citrate process (CA/M = 2.0).

YDT pellets sintered in air had black dots distributed both on the surface and in bulk. These coloured spots disappeared on changing the gas from ambient to 2%H_2–Ar saturated with water vapour whereby clean and milky white pellets free from coloured spots could be obtained. This is due to the fact that the oxygen partial pressure in air (0.21 bar) is several orders higher than the upper electrolytic domain boundary of YDT ($\approx 10^{-6}$ bar, over a wide temperature range) and hence sintering in air resulted in the formation of colour centers due to the creation of electronic (hole) defects. Whereas the oxygen partial pressure of 2%H_2–Ar saturated with water vapour, is well within the electrolytic domain boundaries of YDT and therefore milky white pellets, free of these defects were obtained.

A scanning electron image of a sintered YDT pellet from the amorphous citrate process with CA/M = 2.0 is shown in Fig. 4. As seen from the image, the grains are generally spherical with uniform size distribution. The grain sizes are of the order of ≈400 nm.

4. Summary and conclusion

Three different polymeric precursor methods were compared for synthesising homogeneous solid solutions of 7.5 mol% Y_2O_3–ThO_2. A controlled combustion technique which avoided violent reactions was used for the combustion of gels into precursors. All these processes yielded crystalline powders of solid solutions of yttria in thoria having crystallite sizes of ≈10 nm. The carbon content of the calcined powders prepared by the amorphous citrate process tended to decrease with increase in the CA/M ratio whereas in the Pechini process it increased with increase in ethylene glycol fraction in the fuel. No such systematic trend was observed in the PEG-assisted process. Sintered densities as high as 99% th.d. could be achieved with powders from (i) the amorphous citrate process with CA/M ratios 2.0 and 3.0, (ii) the Pechini processes and (iii) the PEG-assisted process using PEG 4000. The Pechini processes have an advantage among others, as high sintered densities (99% th.d.) were obtained independent of fuel composition. Among these, the PP-1:1 ratio is preferable as the carbon content of the calcined powder obtained from this process is very low.

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