

# Novel wet-chemical synthesis and characterization of nanocrystalline $\text{CeO}_2$ and $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ as solid electrolyte for intermediate temperature solid oxide fuel cell (IT-SOFC) applications

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**Abstract** Novel wet-chemical methods of synthesis have been adopted to synthesize nano-crystalline  $\text{CeO}_2$  and Gd-substituted compositions aiming to explore an efficient oxide ion conducting solid electrolyte for intermediate temperature solid oxide fuel cell (IT-SOFC) applications. Nano-crystalline  $\text{CeO}_2$  powders were synthesized by combustion method using redox mixture of ceric ammonium nitrate or cerium nitrate and maleic acid or 1,3-dimethylurea and compared with high surface area  $\text{CeO}_2$  powders prepared by hydrothermal technique with microwave precipitated precursor from aqueous solutions of  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  and urea. The grain size achieved by the hydrothermal technique is  $\sim 7$  nm which is smaller than that of commercial nano  $\text{CeO}_2$  powders. Conventional or microwave sintering was used to prepare dense  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$  pellets from the ceria powders made of redox mixture of cerium nitrate, 1,3-dimethylurea (DMU) and  $\text{Gd}_2\text{O}_3$  as the starting ingredients. The samples were characterized by X-ray diffractometry (XRD), transmission electron microscopy (TEM), diffuse reflectance spectroscopy (DRS), scanning electron microscopy (SEM), and ac impedance spectroscopy. The ionic conductivity measured for the pellet sintered at  $1400^\circ\text{C}$  is  $1 \times 10^{-2}$  and  $2.4 \times 10^{-2}$  S/cm at  $700^\circ\text{C}$  and  $800^\circ\text{C}$  respectively.

## Introduction

Fluorite structured Ceria ( $\text{CeO}_2$ ) has many applications as oxygen sensor [1], auto exhaust catalysts [2], polishing agents [3], sunscreens [4], and electrolyte materials for intermediate temperature solid oxide fuel cell (IT-SOFC) [5, 6]. Although yttria stabilized zirconia (YSZ) is still the favored electrolyte materials; ceria is considered alternative electrolyte material and could operate at lower temperatures ( $500\text{--}700^\circ\text{C}$ ). The ionic conductivity of ceria is approximately an order of magnitude greater than that of YSZ for comparable doping condition and especially when its nano-crystalline nature is retained. However,  $\text{CeO}_2$  is not a pure ionic conductor but has electronic conduction too, at elevated temperatures and electronic conduction gets enhanced in reducing atmospheres. IT-SOFC stacks operating at reduced temperature offer many exiting advantages, for example, increased material durability and reduced overall cost. They allow the use of gaskets that will permit greater design flexibility for the stack configuration, and allow the metal-supported positive-electrolyte-negative (PEN) structures, which will withstand the rapid temperature cycles during operation of small stacks [7–9].

Ceria is highly refractory oxide and difficult to sinter without sintering aids. However, nano-crystalline ceria can be densified at much lower temperature because of high surface energy of the nanoparticles [10–13]. Many solution based techniques were used to obtain the nanocrystalline ceria powders, such as hydrothermal technique [14], mimic alkoxide technique [15], micro-emulsion technique [16], sol-gel technique [17], precipitation technique [18], glycine-nitrate combustion technique [19], hydrazine technique [20], and spray

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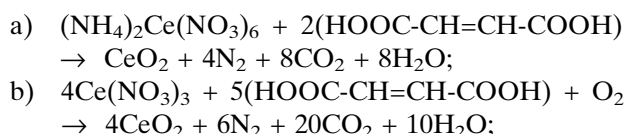
hydrolysis [21]. In the past, nanocrystalline  $\text{CeO}_2$  powders have been prepared by using urea and hexamethylenetetramine-based precipitation [17, 18]. In these experiments precipitation was carried out by conventional heating of the precursor solution at 80 °C. Since microwave heating is rapid and uniform, homogeneous nucleation and agglomerate-free precipitation is expected when the precursor solution is heated by microwaves. In this work emphasis has been given on the preparation of uniform nano-crystalline ceria powders at 200 °C, by hydrothermal treatment of microwave precipitated precursor from aqueous solution of  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  and urea. Nanocrystalline  $\text{CeO}_2$  and  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$  powders were also prepared by solution combustion technique using different kinds of starting reagents for comparison. The ceria powders prepared in this study were characterized by X-ray diffractometry (XRD), transmission electron microscopy (TEM), and diffuse reflectance spectroscopy (DRS), and compared with commercial nanocrystalline ceria powders. Combustion synthesized  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$  powders were made to dense pellets by using a resistance-heating furnace at 1400 °C and 1550 °C; and microwave sintering at 1200 °C. The microstructure of the sintered pellets were examined by scanning electron microscopy (SEM), and their electrical conductivity

was measured by ac impedance spectroscopy (EIS). The results of the experimental observations are discussed in this paper.

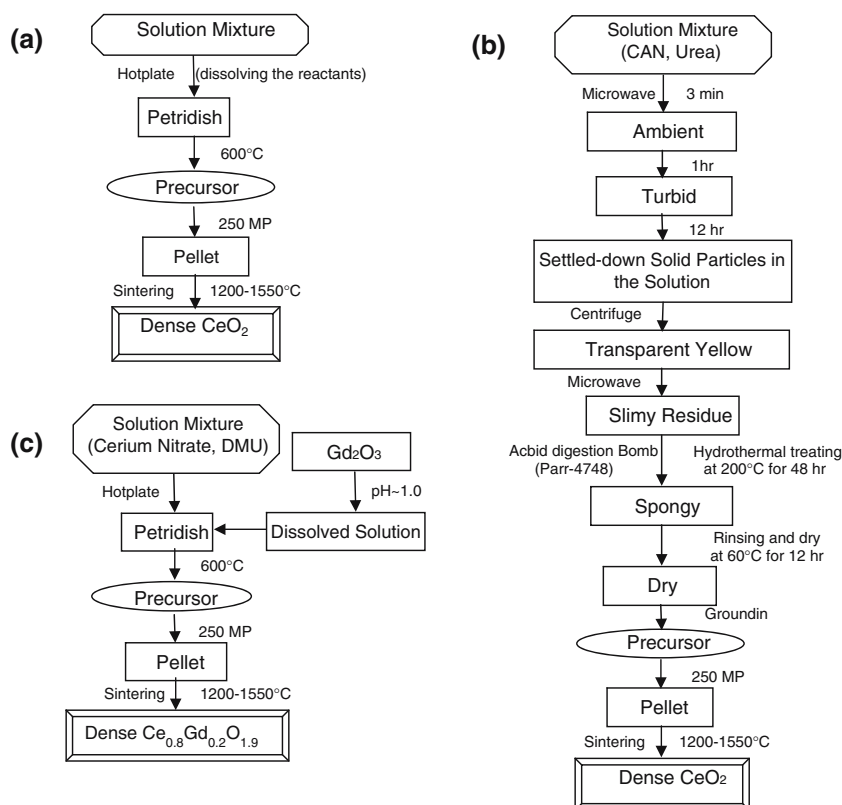
## Experimental

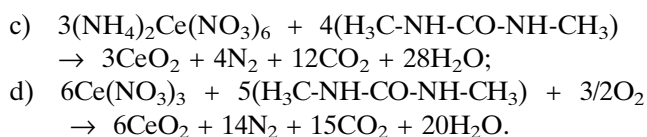
### Synthesis

In this study,  $\text{CeO}_2$  nanocrystalline powders were prepared by solution combustion and hydrothermal techniques. Starting from four kinds of solution mixtures, the  $\text{CeO}_2$  powders were synthesized by the solution combustion route. The four kinds of starting solution were: (a) redox mixture of ceric ammonium nitrate (CAN) and maleic acid; (b) redox mixture of cerium nitrate and maleic acid; (c) redox mixture of ceric ammonium nitrate (CAN) and 1,3-dimethylurea (DMU); and (d) redox mixture of cerium nitrate and 1,3-dimethylurea (DMU). Assuming complete combustion of the redox mixture, the theoretical equation for the formation of  $\text{CeO}_2$  may be written as follows:



**Fig. 1** Flowcharts to synthesize the nanocrystalline ceria powders: **(a)** combustion technique to prepare the  $\text{CeO}_2$  powders; **(b)** combustion technique to prepare the  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$  powders; and **(c)** hydrothermal treatment of microwave precipitated precursor





A typical solution combustion process can be described considering the case (a) as given above as an example: 10 g of CAN were taken in a 250 mL petri-dish dissolved in minimum amount of water, 4.234 g of maleic acid was added to this solution. The redox mixture of CAN and maleic acid was slightly heated on the hot plate to completely dissolve the reactants. Then the petri-dish was introduced into a preheated furnace (600 °C). The solution boiled and frothed leading to self propagating-type combustion after a few seconds. The product was bright yellow in color. The details of the procedure are given in the flowchart (Fig. 1a).

The hydrothermal technique has more processing steps than the solution combustion technique. The aqueous solution of 10 g of  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  and 16 g of urea was heated in a domestic microwave (2.45 GHz, 700Watts) at maximum power for 3 min. No turbidity was observed. When this solution was kept under ambient conditions in an open beaker without stirring for an hour, turbidity was observed. The solid settled down when the turbid solution was kept standing under ambient conditions in an open beaker without stirring overnight. The solution was centrifuged. The microwave reheating at maximum power of the transparent yellow supernatant in open beaker did not result in any significant turbidity. The pale yellow slimy residue obtained from centrifugation was transferred to a teflon container in a steel lined autoclave and hydrothermally treated at 200 °C for 48 h. The product obtained was spongy, swollen and voluminous. It easily separated from the teflon container. The product smelled of little ammonia. The product was rinsed with double distilled water and dried overnight in oven at 60 °C. The product obtained was shrunk in volume. It was ground and the color is lighter than the commercial nano-active  $\text{CeO}_2$ . The detailed steps of the process are given in the flowchart (Fig. 1b). Gd-doped ceria was also prepared by solution combustion technique using redox mixture of cerium nitrate, 1,3-dimethylurea (DMU) and  $\text{Gd}_2\text{O}_3$ . The details are shown as a flowchart in Fig. 1(c). The ceria powders were pelletized under 230 MPa at room temperature into pellets of 1.2 mm thick and 11 mm diameter. The pellets were sintered in resistance heating furnace (Carbolite RHF 1600) at 1400 °C and 1550 °C for 12 h, or sintered in a microwave oven (Panasonic, 2.45 GHz, 1200 W) at 1200 °C for 60 min. The

microwave oven was equipped with a thermocouple and a programmable temperature controller (ThermWave Mod.III, Research Microwave Systems LLC).

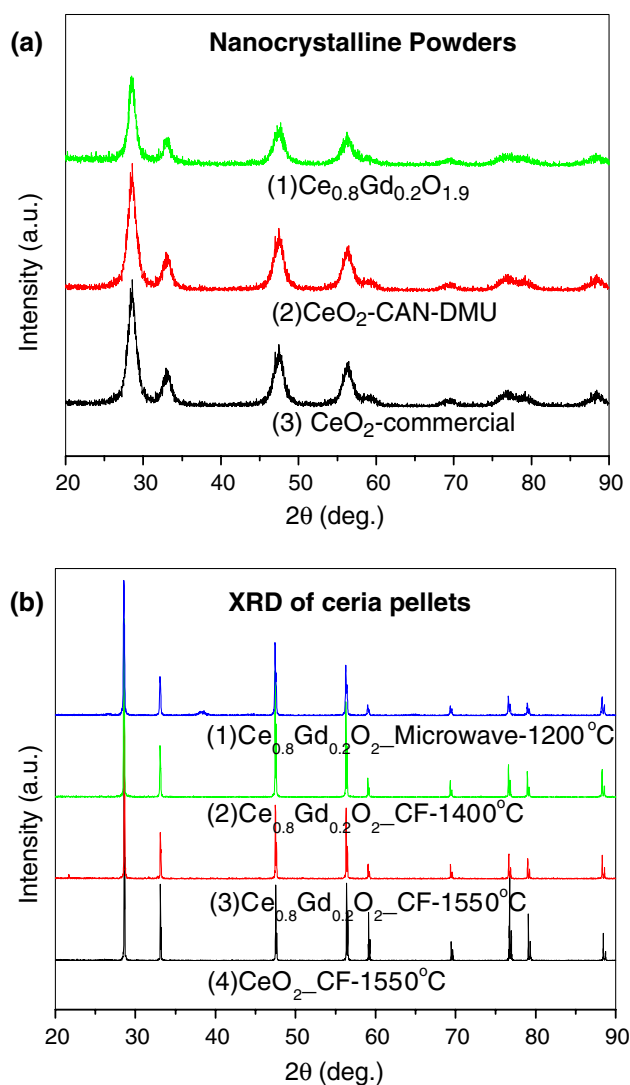
### Characterization

The powder and pellet samples were characterized by XRD, transmission electron microscopy (TEM), diffuse reflectance spectroscopy (DRS), scanning electron microscopy (SEM), and ac impedance spectroscopy (EIS). The XRD data were obtained at room temperature by a Siemens/Bruker D5000 diffractometer using  $\text{CuK}_\alpha$  as the incident X-ray. The TEM was taken by a JEOL 2010 High-resolution Transmission Electron Microscope (HRTEM). The DRS was scanned by a CARY 500 Scan UV-Vis-NIR spectrophotometer. The SEM was taken by a JEOL 6300F microscope using 3–5 kV as the accelerating voltages of the electron beam. The EIS was measured by HP-4192A LF Impedance Analyzer (5–13 MHz) in air at temperature range of 200–900 °C. The two electrodes were formed by applying platinum paste to the two sides of the pellet and firing at temperature 980 °C for 30 min or silver paste firing at 500 °C for 30 min.

## Results and discussion

### XRD of the ceria powders and pellets

The X-ray diffraction of the ceria powders and pellets are shown in Fig. 2. The broad peaks in Fig. 2(a) indicate the ceria powders are nanocrystalline. The XRD pattern of  $\text{CeO}_2$  and  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$  powders synthesized in this work (Fig. 2(a)) have quite similar XRD pattern as that of the commercial powders (NanoActive Cerium Oxide, NanoScale Materials, Inc.), this indicates that their crystal structure is same and their grain sizes are of same order of magnitude. The crystallite size of the particles were also measured by using Scherrer formula;  $t = 0.9\lambda/B\cos\theta$ , Where,  $t$  = Average crystallite size,  $\lambda$  = wavelength of X-rays,  $\theta$  = the position of the reflection in XRD pattern in degrees,  $B$  = integral breadth of a reflection (in radians  $2\theta$ ) located at  $2\theta$  and often calculated by using a solid reference standard, i.e  $B^2 = B_s^2 - B_r^2$ . The particle size measured from TEM and XRD confirms the nanocrystalline nature of the particles. The XRD patterns of the ceria pellets prepared from the laboratory-made undoped and doped ceria powders are shown in Fig. 2(b). In Fig. 2(b) the peaks are very sharp indicating well crystalline nature of the material compared



**Fig. 2** XRD of (a) nanocrystalline ceria powders and (b) ceria pellets

to those in Fig. 2(a) and there is no impurity peak shown except for the microwave-sintered pellet. The XRD data confirms that conventional (resistance heating) sintering produces well crystalline and phase pure  $\text{CeO}_2$  and  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$  pellets.

#### TEM of the ceria powder

In Fig. 3(a–d) TEM and electron diffraction pattern of the ceria powders synthesized by different routes and different compositions has been shown. The undoped ceria in Fig. 3(a–c) have mean grain-size  $\sim 5$  nm, and the doped ceria in Fig. 3d has a bigger mean grain-size  $\sim 20$  nm. It is noticeable that the electron diffraction patterns in Fig. 3c are similar to the pattern of the commercial ceria powder in Fig. 3a.

The similar smooth diffraction rings in Fig. 3c indicate that the ceria prepared in the laboratory through the hydrothermal synthesis has similar grain homogeneity as the commercial ones. The dark diffraction spots scattered along the rings in Fig. 3b and 3d reflect the presence of some big grain in the powders and the grain evenness is not as perfect as the ones in Fig. 3a and c.

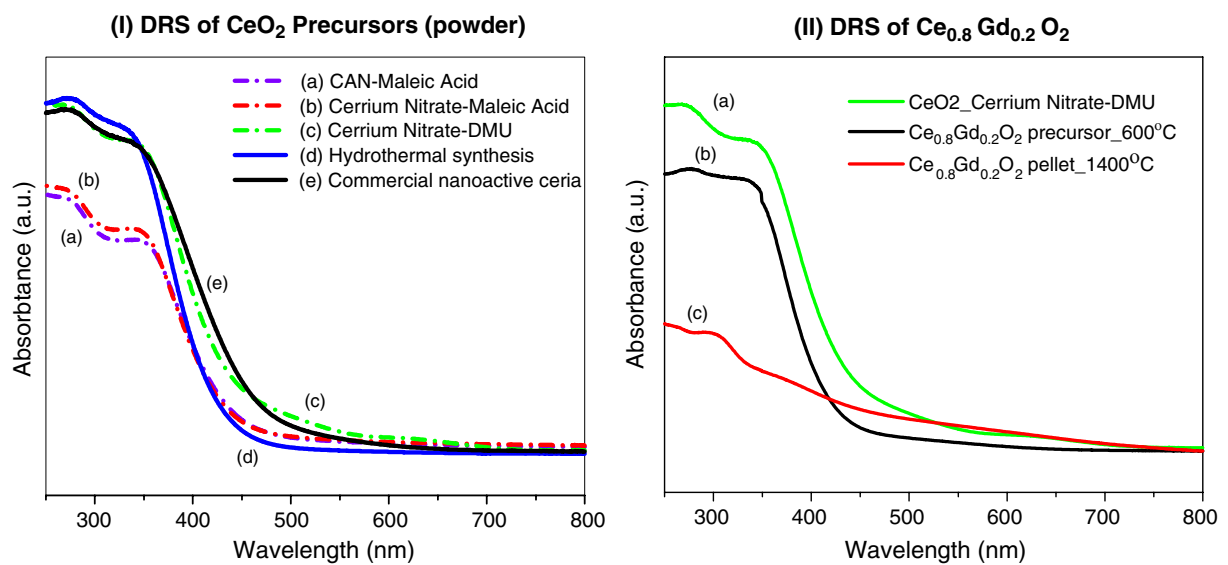
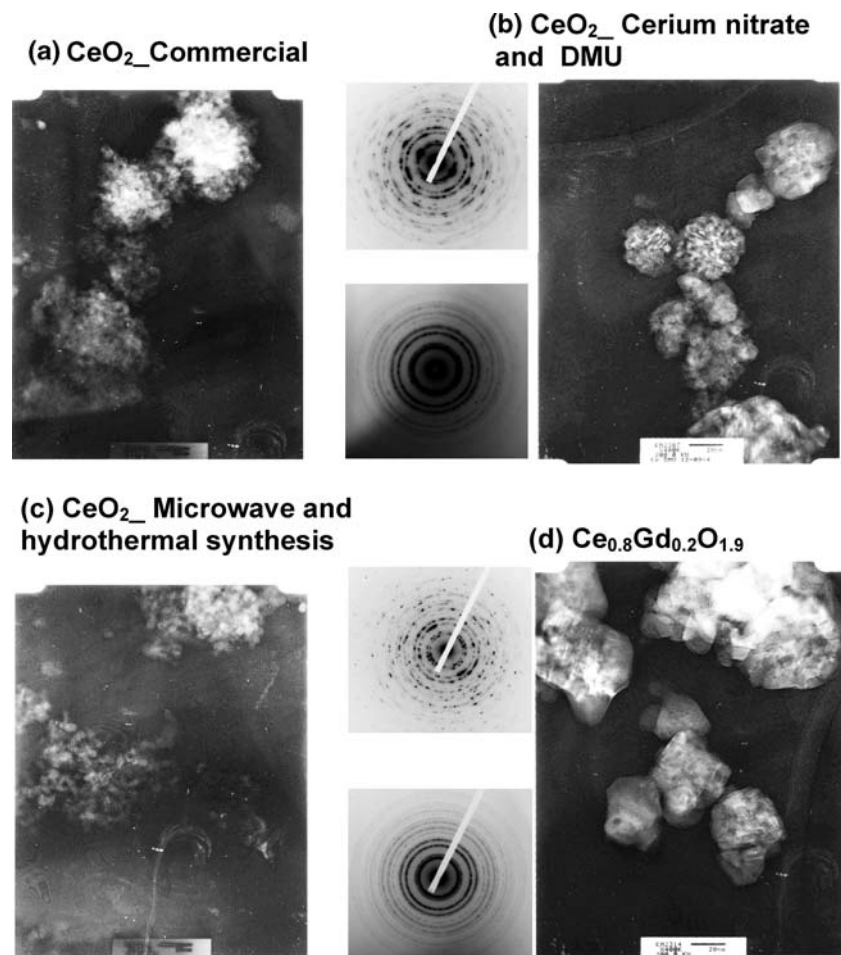
#### Diffuse reflectance spectra (DRS) of the ceria powder

In Fig. 4 the diffuse reflectance spectra of the undoped and doped ceria synthesized through different routes has been shown. For ceria powders synthesized through the conventional solution route as shown in Fig. 1a exhibited similar DRS patterns as the commercial one, ref. Fig. 4I(a), (b), (c) and (e) for  $\text{CeO}_2$ , and Fig. 4II(b) for  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ . However, the powders synthesized through the hydrothermal route in Fig. 1c has an obvious blue shift comparing to the commercial one as shown in Fig. 4(I)-(d) and (f). The ultraviolet absorption is commonly believed a direct charge-transfer transition between O-2p and Ce-4f bands. Due to the quantum size effect, the blue shift is inversely proportional to the nearly square of the particle diameter [22]. In this case, the blue shift of the hydrothermally synthesized ceria in Fig. 4-I-(d) indicates that the ceria synthesized in this work has a smaller mean grain size than the commercial ceria in Fig. 4-I-(e).

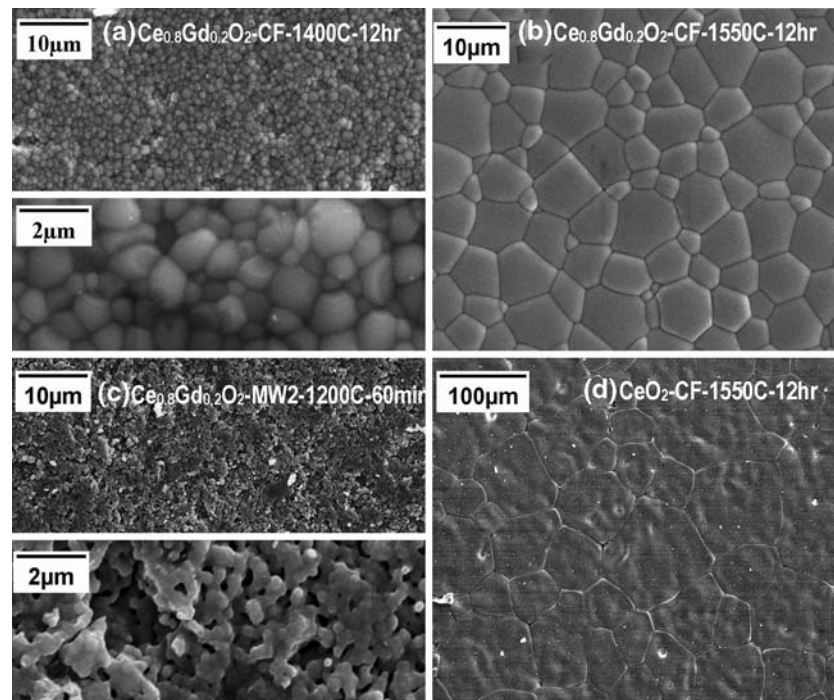
#### SEM of the ceria pellets

Some pellets were made from the nano-crystalline ceria powders. The scanning electron microscopy pictures of the ceria pellets are shown in Fig. 5(a)–(d). Fig. 5(a) and (b) show the sintering temperature effect on the grain size of the doped ceria. The mean grain size of pellet sintered at temperature  $1550^\circ\text{C}$  ( $\sim 7\ \mu\text{m}$ ) is about seven times bigger than the one sintered at  $1400^\circ\text{C}$  ( $\sim 1\ \mu\text{m}$ ). We also sintered the pellet by using microwave, as shown in Fig. 5(c). The pellet was sintered under microwave at  $1200^\circ\text{C}$  for 60 min. The mean grain size is about  $0.2\ \mu\text{m}$ , which is very small comparing to the upper two conventionally sintered pellets. We also made an undoped ceria pellet sintered at  $1550^\circ\text{C}$  as shown in Fig. 5(d). It is noticeable that the grain size is very big, up to  $100\ \mu\text{m}$ . The mean grain size is about ten times bigger than that of the Gd-doped ceria pellet sintered at the same temperature (comparing Fig. 5(d) to 5(b)).

**Fig. 3** TEM of the nanocrystalline ceria powders

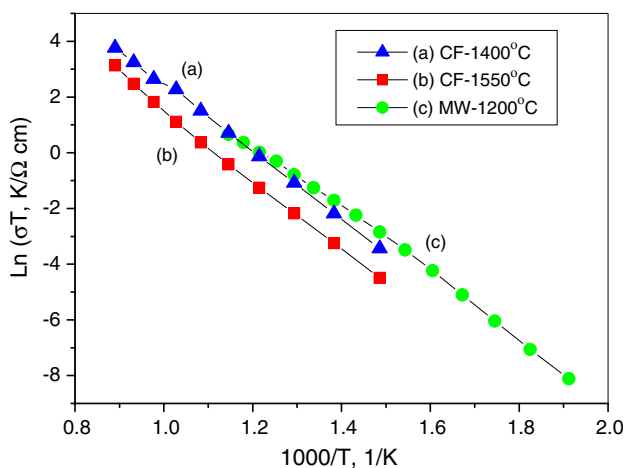


**Fig. 4** Ultraviolet-Visible diffuse reflectance spectra

**Fig. 5** SEM of the ceria pellets

Impedance spectroscopy (EIS) of the ceria pellets

We measured the conductivities of the Gd-doped pellets by ac impedance spectroscopy in air. The transport number is nearly equal to one in air or an inert atmosphere [23]. The Arrhenius relations of conductivity versus temperature are shown in Fig. 6. All the three samples display similar conductivities and Arrhenius slope. Although the grain size of the microwave sintered ceria is as small as submicrometer, the sample (Fig. 6(c)) shows similar conductivity as the conventional sintered and bigger grained  $Ce_{0.8}$

**Fig. 6** Arrhenius relations of the Ceria pellets

$Gd_{0.2}O_{1.9}$  (Fig. 6(a) and (b)). The sample has higher conductivity than the other two samples in the lower temperature region below 600 °C. The sample sintered at 1400 °C has a higher conductivity ( $1.0 \times 10^{-2}$  S/cm at 700 °C and  $2.4 \times 10^{-2}$  S/cm at 800 °C) than the sample sintered at 1550 °C, even though the sample has smaller grain or bigger grain-boundary region. It shows the grain-boundary region has negligible contributions to the total resistance of these pellets.

## Conclusion

Uniformly nano-grained ceria powders were synthesized at 200 °C by hydrothermal treatment of microwave precipitated precursor from aqueous solution of  $(NH_4)_2Ce(NO_3)_6$  and urea. The average grain size (~5 nm) of hydrothermally treated ceria powders is smaller than that of commercial nano-grained ceria (~7 nm) evident from the TEM and DRS studies. The obvious blue-shift in the DRS plot is believed to be caused by smaller nanoscale grain size.

Dense  $CeO_2$  and  $Ce_{0.8}Gd_{0.2}O_{1.9}$  pellets were prepared from the nanocrystalline powders. The pellets sintered by conventional furnace (resistance heating) at 1400 °C and 1500 °C were well-crystallized phase pure. The sample sintered at 1400 °C has ionic conductivities of  $1.0 \times 10^{-2}$  S/cm at 700 °C and  $2.4 \times 10^{-2}$  S/cm at 800 °C. The pellets sintered by microwave oven

at 1200 °C have submicrometer grain size and secondary phase, which needs higher sintering temperature to achieve better crystallization.

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