

# Preparation of nanocrystalline gadolinia doped ceria powders by combustion synthesis process

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*Nanocrystalline gadolinia doped ceria powder was prepared by a combustion synthesis process using polyvinyl alcohol as fuel, with the aim of obtaining nanosized crystallites of this solid solution with high specific surface area. The structures of the polymer gel and the calcined materials were investigated by Fourier transform infrared spectroscopy. Residual carbon content and specific surface area determinations were carried out on calcined powders. Microstructural characterisation was done by X-ray diffractometry and scanning electron microscopy. The results demonstrate that nanocrystalline particles of the solid solution can be prepared with low carbon content and high specific surface area by this one step synthesis technique.*

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## INTRODUCTION

Solid electrolytes based on rare earth doped cerium dioxide are of considerable interest for potential use in solid oxide fuel cells (SOFCs), as a result of their high ionic conductivity and low cost compared with stabilised zirconia and doped lanthanum gallate respectively.<sup>1–4</sup> Among ceria based solid solutions, the highest ionic conductivity occurs with the use of Sm, Gd, and Y as dopants in the 10 to 20 mol-% concentration range. Such solid electrolytes are being considered for use in intermediate temperature (500–700°C) SOFC systems.<sup>3,5</sup>

Several techniques have been used to prepare solid electrolytes.<sup>6–11</sup> The processing technique is of particular importance because it may determine microstructure dependent properties of the sintered ceramic. The combustion technique, originally developed in the former USSR, has been widely used in the last 20 years for the synthesis of materials including ceramics, intermetallics, and composites.<sup>12–14</sup> This synthesis technique is based on a fast exothermic reaction between a redox mixture containing the desired cations and an organic fuel as reducing agent.<sup>15</sup> The cations are in general in the form of salts, especially nitrates, whereas a range of compounds may be used as the organic fuel, for example urea, citric acid, and polymers. The combustion technique has many potential advantages, such as low processing cost, energy efficiency, and high production rate.<sup>14</sup>

The aim of the present work was to prepare nanocrystalline  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$  powders by the combustion of a polymer gel, and to study the effects of subsequent calcination of

the product on some physical properties of the particulate material.

## EXPERIMENTAL PROCEDURES

Cerium nitrate hexahydrate (99.99%, Aldrich) and gadolinium oxide (99.9%, Aldrich) were used as starting materials. Polyvinyl alcohol (PVA) (Fluka, molecular weight = 125000) and other reagents were of analytical grade. Aqueous solutions of the starting materials were prepared using deionised water, and mixed in the desired proportions for 10 min using stirring for homogenisation. A 10 wt-% solution of PVA was then added to the cation solution, and the mixture was heated up to 80°C to form a polymer gel, and to 250°C for the combustion of the material. Ignition occurred in the 200–230°C temperature interval. The product was subsequently calcined at 400 or 600°C for 1 h with a heating rate of 2 K min<sup>-1</sup>.

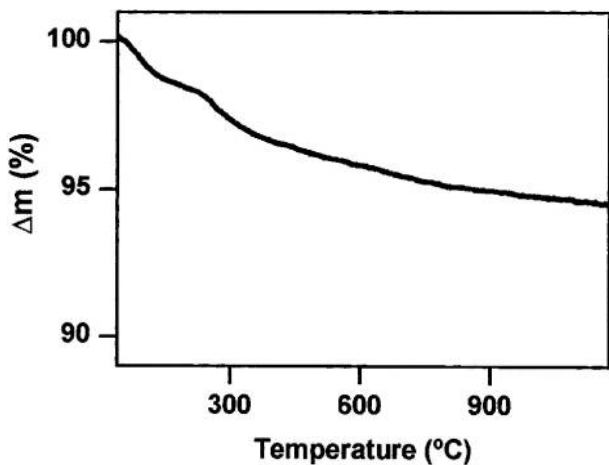
The weight loss of the as reacted material was verified by thermogravimetric analysis (Netzsch, STA 409). The heating and cooling rates were 10 K min<sup>-1</sup>, and the temperature range spanned from room temperature to 1000°C in air. The polymer gel was studied by Fourier transform infrared spectroscopy (FTIR) (Nicolet, Magna IR560) using a He–Ne laser. Calcined powders were characterised by FTIR, and by analysis of residual carbon content (Leco, CS400), particle size distribution (following ultrasonic deagglomeration) by laser scattering (CILAS, model 1064), and specific surface area *S* by nitrogen adsorption (Micromeritics, ASAP 2010). Amorphous and crystalline structures were determined by X-ray diffraction (Bruker-AXS, D8 Advance), operating at 40 kV and 40 mA, and using Cu *K*<sub>α</sub> radiation. The crystallite size was estimated using the Scherrer equation.<sup>16</sup> To observe the morphology of particles and agglomerates, scanning electron microscopy (Philips, XL30) analysis was carried out on powder material.

## RESULTS AND DISCUSSION

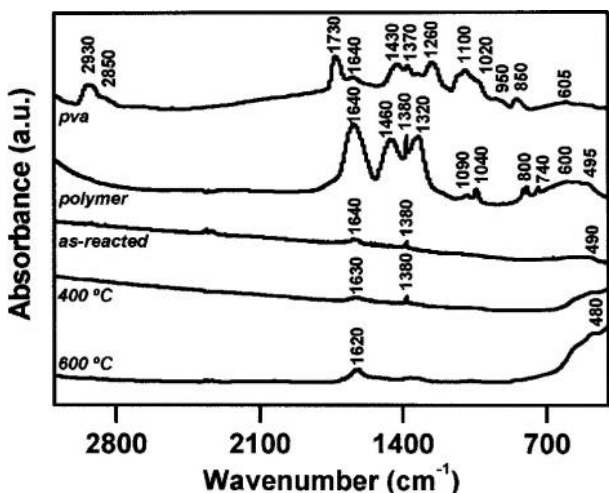
After combustion, the material has the appearance of a pale yellow powder. This colouration, typical of the Ce(IV) oxide, does not change with further heat treatment.

The TG curve of the as reacted material is shown in Fig. 1. The curve shows a total weight loss of 5.5% up to 1000°C. This weight loss is due to the evolution of carbon compounds (CO and CO<sub>2</sub>) and nitrates (NO and NO<sub>2</sub>). The evolution of these gases is attributable to residues of the decomposition of PVA still present in the as reacted material.

The PVA precursor, polymer gel, and calcined powders were characterised by FTIR to gain more insight into the structure and composition of materials and to characterise the gel to ceramic conversion. Figure 2 shows FTIR spectra of the PVA solution, the polymer gel, and calcined powders. In the PVA spectrum, the IR bands related to its polymeric structure can be seen. The strongest bands are related to CH and CH<sub>2</sub> stretches (≈2900 cm<sup>-1</sup>), C=O stretching of the residual acetate group (1730 cm<sup>-1</sup>), and O–H stretching or C–OH stretching (1380 cm<sup>-1</sup>). The spectrum of the polymer gel exhibits bands related to the presence of



1 TG curve of as reacted material



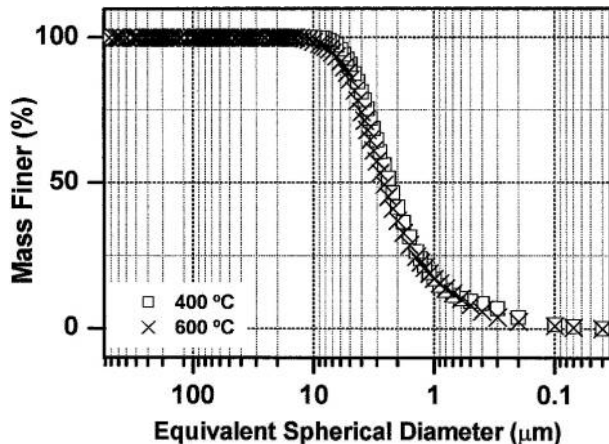
2 FTIR spectra of precursor, polymer gel, and product

carbonaceous materials (at 1640 and 1440–1300 cm<sup>-1</sup>), to C–O symmetric stretching (1090 cm<sup>-1</sup>) and C–O asymmetric stretching (1040 cm<sup>-1</sup>), to the NO<sub>3</sub><sup>-</sup> ion (1380 cm<sup>-1</sup>), and part of the band related to the metal ion–oxygen bond ( $\approx 500$  cm<sup>-1</sup>). The disappearance of the bands due to CH and CH<sub>2</sub> stretches in the 2700–3000 cm<sup>-1</sup> region was probably a result of the degradation of PVA in the presence of a strong oxidising agent (NO<sub>3</sub><sup>-</sup>). In the as reacted material and calcined powders most of these bands disappear. However, low intensity bands related to residual carbon and nitrate ions, and that assigned to the metal–oxygen bond, are still observed.

The residual carbon content decreases slightly with increasing calcination temperature (Table 1). This result agrees with the infrared spectra showing bands related to residual carbon even after calcination at 600°C. The evolution of residual carbon is also responsible for part of the weight loss observed in the TG curve. Thus it may be concluded that the combustion reaction is too fast for the complete elimination of carbon and nitrate ions resulting from the decomposition of the polymer gel. However, this

Table 1 Carbon content *C* and average particle size *d*<sub>50</sub> for powders calcined at 400 and 600°C

Calcination temp., °C	<i>C</i> , wt-%	<i>d</i> <sub>50</sub> , μm
400	0.27	2.3
600	0.20	2.6

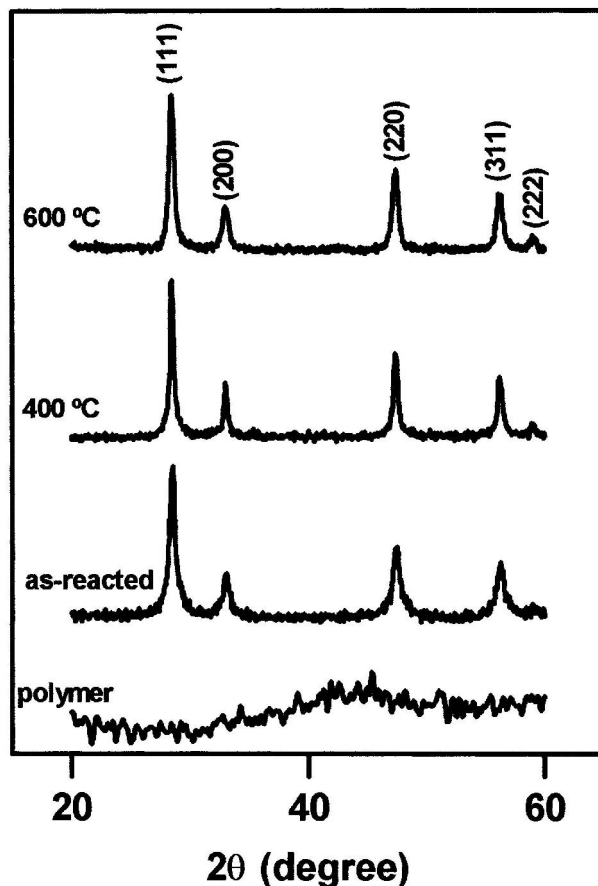


3 Particle size distribution of solid solution after calcination

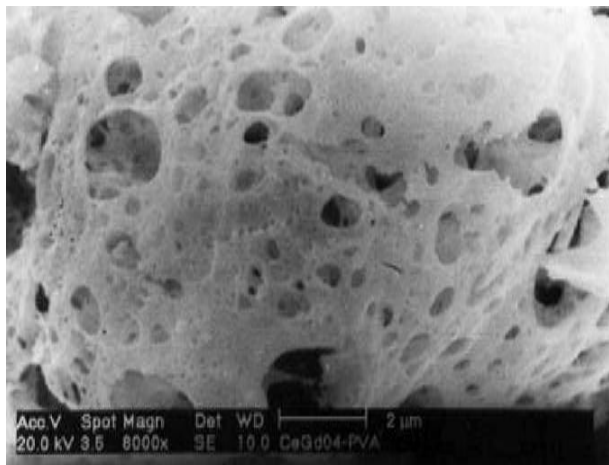
residual carbon should not compromise the performance of the product material since it may be eliminated by subsequent heat treatment, for example during sintering of a powder compact.

The specific surface area measured by nitrogen adsorption, using a three point BET analysis, is 21.2 m<sup>2</sup> g<sup>-1</sup> after calcination at 400°C. The particle size calculated from the BET analysis using the equation  $d_{BET} = 6/(S\rho)$ , where  $\rho$  is the crystallographic density of the material, is approximately 40 nm. These results show that this method of synthesis can produce reactive powders with crystallite sizes in the nanometre range.

The particle size distribution curves after calcination at 400 and 600°C are shown in Fig. 3. As may be seen, the shape and general behaviour of the two curves do not differ.



4 X-ray diffraction patterns of polymer gel and as reacted and product materials



5 SEM micrograph of agglomerate after calcination at 400°C

The equivalent spherical diameters  $d_{50}$  obtained at 50% cumulative mass (Table 1) are also similar, within experimental errors. This result indicates that the temperature reached during the combustion reaction is higher than the ignition ( $\approx 220^\circ\text{C}$ ) and calcination temperatures.

Figure 4 shows X-ray diffraction patterns of powders of the dried polymer gel, after the combustion reaction, and after calcinations. It can be seen from this graph that the polymer gel is amorphous to X-rays, whereas the as reacted material is crystalline in nature. The diffraction peaks in all cases could be indexed according to a cubic fluorite lattice (Fm3m space group). This result shows that the as prepared particulate material is crystalline, and that the material consisted of crystallites with a diameter of  $\approx 15$  nm, calculated from the broadening of the (111) main reflection using the Scherrer equation.

There are no qualitative differences in the morphologies of the as reacted material and the calcined agglomerated powders. These agglomerates consist of porous particles, as shown in Fig. 5 for the material calcined at 400°C. This very porous structure is typical of powders prepared by the combustion technique.<sup>15,17</sup> Calcined materials are also friable, easily breaking under the application of very weak forces. These characteristics (porous structure and friability) probably result from gases released by the redox reaction of PVA and metal nitrates.<sup>18</sup>

The overall results point to the possibility that some organic matter may be entrapped inside the porous structure owing to the short reaction time over which combustion takes place. This would explain the gradual elimination of carbon by heat treatments following synthesis.

## CONCLUSIONS

Nanocrystalline gadolinia doped ceria solid solutions may be prepared by a one step synthesis method using polyvinyl alcohol as a reducing agent. The formation temperature of the solid solution using this technique is rather low compared with the conventional solid state reaction method. High specific surface area and low carbon content can be obtained. The powder is porous, with a specific surface area of  $21\text{ m}^2\text{ g}^{-1}$  and crystallite size lower than 20 nm after calcination at 400°C.

## ACKNOWLEDGEMENTS

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