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EXAFS study of nanocrystalline CeO_2 samples prepared by sol–gel and ball-milling routes

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Abstract

This paper reports a study of nanocrystalline ceria prepared by both sol–gel and ball-milling methods. EXAFS measurements show that the ball-milled samples contain a considerable fraction of amorphous material, whereas there is a high degree of order in the sol–gel samples of similar grain size. In addition, a study has been made of the effect of silica and alumina as effective additives to reduce the grain growth of nanocrystalline ceria at elevated temperatures.

Keywords: Nanocrystals; Ceria; Fuel cells; XAS; EXAFS

1. Introduction

An important technological application of the rare earth oxides is in the electrolyte of solid oxide fuel cells, SOFCs [1,2], where the fuel is hydrogen and the oxidant is air The requirements for the electrolyte are a high oxygen ion conductivity, good mechanical and chemical stability. The dominant material has been cubic stabilized zirconia, where the stabilizing additive is yttrium (as in YSZ) or a rare earth. High oxygen ion conductivity is a result of the open nature of the fluorite structure and the high concentration of oxygen ion vacancies (the mobile defects) introduced to charge compensate for the aliovalent dopant. However, a zirconia based SOFC has to be operated at temperatures around 1000 °C for the conductivity of the electrolyte to be sufficiently high for useful power. This places severe constraints on the other components of the SOFC, such as electrodes gas-seals and gas feeds, and has been an obstacle in the commercial exploitation of SOFCs. Amongst the possible alternatives to zirconia the most promising electrolyte material is gadolinium doped cerium oxide, CGO. This material also has the fluorite structure and similar defect chemistry to YSZ, but the conductivity at moderate temperatures is higher with the promise of lowering the operating temperature to 400–600 °C.

There is now considerable interest in nanomaterials [3–5] because of their unusual chemical and physical properties when compared to the parent bulk materials. One of the properties reported is exceptionally high diffusion coefficients, and consequently enhanced ionic conductivity in solid electrolytes [6,7]. Although some of the evidence has been the matter of debate [8] there are now convincing reports of conductivity enhancement which have potential consequences for applications, such as SOFC electrolytes. Recent data for two doped CeO_2 samples, nanocrystalline Gd doped CeO_2 [6] (Fig. 1) and Sm doped CeO_2, which are different in terms of the compositions and temperature ranges studied and also in respect to the physical nature of the samples, show a very significant increase in conductivity.

Understanding the origin of the conductivity enhancement in nanocrystalline ionic solids requires a detailed understanding of the microstructure of the material. We have been investigating the microstructure of a range of nanocrystalline oxides using X-ray absorption spectroscopy (XAS) as the structural probe [9], including preliminary studies of CeO_2 films and powders [9,10]. In this contribution we report an EXAFS study of nanocrystalline CeO_2 and the dependence of microstructure on the preparative route. We also report the effect of using silica and alumina additives to pin the boundaries in ceria to reduce grain growth.

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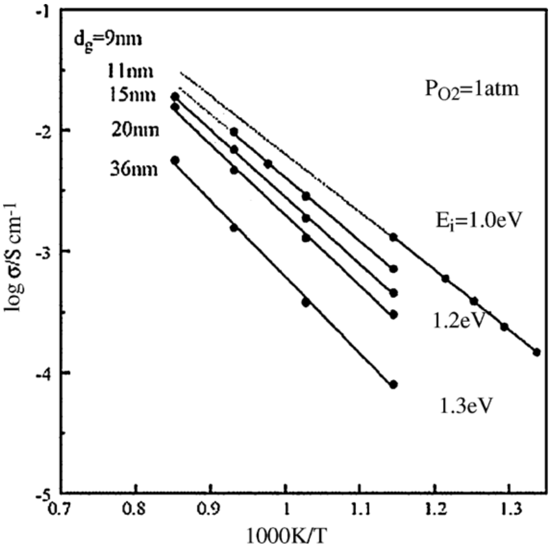

Fig. 1. The ionic conductivity of Gd doped CeO_2 ($Ce_{0.8}Gd_{0.2}O_{1.9}$) nanocrystalline thin films (after [6]).

2. Experimental

The preparation of the nanocrystalline ceria samples is described below.

2.1. *Nanocrystalline CeO_2 via precipitation*

Nanocrystalline CeO_2 was prepared by precipitation from an aqueous solution of cerium(III) nitrate hexahydrate by the addition of ammonia solution. The resulting solid was filtered, washed and dried at 60 °C overnight, ground using a pestle and mortar and portions calcined at temperatures in the range 400–1200 °C for 1 h.

2.2. *Nanocrystalline CeO_2–SiO_2 via sol–gel pinning*

Nanocrystalline CeO_2–SiO_2 (to give 15% by weight of SiO_2 in the final material) was prepared by precipitation from an aqueous solution of cerium(III) nitrate hexahydrate, tetraethylorthosilicate and ethanol by the addition of ammonia solution. The resulting solid was filtered, washed and dried at 60 °C overnight, ground using a pestle and mortar and portions calcined at temperatures in the range 400–1200 °C for 1 h.

2.3. *Nanocrystalline CeO_2–Al_2O_3 via sol–gel pinning*

Nanocrystalline CeO_2 was prepared by precipitation as described in Section 2.1. The powder was mixed with butan-2-ol to form a slurry and the required amount (to give 10% by weight of Al_2O_3 in the final material) aluminium tri-*sec*-butoxide was added and mixed for 1 h. Sufficient water was added to gel the slurry, this was dried at 80 °C overnight. The resulting solid was ground using a pestle and mortar and portions calcined at temperatures in the range 400–1200 °C for 1 h.

2.4. *Nanocrystalline CeO_2 via high energy ball milling*

Eight grams of bulk cerium(IV) oxide was ball milled using a stainless steel vial and balls (initial ball-to-powder ratio = 2) using a SPEX 8000M Mixer Mill. Portions were removed after various milling times for analysis (final ball-to-powder ratio = 3.2).

XRD patterns were collected using a Philips PW 1720 diffractometer with Cu Kα radiation (1.514 Å) and the data were analysed using Traces v3.0 (Diffraction Technology, Pty) commercial software, which also performed the calculation of the average particle sizes *via* the Scherrer equation. The Ce L_3-edge EXAFS were collected on station 9.3 at the CCLRC Daresbury Synchrotron Radiation Source, operating at an energy of 2 GeV and an average ring current of 150 mA in transmission mode. The EXAFS results were analysed using the Daresbury suite of programme; EXCALIB, EXBACK and EXCURV98 [11].

Table 1
The particle sizes of the nanocrystalline CeO_2 samples after 1 h calcining at the specified temperature

	Calcination temperature (°C)					
	400	600	800	900	1000	1200
Average particle size (nm)						
Pure CeO_2	32	34	61	116	270	1352
CeO_2–SiO_2	7	7	8	11	19	104
CeO_2–Al_2O_3	23	23	31	53	88	811

3. Results and discussion

The grain growth of nanocrystalline oxides is very rapid even at moderate temperatures [12]. The effect of adding silica and alumina as a pinning agent to reduce the growth has been shown to be effective for several oxides [12]. The results of the present experiments, shown in Table 1, demonstrate that the pinning agents are also very effective for CeO_2. Clearly SiO_2 is the most effective of the additives, maintaining a particle size less than 20 nm even after calcining at 1000 °C. It is interesting to note that no peaks for SiO_2 or Al_2O_3 were detected in the XRD patterns indicating that the additives were amorphous in the samples. The effect of milling time on the average particle size of the ball-milled CeO_2 is shown in Fig. 2. This clearly shows that increasing the milling times leads to a decrease in the average particle size. It is interesting to note that there is a significant reduction in average particle for milling times up to 300 min, but further increasing the milling time leads to only a slight reduction in particle size.

The EXAFS spectra and corresponding Fourier transforms for the Ce L_3-edge EXAFS spectra for bulk CeO_2 (507 nm), nanocrystalline CeO_2 annealed at 600 °C (34 nm), Al_2O_3-pinned CeO_2 annealed at 600 °C (23 nm) and CeO_2 ball milled for 1800 min (25 nm) are shown in Fig. 3. This figure shows that there is a reduction in the intensity of the EXAFS, compared to the bulk sample, for the nanocrystalline samples. This

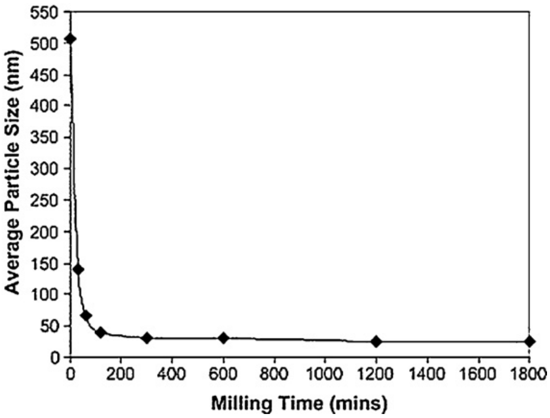

Fig. 2. The effect of milling time on average particle size of ball-milled CeO_2 (the line is a guide).

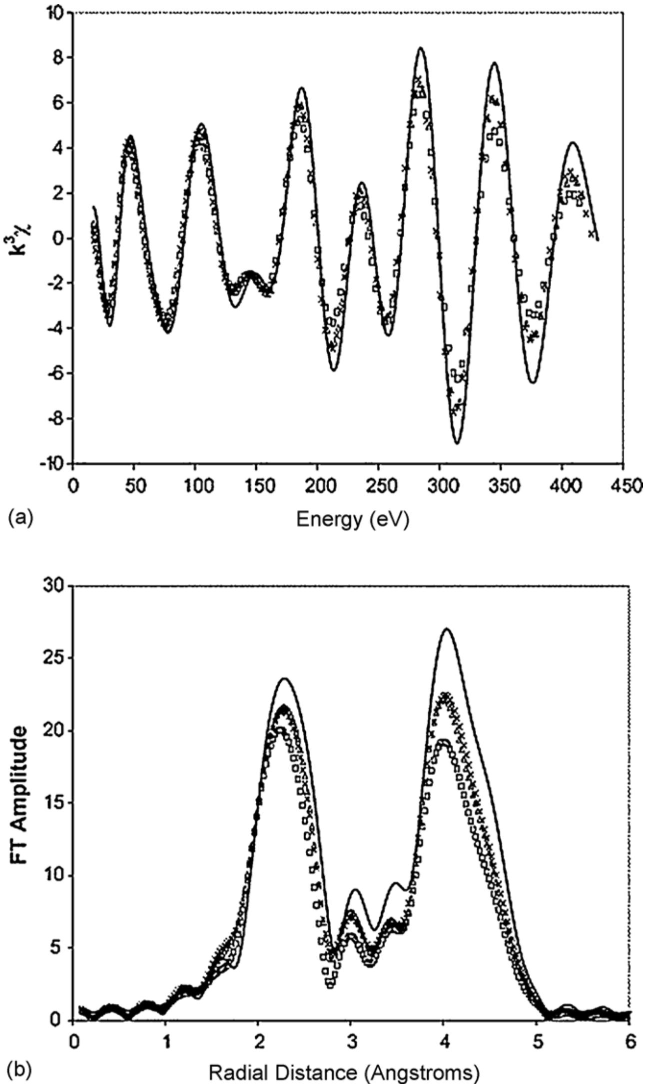

Fig. 3. The normalised EXAFS (a) and corresponding Fourier transforms (b) of the Ce L_3-edge EXAFS data for bulk CeO_2 (solid line), Al_2O_3 pinned CeO_2 600 °C (triangles), nanocrystalline CeO_2 600 °C (crosses) and CeO_2 ball milled 1800 min (squares).

reduction in amplitude can arise from (i) the particle is so small (<5 nm) that the average coordination numbers for the neighbouring shells is reduced or (ii) there is sufficient disorder in the sample that the Debye–Waller factors are increased. In this work the nanocrystalline samples are all 20–30 nm meaning that (i) cannot be the cause of the reduction in amplitude [9]. In the case of the nanocrystalline CeO_2 and Al_2O_3-pinned CeO_2, this reduction could be due to incomplete crystallisation of the samples. Since they were only heated at 600 °C, they may still contain some amorphous material that is not detected by XRD analysis. This has been shown previously in the case of sol–gel prepared nanocrystalline ZrO_2, where annealing at temperatures above 600 °C was required to fully crystallise the material [13], while low temperature (17 K) EXAFS spectra have shown that there is no reduction in amplitude for well crystallised 10 nm tetragonal ZrO_2 compared with bulk tetragonal ZrO_2 [14]. However, the ball-milled sample shows a greater reduction in the amplitude of the Fourier transform, than the Al_2O_3-pinned CeO_2 even though the particle sizes are similar. In this case, the reduction in amplitude cannot be due to incomplete crystallisation of the sample, but is likely to be due to presence of amorphous material produced during the preparation. Ball milling has been shown previously to produce nanocrystalline materials with a significant amorphous fraction [12,15] and EXAFS studies of ball-milled SnO_2, ZrO_2 [16,17] and $LiNbO_3$ [18] have all shown a large decrease in the amplitude of the EXAFS oscillations.

The EXAFS results reported here are for the nanocrystalline powders of a similar particle size. Previous studies of nanocrystalline ceria thin film prepared by polymer spin-coating show no reduction in the EXAFS intensity even at particle sizes of 4 nm [9,10], adding further evidence that the ball-milled samples in particular contain amorphous material. XAS studies of the SiO_2 pinned samples with particle sizes less than 20 nm are currently in progress.

4. Conclusions

The present work yields a number of interesting results. Firstly it is possible to restrict the grain growth of nanocrystalline CeO_2 at elevated temperatures by the addition of Al_2O_3 and SiO_2, the latter being the more effective. Secondly, the EXAFS measurements show that ball-milled samples of CeO_2 contain a large fraction of amorphous material when compared to sol–gel samples of a similar particle size. Both these results have consequences on the ionic conductivity studies of nanocrystalline CeO_2. The ability to reduce grain growth will be useful in extending conductivity to high temperatures. The highly ordered nature of the sol–gel samples will help in the modelling of the transport experiments.

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