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Combustion synthesis of 5 and 10 mol% $YO_{1.5}$ doped ThO_2 powders

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Abstract

Nanocrystalline 5 and 10 mol% $YO_{1.5}$ doped ThO_2 powders were prepared by the combustion technique using citric acid as a fuel and nitrates as oxidants. The auto-ignition of the fuel-deficient precursors (prepared by thermal dehydration of the aqueous solutions containing metal nitrates and citric acid in required molar ratio) directly resulted in the well crystalline powders of the desired solid solutions along with traces of carbonaceous material. The as-prepared and calcined powders were characterized by X-ray diffraction (XRD), high-temperature XRD and by their sinterability. The $YO_{1.5}$ doped ThO_2 powders when cold-pressed and sintered at 1300 °C for 2 h resulted in $\geqslant 95\%$ of their theoretical densities with nanograin microstructure.

1. Introduction

Thoria–yttria solid solutions are candidate materials for electrolyte used in solid oxide fuel cells (SOFC) [1]. The basic requirement of the electrolyte in a SOFC device is that it should be nearly theoretically dense to results in the desired electrical characteristics and to avoid any kind of leakage of the fuel and oxidant in the form of gases [2].

Apart from low electrical conductivity compared to yttria stablized zirconia electrolyte and alpha emission from thorium (even though its specific activity is very low), one of the parameters which restrict the use of thoria is to achieve a high sintered density due to its very high melting point (i.e., 3300 °C). The use of dopants such as Y^{3+} in thoria introduces oxygen vacancies in it, which enhance its oxygen ion conductivity.

Thoria–yttria solid solutions were reported to be prepared by various processes including solid-state synthesis [3], oxalate route [3] and modified Pechini process [4]. Shridharan and co-workers [5] also prepared 15 mol% $YO_{1.5}$ doped ThO_2 powder using a polymeric gel combustion process. Wet-chemical processes are advantageous over conventional solid-state synthesis in terms of homogeneity and powder characteristics specially in case of electro-ceramics for which electrical functions are governed by small amounts of dopants. Among the various wet-chemical processes, the combustion technique has recently attracted much attention due to its simplicity and capability to deliver the nanocrystalline powders in a surprisingly short time with improved characteristics such as high surface area and better sinterability [6,7].

The combustion technique basically involves the preparation of a homogeneous fuel-oxidant precursor (mostly in the form of viscous liquid or gel) and its exothermic decomposition. The resultant powder is in the form of friable agglomerates having nanoparticles as the building blocks. Phase purity and powder characteristics of the combustion-synthesized powder are

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primarily depend upon nature and amount of the fuel used in the process which decides the enthalpy of combustion (or flame temperature), amount of gas evolution and rate of combustion (or nature of decomposition) [8–10]. In order to obtain the phase pure, nanocrystalline powder with high surface area and without hard agglomerates, the rate of decomposition of the precursor should be very fast (preferably single-step decomposition), and enthalpy of combustion (or flame temperature) should be just sufficient for producing the desired phase-pure powder along with the evolution of high volume of gaseous products.

It is well known that citric acid has a better complexing ability, low ignition temperature (i.e., 200–250 °C) and controlled combustion reaction with nitrates [11,12]. Hence, citric acid was selected as a fuel for the preparation of thoria–yttria solid solutions.

2. Experimental

In order to prepare 5 and 10 mol% $YO_{1.5}$ doped ThO_2 (i.e., $Th_{1-x}Y_xO_{2-x/2}$, $x = 0.05$ and 0.1) powders, thorium nitrate, yttrium nitrate and citric acid were used as the starting materials. Yttrium nitrate was prepared by dissolving the yttrium oxide in a minimum amount of dilute nitric acid. The metal nitrates and citric acid were mixed, in a required molar ratio, in a minimum amount of de-ionized water to obtain citrate–nitrate solutions. The total metal ion-to-citric acid molar ratio used in the process was 1:0.5. Thermal dehydration of the citrate–nitrate solutions on a hot plate at about 80 °C initially resulted in white precipitates, which on further heating slowly got re-dissolved to result in the viscous gels. As soon as these gels formed, the temperature of the hot plate was raised to about 200 °C. The gels swelled and auto-ignited with the evolution of a large volume of the gases to result in the white voluminous powders along with traces of carbonaceous material. The as-prepared powders were calcined at 600 °C for 1 h to remove unwanted impurities before sintering.

X-ray diffraction (XRD) measurements on the as-prepared and calcined powders were carried out for phase identification and crystallite size measurement using a Philips X-ray diffractometer, Model PW 11830. The lattice parameters were estimated using a standard least-squares refinement program. High temperature X-ray diffraction (HT-XRD) was used to study the variation in the crystallite size of the thoria–yttria solid solution with calcination temperature. The instrument used was Philips X'pert Pro with 'Anton Paar HTK-16' sample stage and 'TCU 2000' controller. The XRD patterns were recorded (covering the most intense peak i.e., from 25° to 30° with a scan speed of 1°/min from room temperature to 1400 °C with a temperature difference of 100 °C. The temperature of measurement was reached with a heating rate of 20 °C/min. The calcined powders were pressed in the form of 12 mm diameter pellets at a compaction pressure of about 200 MPa using an uniaxial hydraulic press and sintered at 1300 °C for 2 h in static air atmosphere. The sintered densities were measured using Archimedes's principle. The microstructure of the as-sintered samples was investigated using a Jeol Scanning Microscope, Model JSM-T330A (Japan).

3. Results and discussion

In order to achieve the low-temperature synthesis with the improved powder characteristics (e.g. fine crystallite size without premature local partial sintering), the amount of the fuel should be adjusted in such a manner that the combustion reaction should produce the exothermicity just sufficient for the required phase formation via single-step decomposition of the precursor. It was shown [8,9] that higher amounts of nitrates in the precursor (i.e., fuel-deficient precursor) help in achieving the single-step decomposition of the precursor and result in the improved powder characteristics. Therefore, fuel-deficient precursors were selected in case of the combustion synthesis of thoria–yttria solid solutions.

We know that the valencies of the elements Th, Y, C, H and O are 4+, 3+, 4+, 1+ and 2−, respectively. Nitrogen is assumed to be having a valency of zero, as it is evolved as N_2 in the combustion process. Using the valencies of these individual elements, the net oxidizing valencies of thorium nitrate and yttrium nitrate were worked out to be 20− and 15−, respectively, whereas the net reducing valency of citric acid was worked out to be 18+. According to the principle of propellant chemistry [13], for a stoichiometric combustion reaction among metal nitrates and citric acid to produce one mole of 5 and 10 mol% $YO_{1.5}$ doped ThO_2 powders require a total metal ions-to-citric acid molar ratio as 1:1.0972 and 1:1.0833, respectively. In order to prepare fuel-deficient precursors for thoria–yttria solid solutions, the total metal ions-to-citric acid molar ratio was selected as 1:0.5.

The precursors of the thoria–yttria solid solutions decomposed accompanied with fire in a self-sustaining manner to result in the almost white coloured powder with a small amount of carbonaceous material. The as-prepared powders were found to be well-crystalline in nature and the weight loss observed during calcination was only around 2–3%, which indicate nearly a single-step decomposition of the precursors during auto-ignition.

Fig. 1 shows an XRD pattern of the as-prepared powder obtained after auto-ignition of the $Th_{0.90}Y_{0.10}O_{1.95}$ precursor. The pattern illustrates that the powder is

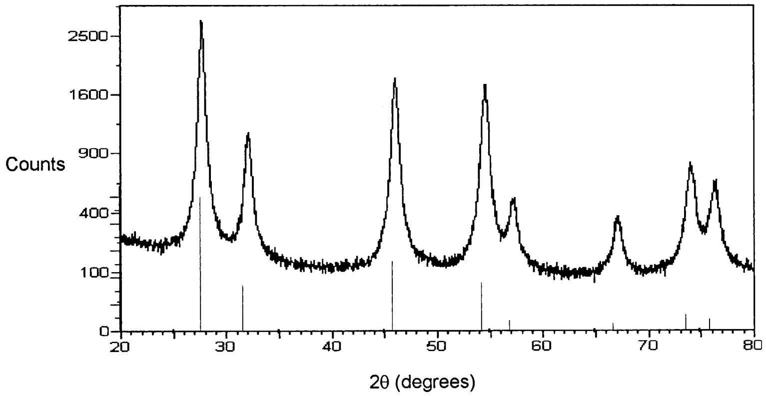

Fig. 1. XRD pattern of as-prepared $Th_{0.90}Y_{0.10}O_{1.95}$ powder obtained after auto-ignition and its comparison with the standard pattern of ThO_2. Vertical lines show the position of pure ThO_2 peaks.

well crystalline in nature. The pattern showed the characteristic peaks of ThO_2 [14] with a slight decrease in *d*-spacings (or increase in 2θ values), which indicates the formation of the required solid solution. The calculated lattice parameter (using a least-squares refinement program) was 0.5574(3) nm whereas the lattice parameter of ThO_2 is 0.5597 nm, which confirms the formation of the required solid solution. The in situ formation of the solid solution was attributed to atomistic level blending in the gel precursor and almost a single-step, exothermic decomposition of the precursor. The powder calcined at 600 °C (to remove the traces of the leftover carbonaceous material) also showed a similar kind of the pattern without any significant change in *d*-spacing but with comparatively increased crystallinity. No characteristic peaks of Y_2O_3 were obtained in the XRD patterns.

The as-prepared powder obtained after auto-ignition of the $Th_{0.95}Y_{0.05}O_{1.975}$ precursor also showed an XRD pattern similar to that for $Th_{0.90}Y_{0.10}O_{1.95}$ with a lattice parameter of 0.5580 nm, which confirms the formation of the required solid solution. The calcined powder showed the pattern similar to that of the as-prepared powder without any significant change in *d*-spacings but with comparatively increased crystallinity. No characteristic peaks of Y_2O_3 were obtained in the XRD pattern in this case also.

However, different researchers have reported the lattice parameters for thoria–yttria solid solutions containing different amounts of the dopant. The slight difference in the reported lattice parameters may be due to the different experimental conditions, defect structures and the extent of solid solubility achieved. The lattice parameters of the thoria–yttria solid solutions synthesized through the auto-ignition of the gel by us are in fair agreement with those reported in the literature [4,5,15].

The crystallite sizes of the $Th_{0.95}Y_{0.05}O_{1.975}$ and $Th_{0.90}Y_{0.10}O_{1.95}$ powders estimated using the standard Scherrer formula were found to be about 8 and 10 nm, respectively, which shows the nanocrystalline nature of the powders.

The variation in crystallite size of the $Th_{0.90}Y_{0.10}O_{1.95}$ powder was studied as a function of temperature using HT-XRD. Table 1 shows the crystallite sizes at different temperatures. As expected, the crystallite size increases with temperature but even at very high temperature (i.e., 1300–1400 °C), the powder is nanocrystalline in nature. This indicates the possibility of maintaining the nanograin size in the sintered product of $Th_{0.90}Y_{0.10}O_{1.95}$.

Sintering of $Th_{0.95}Y_{0.05}O_{1.975}$ and $Th_{0.90}Y_{0.10}O_{1.95}$ at 1300 °C for 2 h resulted in relative densities of about 95% and 97%, respectively. The high density achieved is due to the nanocrystalline nature of the starting powders and the vacancies (or defects) created by the doping. The comparatively higher density achieved in the case of 10 mol% Y^{3+} doped ThO_2 is probably due to the relatively higher number of vacancies created in this case, which enhanced the diffusion process during sintering. The microstructure of the sintered $Th_{0.90}Y_{0.10}O_{1.95}$ pellet was also investigated using SEM and is shown in Fig. 2. The micrograph illustrates the high dense microstructure

Table 1
Variation in crystallite size of $Th_{0.90}Y_{0.10}O_{1.95}$ as a function of calcination temperature

Temperature (°C)	Crystallite size (nm)
600	10
900	11
1100	13
1300	21
1400	27

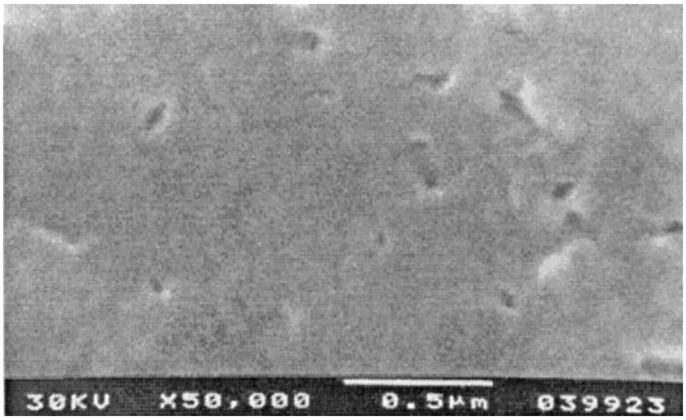

Fig. 2. SEM micrograph of $Th_{0.90}Y_{0.10}O_{1.95}$ sintered at 1300 °C for 2 h.

without much porosity. The micrograph reflects the grain size of ≈50–100 nm. The retention of ultrafine grains after sintering was attributed to a very fine crystallite size (i.e., 10 nm) of the starting powder. However, it may be noted that there is a considerable difference in the grain size obtained through HT-XRD (i.e., 21 nm) and SEM (≈50–100 nm) under identical conditions (i.e., 1300 °C for 2 h). This is because in case of HT-XRD, the heating rate was very high (i.e., 20 °C/min) and the measurement time was very low (i.e., only 5 min) and hence, crystallites did not get much time for their growth whereas in case of sintering, due to comparatively low heating rate and more sintering time (i.e., 2 h), a relatively higher grain size was obtained. Furthermore, in case of sintering, the material was used in the form of well-pressed pellets whereas in case of HT-XRD, the material was used in the form of well-dispersed powder. Therefore, in case of sintering, the crystallites have a higher possibility for their growth due to better contact among them.

However, the process developed by us is similar to that of the polymeric gel combustion process [5] but we have not used ethylene glycol as an extra gelling agent. In addition, the total amount of organic matter used in our process is much less than compared to the polymeric gel combustion process. The sintered density reported in the case of polymeric gel combustion process is higher compared to the auto-ignition route but the sintering temperature, time and amount of the dopant used were also higher in this case. The auto-ignition route is unique in the sense that it utilizes the high exothermicity generated during auto-ignition (of the homogeneous precursor having atomistic level blending of constituents) to form the desired solid solution and hence, does not require the additional high calcination temperature. The grain size of the powders and the sintered products derived through the auto-ignition route is lowest among the reported processes including polymeric gel combustion process.

4. Conclusions

A simple wet-chemical process based on the exothermic decomposition of fuel-deficient citrate–nitrate gel precursors was developed to obtain the nanocrystalline powders of 5 and 10 mol% $YO_{1.5}$ doped ThO_2. The powders when cold pressed and sintered at 1300 °C for 2 h reached $\geqslant 95\%$ of their theoretical density with nanograin microstructure.

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