High-throughput continuous hydrothermal flow synthesis of Zn–Ce oxides: unprecedented solubility of Zn in the nanoparticle fluorite lattice

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High-throughput continuous hydrothermal flow synthesis has been used as a rapid and efficient synthetic route to produce a range of crystalline nanopowders in the Ce–Zn oxide binary system. High-resolution powder X-ray diffraction data were obtained for both as-prepared and heat-treated (850°C for 10 h in air) samples using the new robotic beamline I11, located at Diamond Light Source. The influence of the sample composition on the crystal structure and on the optical and physical properties was studied. All the nanomaterials were characterized using Raman spectroscopy, UV–visible spectrophotometry, Brunauer–Emmett–Teller surface area and elemental analysis (via energy-dispersive X-ray spectroscopy). Initially, for ‘as-prepared’ Ce1−xZnxOy, a phase-pure cerium oxide (fluorite) structure was obtained for nominal values of x = 0.1 and 0.2. Biphasic mixtures were obtained for nominal values of x in the range of 0.3–0.9 (inclusive). High-resolution transmission electron microscopy images revealed that the phase-pure nano-CeO2 (x = 0) consisted of ca. 3.7 nm well-defined nanoparticles. The nanomaterials produced herein generally had high surface areas (greater than 150 m² g⁻¹) and possessed combinations of particle properties (e.g. bandgap, crystallinity, size, etc.) that were unobtainable or difficult to achieve by other more conventional synthetic methods.

Keywords: continuous hydrothermal flow synthesis; supercritical water; cerium oxide; zinc oxide

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1. Introduction

There is considerable interest in the development of advanced functional nano and bulk metal oxides for applications, including fine chemical catalysis (Mo et al. 2005), cosmetic sunscreens (Yabe & Sato 2003), photocatalysis (Mishra & Rao 2006), gas-sensing (Al-Kuhaili et al. 2008), pigments (Vishnu et al. 2009) and solid oxide fuel cells (Murray et al. 1999). It is well known that the chemical and physical properties of the nanoceramics can be tuned towards desired applications by doping the host metal oxide structure with various elements (Morinaga et al. 1997; Li et al. 2002a, b; Jang et al. 2009; Shi & Jin 2009). For example, doping can introduce significant changes in the structure of the host material, creating various lattice defects such as oxygen vacancies, resulting in different functional properties from those of the host material (Yabe et al. 2001).

The Ce–Zn oxide binary system has attracted interest for use in efficient UV filters (Chai & Wang 2007), up-converting phosphors (El Jouad et al. 2009) or gas sensors (Ge et al. 2007). CeO$_2$ (fluorite structure), with a bandgap of ca 3.0 eV, is usually an insulator and exhibits a wide range of interesting physical properties such as good optical transparency and strong UV absorption, similar to those of ZnO, which is a semiconductor with a wide bandgap of ca 3.36 eV (Li et al. 2002a). The synthetic route of manufacture for such materials greatly affects the particle properties (e.g. size, aggregation, morphology, surface area), and hence affects their physical properties. Conventional synthetic routes to Ce–Zn oxides include high-temperature solid-state reactions, high-energy ball-milling, precipitation in micro-emulsions (Kockrick et al. 2008), sol–gel syntheses (Evans 2008; Yang et al. 2008), etc. Unfortunately, many of these synthetic processes are energy or chemically intensive (environmentally unfriendly), time-consuming, multi-step and offer poor control of reaction conditions. Consequently, more efficient methods of synthesis are highly desirable. In particular, batch syntheses and continuous hydrothermal flow synthesis (CHFS) methods (Cabanas et al. 2000, 2001; Weng et al. 2009a) have been used to prepare fluorite-phase nanomaterials, with the latter route giving nanosized homogeneous ceria–zirconia solid solutions with unusual phase behaviour. Conventional CHFS methods have been used previously by the authors and others for the synthesis of a range of nanoceramic oxides. Typically, up to 10 samples per day can reasonably be made (at a level of a few grams per sample) for more conventional CHFS (Adschiri et al. 1992a, b; Darr & Poliakoff 1999; Cabanas et al. 2000, 2001; Sue et al. 2004; Hakuta et al. 2005; Chaudhry et al. 2006; Lester et al. 2006; Norton et al. 2006; Boldrin et al. 2007; Weng et al. 2007, 2008, 2009b; Chaudhry et al. 2008; Lin et al. 2009; Thompson et al. 2009; Zhang et al. 2009a, b). Recently, the authors described a new and more efficient manual CHFS route that allowed the synthesis of multiple nanoceramics compositions in a short time, called HiTCH (high-throughput continuous hydrothermal) flow synthesis. The HiTCH reactor used a flow of superheated water to generate a complete 66-sample library of Ce$_x$Zr$_y$Y$_z$O$_{2-x}$ in less than 12 h (Weng et al. 2009a). Zn–Ti and Ce–Ti binary systems have also been synthesized by the authors using a similar route (Norton et al. 2006; Zhang et al. 2009a, b).

In this work, a new type of HiTCH flow synthesis reactor was used to produce, rapidly and controllably, a binary Ce–Zn oxide nanoparticle sample library. The samples were analysed using a range of techniques, including high-resolution
Synthesis of Zn–Ce oxide nanoparticles

powder X-ray diffraction (PXRD) at the new robotic PXRD beamline I11 facility of the Diamond synchrotron at the Rutherford Appleton Laboratory, UK (Weng et al. 2009a).

2. Experimental

(a) Materials

Zn(NO$_3$)$_2$·6H$_2$O (technical grade, >98%) and (NH$_4$)$_2$Ce(NO$_3$)$_6$ (≥98.5%) were supplied by Sigma–Aldrich Chemical Company (Dorset, UK). Potassium hydroxide pellets (KOH, ≥85%) supplied by VWR International (Leicestershire, UK) were used to adjust the pH. All experiments were conducted using deionized water (10 MΩ).

(b) Apparatus and syntheses

(i) Details of the HiTCH apparatus design

All Ce–Zn oxide samples (as shown in the electronic supplementary material, table S1) were made using a new HiTCH flow synthesis reactor (Weng et al. 2009a; figure 1), the experimental set-up of which is described herein.

The system is rather complex and therefore the authors offer a simplified explanation of the process initially. The system consists of several pumps that deliver the particular reagents together under pressure (figure 1). In essence, water via HPLC pump 1 (which is heated in process to become supercritical) is pumped to meet a mixture of a composite solution from pumps 1 and 2. Pump 2 has cold water and can contain a base or auxiliary solution and these two feeds will mix at a T-piece before they meet the supercritical water flow (at the reactive mixer, R). Periodically, the cold water feed from P3 is bypassed and replaced via a flow from a syringe pump (Isco) containing an aqueous solution of one or more metal salts as required. Hence, the metal salt mixture in flow (premixed with the P2 base feed at the T-piece) now meets the supercritical water at the reactive mixer R and nanoparticles are formed instantly in flow. The particles are cooled and then pass out of the system (to atmospheric pressure) via a back-pressure regulator valve. They are collected as a slurry, which is then cleaned and dried. After collection, the Isco pump can be swapped back with pump 3 to clean the system out. This process is repeated for the next composition of metal salts until all compositions are made. In this way, several nanoceramic samples can be made in a short time. Due to the method of mixing hot and cold shown herein, and the high dilution of the feeds and products, the system (as others have reported before) is able to run for prolonged periods and does not block at all. The authors suggest that the concentrations used herein are suitable for prolonged continuous operation; however, running at higher concentrations can lead to problems of clogging or failure of the back-pressure regulator.

For more technical readers, the authors offer the following description of the system. The system contains three Gilson 305 HPLC pumps fitted with 25 ml pump-heads and an Isco 260D syringe pump arranged as shown in figure 1. 316SS Swagelok 1/8-inch stainless steel fittings and tubing were used for all parts unless described otherwise. Additionally, a two-way Rheodyne switch valve

Phil. Trans. R. Soc. A (2010)
(labelled as ‘SV’ in figure 1) was used to allow the fluid diversion between the Isco pump and pump P3 into the apparatus. The new HiTCH system differs from the old system as described below.

(ii) New versus old HiTCH reactor

The new HiTCH system is a modified version of the previously described HiTCH reactor (Weng et al. 2009a). The new modified HiTCH flow synthesis reactor used an Isco syringe pump for the delivery of metal salts into the flow reactor (via a Rheodyne switch valve), whereas the previous HiTCH flow synthesis reactor used manual filling of a 2ml loop on the Rheodyne switch valve for introducing pre-mixed metal salts. In this way, the new HiTCH reactor allowed controlled and sustained delivery of the mixed metal salts to the mixing point (supercritical water) up to a volume of 260ml, rather than the previous limited 2ml of the Rheodyne loop. There is of course an additional requirement to flush out the Isco pump and the reactor with clean water between each composition to ensure that cross contamination does not occur (Weng et al. 2009a). Furthermore, in the previous HiTCH report, nanoparticles were mixed
with additional cooling water (from a fourth pump) before being passed through a vertical water cooled pipe. This fourth pump was not used in the new system described herein.

The new HiTCH reactor has also been developed by the authors into a fully automated robot called RAMSI (Rapid Automated Materials Synthesis Instrument), which automatically mixes the metal salt precursors, introduces them sequentially into the reactor via an Isco pump (includes auto-cleaning of the pump and reactor between each composition), and then makes, collects, cleans and prints many unique composition slurries in a few hours (Lin et al. 2009; Thompson et al. 2009).

(iii) Experimental synthesis parameters

— The flow rates used herein for the new HiTCH flow synthesis reactor were 20/10/10 ml min⁻¹ for water, the metal salt solution and base solution, respectively, compared with the flow rates of 10/5/5 ml min⁻¹ used in the previous work (Weng et al. 2009a).

— In a typical experiment, each pre-mixed aqueous solution of cerium(IV) ammonium nitrate (0.2 M) and zinc nitrate (0.2 M) was first drawn into the Isco syringe pump (under suction from the barrel) and then delivered into the HiTCH reactor by diverting the pre-primed feed from the Isco pump towards the superheated water feed via the Rheodyne switch valve and thereby diverting the cold water from HPLC pump P3 to the drain via BPR2. In practice, the metal salt mixture then met a 1 M base solution of potassium hydroxide feed from pump P2 at 1/4-inch stainless steel T-piece.

— This mixture was then brought into contact with superheated water (400°C, 24.1 MPa) inside an in-house built 1/4-inch counter-current mixer (Lester et al. 2006; shown as R in figure 1) of similar design to that published elsewhere for a 3/8-inch mixer (Boldrin et al. 2007) at which point nanoparticles were formed (figure 1).

— The temperature measured inside the counter-current varies depending on the location of measurement. A guide to temperature fluctuations under these conditions is as follows: at a position approximately at level with the outlet of the inner tube (of the counter-current mixer) the temperature was 200°C (i.e. immediately after the supercritical water mixed with the cold water). This is significantly below the maximum theoretical temperature of 309°C, determined by enthalpy balance using the thermodynamic properties of water. The temperature measured (by a J-type thermocouple inside the system) at the outlet of the mixer was 297°C, approaching much more closely the expected maximum theoretical temperature.

— After synthesis, the nanoparticles passed through a long vertical water-cooled pipe (1/4-inch SS tube) and out of the back-pressure regulator (labelled as ‘BPR1’ in figure 1).

— Each high pressure line for each Gilson pump also incorporated a pressure gauge (RS model no. 540–255), Nupro SS-4R3A pressure-release safety valves (set to 29 MPa) and Swagelok non-return valves (not shown in figure 1 for clarity).

Phil. Trans. R. Soc. A (2010)
Experimental work-up of samples

- The individual nanopowder slurries were cleaned up via centrifugation at 4500 r.p.m. (model Sigma 4k-15) and up to 40 ml of clear liquid was replaced with clean water (a minimum of 80 ml being replaced in total for each) until the final centrifugation step after which 40 ml of clear liquid was removed to give a slurry volume of ca 10 ml.

- The wet clean Ce–Zn oxide samples were re-dispersed in water using an analogue vortex mixer (VWR, model VM-3000, Leicestershire, UK) on its maximum setting for 2 min, to give a final concentration of ca 40 wt%.

- The slurries were then printed in duplicates as shown in the electronic supplementary material, figure S1a (spot size of 50–100 µl) using an Eppendorf pipette (20–200 µl, VWR, Leicestershire, UK) onto a silicone release paper (Zhan et al. 2007; double-side coating, serial no. SPT/50/12, Cotek, Gloucestershire, UK).

- Dots were mounted with PVA glue into an in-house designed 86 × 123 mm size aluminium 96-well plate library (wells are rounded bottoms of 4 mm well diameter × 1.5 mm well depth; see electronic supplementary material, figure S1b).

- A further set of air-dried nanoceramic discs were also heat-treated at 850°C for 10 h in air (ramp rates for heating and cooling were 10 and 20°C min⁻¹, respectively).

Samples were assigned names on the basis of their nominal Zn contents, e.g. sample 30 Zn–Ce was assumed to have 30:70 ratio of Zn:Ce. In total, 10 samples were made herein in 4 h using a volume of 200 ml of metal salt solution for each sample (excluding ZnO which was made on a separate occasion under the same conditions, and allowing time for purging the HiTCH reactor between samples) and the yields were all more than 70 per cent. Compared with the 12 h required to make 66 samples previously, each sample here took longer but of course the number of samples typically made here was much more as a result of longer running times for metal salts herein by virtue of using an Isco syringe pump to ‘inject’ each composition into the high-pressure apparatus (Weng et al. 2009a). This is still typically at least five times faster than nanomaterials made using conventional methods and of course does not offer the same sets of particle properties as are described herein.

(c) Analytical and other equipment

Freeze-drying was performed using a Virtis Genesis 35XL freeze dryer. The solids were frozen in liquid nitrogen and then freeze-dried for ca 22 h at 1.3 × 10⁻⁷ MPa. The samples were then heat-treated at 850°C in air for 10 h using a Carbolite CWF1300 furnace (using a heating rate of 10°C min⁻¹ and cooling rate of 20°C min⁻¹). An Oxford Instruments Inca 300 EDX detector, connected to a JEOL JSM-6300 scanning electron microscope, was used to carry out the elemental analysis for all the samples. An average of 10 areas per scan was used to calculate the average elemental composition. Brunauer–Emmett–Teller (BET) surface area measurements were performed on a Micromeritics ASAP 2420 analyser equipped with 12 degass and six analysis stations. The powders were degassed at 200°C with N₂ (purge gas supplied by BOC, UK) for 5 h,
prior to the BET analyses. Raman spectra of all samples were recorded at room temperature with a Renishaw InVia Raman microscope system equipped with a 1200 lines mm$^{-1}$ grating and a 785 nm diode laser. The spectral resolution of the instrument was 1 cm$^{-1}$. The most intense band of silicon at approximately 520 cm$^{-1}$ was checked before and after measurements to ensure the wavenumber stability of the instrument. The absorption spectra of the photocatalyst powders were measured using an Ocean Optics USB4000 UV–visible spectrophotometer with a DH2000-BAL light source. Spectralon was used as a reference material. CIE $L^*a^*b^*$ colour data were calculated from the reflectance spectra using the Ocean Optics SPECTRASUITE software. Colour measurements were conducted using a 2° viewing angle and a D65 light source. Additionally, the bandgaps were calculated using the Kubelka–Munk function via conversion of the reflectance spectra into the equivalent absorption coefficient for direct transitions (Tauc et al. 1966). Particle size and morphology of the Ce–Zn oxide samples were investigated using a Titan 80–300S/TEM high-resolution transmission electron microscope (HR-TEM; acceleration voltage 300 kV). Samples were collected on carbon-coated copper grids (Holey Carbon Film, 400 mesh Cu, Agar Scientific, Essex, UK) after being dispersed in absolute ethanol in a 60 W Engis B2200 E2 ultrasonic bath (Branson Ultrasonics, Berkshire, UK). Image analysis was performed using a fast Fourier transform (FFT) algorithm in the IMAGEJ software package (developed by the US National Institutes of Health, MD, USA).

(i) Details of HiTCH heaters and their design

A 2.5 kW electrically powered water pre-heater was used in the system and was built from 1/4-inch fittings and consisted of a 1 kW Firerod (Watlow, Nottingham, UK) heater cartridge encased in a rod of aluminium metal around which 6 m of 1/4-inch stainless steel high-pressure tube was wound. The whole pre-heater assembly was then insulated with a custom-made Watlow heater jacket (1.5 kW). Additionally, a small 5 cm long, 200 W band heater (Watlow) set to 400°C that was controlled via a Eurotherm controller (model 2216e) was used outside the counter-current mixer to maintain the highest possible reaction temperature (not shown in figure 1 for clarity).

(ii) Powder X-ray diffraction

Each of the 45 detectors on Diamond beamline I11 (Weng et al. 2009a) was calibrated (using a standard Y$_2$O$_3$ sample sintered at 1200°C for 5 days and measured for 3 h in a 0.5 mm capillary) for relative detector response and precise angular 2$\theta$ separation (nominal spacing of 2° within a bank of nine detectors and 14° separation between each of the five banks). Diffraction patterns from each detector were corrected for detector response but not beam decay, as the synchrotron ring was in continuous top-up mode with a beam current of 250 mA. Corrected patterns from individual detectors were checked for consistency and merged into a single PXRD pattern covering the 2$\theta$ range of 0–155° in 0.01° steps. The wavelength used was 0.826017 Å and each pattern took 20 min to collect. Samples were put in 0.5 mm borosilicate glass capillaries (CST, Reading, UK) on self-aligning holders and placed on a 200 position carousel (Weng et al. 2009a). A robotic arm automatically selected and mounted the samples on the diffractometer in turn. The individual patterns

Phil. Trans. R. Soc. A (2010)
were fitted and unit cell dimensions were monitored in Rietica using the Le Bail profile fitting method with the CeO₂ and ZnO models. Structure fitting was neither required nor possible as absorption of X-rays by cerium was severe and beyond the functional limits of the available refinement packages. Crystallite size was calculated from XRD peak half-widths using the Scherrer equation (Zhang et al. 2009b).

3. Results and discussion

The authors used a new CHFS reactor (Adschiri et al. 1992a,b; Darr & Poliakoff 1999; Cabanas et al. 2000, 2001; Sue et al. 2004; Hakuta et al. 2005; Chaudhry et al. 2006; Lester et al. 2006; Norton et al. 2006; Boldrin et al. 2007; Weng et al. 2007, 2008, 2009a,b; Chaudhry et al. 2008; Zhang et al. 2009a,b) known as a HiTCH flow synthesis reactor that allowed controlled delivery of mixed metal salt solutions into the system. Cerium ammonium nitrate and zinc nitrate were used as the metal ion feeds and all nanoparticles were produced under alkaline conditions because of the presence of potassium hydroxide in flow. The individual metal salt solutions were first prepared manually to produce a desired Ce⁴⁺:Zn²⁺ ratio (mol%), in the sample from 100:0 increasing in increments of 10 mol%. In all cases herein after clean-up, one portion of each concentrated nanoparticle slurry (40 wt%) was printed onto a silicone release paper and dried in air to give dome-shaped discs, which were mounted flatside up into the custom-made round-bottomed 96-well aluminium plate library (electronic supplementary material, figure S1b, samples 1–10).

For the CeO₂ sample, HR-TEM was used to investigate the particle size and morphology. Figure 2a reveals a characteristic HR-TEM image for CeO₂ nanoparticles made via HiTCH with particle size distribution (electronic supplementary material, figure S2) in the range ca 3.1–4.6 nm (mean particle ca 3.7 ± 0.3 nm, 242 particles sampled) with typical cerium oxide (111) lattice spacing of 0.30 ± 0.02 nm, which is in agreement with the literature value (Kockrick et al. 2008). By contrast, the pure zinc oxide (Zhang et al. 2009a,b) sample had a polygonal shape and a mean particle size of ca 120.1 ± 19 nm (figure 2b).

A summary of the samples, the nominal ratios of Ce⁴⁺:Zn²⁺ in the precursor and the EDX metal analytical results for all samples is shown in the electronic supplementary material, table S1. In most cases, the Ce⁴⁺:Zn²⁺ ratios were similar to that of precursor of the feed. The largest divergence was for the nominal composition of 30 Zn–Ce, which was shown to contain 27.53 mol% Zn and the best fit was for the 20 Zn–Ce, which had 19.95 mol% Zn (average difference in Zn mol% was 1.15 mol% across all samples).

Figure 3 shows the trend in BET surface areas that varies from CeO₂ (180 m² g⁻¹) to ZnO (30 m² g⁻¹). As-prepared samples 10 Zn–Ce and 20 Zn–Ce (phase-pure fluorite structure) had high surface areas of 244 and 243 m² g⁻¹, respectively. This suggested that Zn substitution into CeO₂ retarded the growth of these particles from solution under these conditions. The BET surface area of sample 30 Zn–Ce was ca 222 m² g⁻¹, which coincided with the first appearance of ZnO peaks in the XRD plots (figure 4) and a slight reduction in the surface area from 20 Zn–Ce, which did not contain the ZnO phase. In most cases thereafter,
Synthesis of Zn–Ce oxide nanoparticles

Figure 2. A HR-TEM image of (a) CeO$_2$ nanoparticles made via HiTCH flow synthesis. The inset plots are intensity profiles of the lattice fringes where the spacing of a set of fringes is proportional to the lattice spacing as the corresponding lattice planes meet the Bragg condition. In this case, the $d$-spacing value of 0.31 ± 0.02 nm (five particles sampled) corresponding to the ceria (111) reflection and 0.19 ± 0.01 nm to the ceria (220) reflection were measured from the TEM images using a fast Fourier transform algorithm in the IMAGEJ software package. (b) ZnO$_2$ nanoparticles showing the polygonal nature of the particles. Scale bars, (a) 5 nm and (b) 50 nm.

the BET surface area decreased almost linearly with increasing zinc content. This was unsurprising given that the particle size of pure ZnO (ca 120 nm) is much larger than that of pure CeO$_2$ (ca 3.7 nm), hence a mixture of a high (doped ceria) and low (ZnO) surface area phases would be expected to follow such a gradual trend with increasing ZnO phase content.

*Phil. Trans. R. Soc. A* (2010)
Figure 3. BET surface areas and measured zinc content (from EDX) of as-synthesized and freeze-dried pure CeO$_2$, pure ZnO and Zn–Ce oxide samples with different nominal zinc content.

Figure 4. PXRD patterns of as-synthesized and freeze-dried pure CeO$_2$, Zn–Ce oxide and pure ZnO nanoparticle samples. Asterisks, fluorite; dots, wurtzite.

High-resolution PXRD data were collected at the synchrotron for all as-synthesized and heat-treated samples to investigate how Zn$^{2+}$ content affected the phase composition. The PXRD data for CeO$_2$ (as-synthesized) shown in figure 4 gave a good match with the reference line pattern for the crystalline fluorite structure of CeO$_2$ (ICDD pattern 78–694). It should be noted that the PXRD
Synthesis of Zn–Ce oxide nanoparticles

Figure 5. PXRD patterns for heat-treated (850°C for 10 h) pure CeO₂, Zn–Ce oxide and pure ZnO samples.

data collected at the synchrotron (XRD wavelength was 0.826017 Å) appear at different 2θ values to PXRD data collected on a laboratory machine as expected (owing to different wavelength of radiation used).

The PXRD data for ZnO (as-synthesized) were indexed to the hexagonal close-packed ZnO wurtzite structure (ICDD 79–2205; see indexed pattern in figure 4). Samples 30 Zn–Ce up to 90 Zn–Ce were identified as biphasic mixtures with a good match to the aforementioned patterns for CeO₂ and ZnO, respectively. The formation of Ce_{1-x}Zn_{x}O_{2-x} solid solutions is known to be limited because of the size mismatch of the cerium and zinc ions. In comparison with the previous literature for similar materials, some subtle differences are noted. The literature reports that the phase boundary exists at less than 10 mol% Zn (Mishra & Rao 2006; Ge et al. 2007). However, our results suggested that a single fluorite phase was exclusively observed to and including the doping level of 20 mol% Zn in CeO₂ (20 Zn–Ce sample), which indicated that the solid solubility limit for Zn in CeO₂ was between 20 and 30 mol% (for the as-synthesized nanomaterials). The differences between the literature and our results may partly be due to the formation of what is in effect a low-temperature metastable phase and because of the excellent homogeneity afforded by rapid precipitation of the material made by HiTCH flow synthesis reactions, which are difficult to achieve with more conventional routes (Cabanas et al. 2000, 2001; Weng et al. 2009a). Other reasons such as differences in phase behaviour compared with conventional bulk materials could also be due to small particle sizes obtained herein, which may allow non-equilibrium compositions to be stabilized in solid form.

In order to investigate the thermal stability of the as-prepared nanoceramics, the Ce–Zn oxide samples were heat-treated at 850°C for 10 h in air (figure 5 shows XRD patterns). Only phase-pure fluorite, wurtzite and biphasic mixtures of the
two were observed. The solubility of ceria in the ZnO was limited mainly by the mismatch in the ionic radii; thus, fluorite peaks were observed for high Zn loadings from 90 Zn–Ce inclusive and for less Zn loadings. The lattice constants of the undoped ZnO \((a = 3.250 \text{ Å} \text{ and } c = 5.206 \text{ Å})\) and CeO\(_2\) \((a = 5.412 \text{ Å})\) determined from the PXRD pattern (see electronic supplementary material, table S2) were consistent with the published comparable literature (Morinaga et al. 1997; Cabanas et al. 2000). On the basis of lattice cell parameters (electronic supplementary material, table S2), it was possible to observe a modification of the primitive cell volume as a function of Ce loading, which indicates that Ce\(^{4+}\) ions had been incorporated into the ZnO lattice (electronic supplementary material, figure S3). This phenomenon has been reported previously in the literature, even though the ionic radius of Ce\(^{4+}\) (1.03 Å) is much bigger than that of Zn\(^{2+}\) (0.74 Å).

There are also reports in the literature regarding the incorporation of zinc ions into cerium oxide lattice. However, in our case there were no noticeable trends in the cerium oxide lattice parameters.

For the heat-treated samples, a very weak peak corresponding to ZnO was first observed for the sample nominally with 10 mol% Zn (sample 10 Zn–Ce), though this was not present for the as-precipitated sample, indicating that phase separation occurred because of the heat treatment. By 30 mol% Zn (sample 30 Zn–Ce), the intensities of the ZnO peaks in the PXRD were significant and sufficient to give stability to the whole-pattern fits. Moreover, the peak intensities of any phase increased with an increase in the proportion of that phase.

The crystallite sizes of the samples were estimated from peak half-widths in the XRD pattern by applying the Scherrer equation and are given in the electronic supplementary material, table S1. The peak half-widths of the ceria (111) patterns were used while the (101) peak was used for the wurtzite-containing patterns (because the peak does not interfere with ceria peaks). Generally, from 10 Zn–Ce to 40 Zn–Ce, the particle size of the fluorite phase was similar with a relatively narrow range of ca 3.8 ± 1.2 nm for the particles of the Ce–Zn–O solid solutions, similar to the particle size for pure CeO\(_2\) obtained from the TEM analysis.

Raman spectroscopy was used to analyse the samples and complement the PXRD data for the identification of compositional phases in the Ce–Zn oxide samples. Figure 6 shows the room temperature Raman spectra of CeO\(_2\), ZnO and all the binary mixtures.

The Raman spectrum of nano-CeO\(_2\) (which has a fluorite structure) shows a strong band at approximately 457 cm\(^{-1}\) because of its F\(_{2g}\) Raman active band (Weber et al. 1993; Martínez-Arias et al. 2000; Yue & Zhang 2008). Additionally, the peak located at ca 600 cm\(^{-1}\) is reported to be due to the formation of defects arising from oxygen vacancies in the CeO\(_2\) lattice (Lyu et al. 2003). The intensities of all of the Raman bands of the samples decreased progressively on changing from 10 Zn–Ce (10 mol% Zn-substituted CeO\(_2\)) to 70 Zn–Ce (70 mol% Zn-substituted CeO\(_2\)). Increase of zinc content to 70 mol% (and above) resulted in the appearance of new bands at approximately 332 and 437 cm\(^{-1}\), which corresponded to the Raman active bands of ZnO. However, in PXRD data (figure 4), the appearance of ZnO phase was first observed in the as-prepared sample 20 Zn–Ce. This could be due to the fact that ZnO and CeO\(_2\) both have intense Raman bands in the same wavenumber region. Further, the strongest band of CeO\(_2\) at approximately 457 cm\(^{-1}\) was much more prominent and broad than the ZnO band at 437 cm\(^{-1}\). The Raman spectrum of the ZnO sample showed bands at approximately 332, 382
Synthesis of Zn–Ce oxide nanoparticles

150 Zn–Ce
20 Zn–Ce
30 Zn–Ce
40 Zn–Ce
50 Zn–Ce
60 Zn–Ce
70 Zn–Ce
80 Zn–Ce
90 Zn–Ce
ZnO

Figure 6. Raman spectra in the range of 150–650 cm$^{-1}$ of as-synthesized and freeze-dried pure CeO$_2$, Zn–Ce oxide and pure ZnO samples. Note that the peak corresponding to ZnO can be clearly seen as a shoulder in the 80 Zn–Ce spectrum and increases for samples with higher zinc loading. Unmarked peaks denote cerium oxide, asterisks denote zinc oxide.

and 437 cm$^{-1}$, which were attributed to the ZnO wurtzite phase (Jang et al. 2009). A slight blue shift in the Raman bands of Zn–Ce oxide samples with respect to those of ZnO itself was observed. This could be due to change in lattice constant upon Ce incorporation into the ZnO lattice (Yang et al. 2008; Phoka et al. 2009).

The optical properties of Ce–Zn oxide samples were analysed using UV–visible spectrophotometry and the plots are shown in figure 7. The UV–visible spectra revealed that the optical absorption edge was highly influenced by the zinc content. The CeO$_2$ absorption spectrum revealed a broad absorption centred at 380 nm with a broad shoulder understood to originate from the charge transfer transition from O (2p) to Ce (4f) (Singh & Hegde 2008). Upon doping of 10 mol% Zn into the nanoceria (i.e. sample 10 Zn–Ce), the absorption profile showed a reduction of the intensity of this charge transfer band. Thereafter, for increasing Zn loadings up to 50 mol% (sample 50 Zn–Ce), the absorption edge became gradually ever steeper, with the absorption profiles of samples 60 Zn–Ce to 90 Zn–Ce appearing to display an ever increasingly ZnO-like profile (inset of figure 7 for profiles 70 Zn–Ce to 90 Zn–Ce).

In contrast, Ce–Zn–O materials reported in the literature by Yuan and co-workers (made using more conventional batch hydrothermal processing) showed absorption much more like pure ZnO across most of the compositional spread (i.e. they have a very steep rise towards a plateau, even at relatively low Zn contents; Ma et al. 2010). The gradual change seen herein could be as a result of good atomic or particulate mixing due to the rapid nature of the crystallization process reported herein.

The optical bandgaps (shown in the electronic supplementary material, table S1) were determined herein from the absorption edges and using the Kubelka–Munk (KM) model for a direct transition (Tauc et al. 1966). The
estimated bandgap of the CeO$_2$ nanoparticles was 3.00 eV (or 2.29 eV using the KM function), which was within the range of 3.00–3.63 reported in the literature (Masui et al. 1997; Phoka et al. 2009). A gradual change (blue shift) in the optical bandgap was observed for samples 10 Zn–Ce at 3.28 eV (KM = 2.79 eV), 20 Zn–Ce at 3.35 eV (KM = 2.88), 30 Zn–Ce at 3.45 eV (KM = 2.98) and 40 Zn–Ce at 3.4 eV (KM = 3.02 eV). There was a reduction in the optical bandgap (to 3.3 eV) between samples 50 Zn–Ce and 70 Zn–Ce with the bandgap moving towards the ZnO value of 3.35 eV (KM = 3.15 eV) with further increase in Zn content. This is thought to be due to an increase in the UV absorption owing to the transition to a majority ZnO phase.

As-synthesized materials were obtained over a wide range of colours starting from pure cerium oxide (the darkest) to very light yellowish colour for high zinc loadings to white powder for nano-ZnO. The colorimetric data for all samples are summarized in the electronic supplementary material, table S1, and plotted as shown in figure 8. $L^*$ is the lightness axis (black = 0 to white = 100), $a^*$ is the green (−) to red (+) axis and $b^*$ is the blue (−) to yellow (+) axis. The lightness ($L^*$) increased almost linearly with increasing zinc concentration for samples 20 Zn–Ce up to ZnO as shown in figure 8a. On the other hand, $a^*$ values considerably decreased and $b^*$ values generally decreased for the same
samples, which are consistent with the change of colour from dark brown for CeO$_2$ (suggesting a majority of 4+ oxidation state for cerium ions as observed elsewhere for high cerium content ceria-containing solid solutions; Weng et al. 2009b) to very light yellowish or white for ZnO. The pure CeO$_2$ and 10 Zn–Ce did not appear to follow the trends of the other samples, which suggested that the presence (or absence) of separate ZnO nanoparticles dominated the trends in $L^*a^*b^*$ properties. The colour change with increasing Zn content thereafter could be attributed to an expected rise in Ce$^{3+}$ (relative to Ce$^{4+}$) as Zn is added to the fluorite as a +2 dopant (Ce$^{3+}$ would give a more yellow colour; Ma et al. 2010). Further studies using X-ray photoelectron spectroscopy are currently in progress to identify the relative amounts of Ce$^{3+}$ and Ce$^{4+}$ and will be reported in due course.

Phil. Trans. R. Soc. A (2010)
4. Conclusions

In conclusion, we report the use of a new HiTCH flow synthesis method, which enabled a complete range of Ce–Zn oxide nanomaterials to be sequentially synthesized in a relatively short timeframe (few hours). A new high-resolution powder diffraction facility at Diamond was employed to obtain high-quality diffraction data on the entire as-prepared and heat-treated library in a rapid and time-efficient manner. The new HiTCH flow synthesis reactor allowed the production of as-prepared nanomaterials in a few seconds with particle sizes well below 100 nm and as small as 3.7 nm, all of which generally had high surface areas (in many cases greater than 100 m$^2$ g$^{-1}$). Unprecedented solubility of Zn in the nanoparticle fluorite lattice was observed with a solid solubility limit of 20–30 mol% (zinc in ceria) for the as-prepared nanomaterials. Furthermore, doping of as little as 10–20 mol% Zn into the nanoceria in the form of a solid solution dramatically altered the shape and position of the UV–visible absorption edge (much steeper and akin to a ZnO-like absorption profile). There was also a gradual transition of the UV–visible absorption edge profiles thereafter (with increasing Zn content). In summary, the HiTCH flow synthesis route allowed a combination of particle properties to be achieved (e.g. unusual phase stability, tuneable optical bandgap, high crystallinity and small particle size) that was difficult or impossible to achieve using more conventional synthesis routes.

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References


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