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Low-temperature synthesis and characterization of ceria-based oxide ion conductors

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Solid solutions of the general formula $Ce_{1-x}Ln_xO_{2-x/2}\square_{x/2}$ (Ln = lanthanide (III) and $\square$ = anion vacancy), were prepared by a novel sol–gel route. These materials were characterized by powder diffraction and scanning electron microscopy. The gels formed on sol evaporation were found to be solid solutions with the fluorite structure and a crystallite size of approximately 6 nm. This is the lowest temperature of formation to date. The gels densified readily at 700 °C and the lattice parameter of these materials was found to be directly proportional to the ionic radius of the dopant.

1. Introduction

Lanthanide-doped CeO_2 of the general formula $Ce_{1-x}Ln_xO_{2-x/2}\square_{x/2}$ (Ln = lanthanide (III) and $\square$ = anion vacancy) possesses the fluorite structure over a range of dopant concentrations. The substitution range of fluorite structure stability depends on the individual dopant. Partial replacement of Ce^{IV} ions with Ln^{III} ions in the lattice creates a corresponding number of anion vacancies and the resulting solid solutions have high ionic conductivity and as such have been widely studied with possible applications as oxygen sensors [1] and in electrochemical fuel cells [2, 3]. The magnitude of conductivity does not increase linearly with increasing dopant concentration, but increases to a maximum between 10 and 20 mol% before falling off sharply [4]. The magnitude of this maximum in turn depends on the ionic radius of the dopant. Several authors have attempted to explain these complex phenomena in terms of oxygen vacancy–dopant cation pairs and clustering of oxygen ion vacancies [5–8]. These authors used various theoretical models in order to calculate the ionic conductivity of these materials and compared them with experimental data.

Solid solutions of this type are normally prepared by ceramic powder processing techniques where oxides and/or nitrates are intimately ground and fired at 1200–1600 °C for a prolonged period of time to achieve homogeneity [4, 9]. However, prolonged heating at high temperatures often causes considerable metal evaporation and oxygen loss making it difficult to maintain compositional stoichiometry. Owing to point defects thus created, the behaviour of these materials deviates from their expected behaviour.

This paper reports a novel sol–gel route using inorganic sol precursors to synthesize solid solutions of $Ce_{1-x}Ln_xO_{2-x/2}\square_{x/2}$ at low temperature. It is expected that this route will produce better quality materials with desired compositional stoichiometry, minimized point-defect concentration and grain boundaries with negligible silica content. It is expected that these materials produced by sol–gel methods will have improved electrical properties. Initial studies have previously been presented [10].

2. Experimental procedure

2.1. Sample preparation

Solid solutions $Ce_{1-x}Ln_xO_{2-x/2}\square_{x/2}$ where Ln = La, Gd, Sm, Nd, Yb and $x = 0$–0.3 were prepared by a novel inorganic sol–gel method. $Ce(NO_3)_3 \cdot 6H_2O$ (99.9% Aldrich Chemicals) was simultaneously precipitated and chemically oxidized to produce a cerium (IV) oxide hydrate with crystallite size of ~5 nm. This was then impregnated with a requisite quantity of lanthanide nitrate (99.9%, Aldrich Chemicals) and the dried mixture heated in a muffle furnace under strict temperature–time parameters. The resulting solid was powdered and dispersed in deionized water to yield a translucent sol, which was dried to yield a characteristic glassy transparent gel. The gels were then characterized as-prepared or after calcination at increasingly elevated temperatures in a muffle furnace.

2.2. Characterization

2.2.1. Scanning electron microscopy (SEM) and energy dispersive analysis of X-rays (EDX)

Morphology and elemental analysis of the samples were carried out on a Jeol scanning electron microscope (JEM 6100) operating at 20 kV and equipped with an energy dispersive X-ray analyser. Conducting samples were prepared by either carbon coating or gold sputtering finely ground powder specimens. Both broad beam and point EDX analysis of powder particles were performed using pure manganese as a reference standard.

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2.2.2. X-ray powder diffraction measurement (XRD)

X-ray powder diffraction patterns of the samples were recorded in the region of $2\theta = 10°–80°$ with a scanning speed of $\frac{1}{4}° \text{ min}^{-1}$ on a Philips diffractometer (Model PW1710) using CuK_α radiation with a nickel filter. The Philips APD1700 software was used to calculate the average crystallite size of each composition from the broadening of a specific diffraction peak using the well-known Scherrer equation

$$D = k\lambda/h_{1/2}\cos\theta \tag{1}$$

where D is the average size of the crystallites, k the Scherrer constant, λ the wavelength of radiation, $h_{1/2}$ the peak width at half-height, and θ corresponds to the peak position.

3. Results and discussion

The scanning electron micrograph of a sample of dried (105 °C) samarium-doped ceria gel with a nominal composition of $x = 0.2$ is shown in Fig. 1. The particles are seen to be glassy in nature. The results of a broad beam EDX analysis of the sample is shown in Table I. The EDX analysis of three randomly selected particles using a spot size of 100 nm, was averaged and is also shown. Similar data for all other samples are also included in the table. These results clearly show that all gels with different dopants studied in the present investigation are homogeneous on a nanoscale, and the analysed compositions agree well with their nominal compositions.

The XRD pattern of a sample of dried (105 °C) samarium-doped ceria gel with a nominal composition of $x = 0.2$ is shown in Fig. 2c. For comparison, the XRD pattern of Sm_2O_3 obtained by nitrate decomposition and that of CeO_2 reference standard (JCPDS file no 34-394) are also included. It can be seen that the gel possesses the fluorite structure with complete absence of any reactant peaks indicating the formation of a solid solution at the gel stage. It is interesting to note that on evaporation of the sol to form the gel, the dopant exists not as an evenly distributed individual component but within the crystalline fluorite lattice. The broadness of the peak observed also indicates nanoscale crystallite size.

The XRD patterns obtained after heating the dried gel to sequentially higher temperatures are shown in Fig. 2d–f. Two observations can be made.

(i) Heating the gel to 500 °C has little effect on peak width and intensity, indicating little change in crystallite size.

(ii) At 700 °C the peaks become very narrow and intense indicating rapid increase in growth of crystallite size and densification.

The XRD patterns of the other systems also showed the formation of fluorite solid solutions at the gel stage. These are the lowest formation temperatures for these materials reported to date.

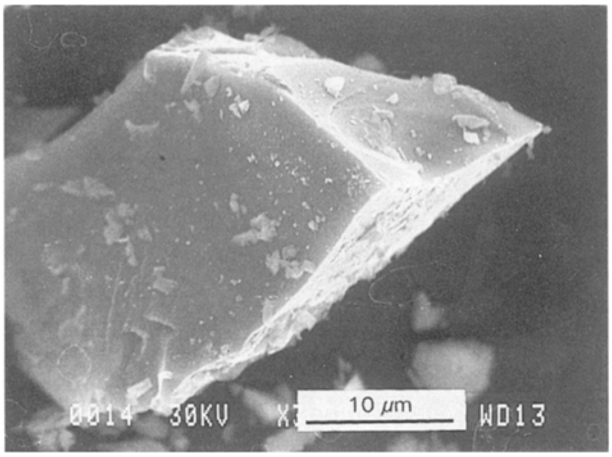

Figure 1 Scanning electron micrograph of ground gel fragments.

TABLE I Results of the EDX analysis of dried (105 °C) lanthanide-doped ceria gels[a]

Nominal composition	Average spot analysis (at %)		Broad beam analysis (at %)	
	Ce	Ln[a]	Ce	Ln[a]
$Ce_{0.8}La_{0.2}O_{1.9}$	80.20	19.80	79.40	20.60
$Ce_{0.8}Gd_{0.2}O_{1.9}$	79.19	20.81	79.14	20.86
$Ce_{0.8}Nd_{0.2}O_{1.9}$	79.94	20.06	79.99	20.01
$Ce_{0.8}Sm_{0.2}O_{1.9}$	79.20	20.80	79.54	20.86
$Ce_{0.8}Yb_{0.2}O_{1.9}$	79.60	20.40	80.06	19.94

[a] Respective lanthanides.

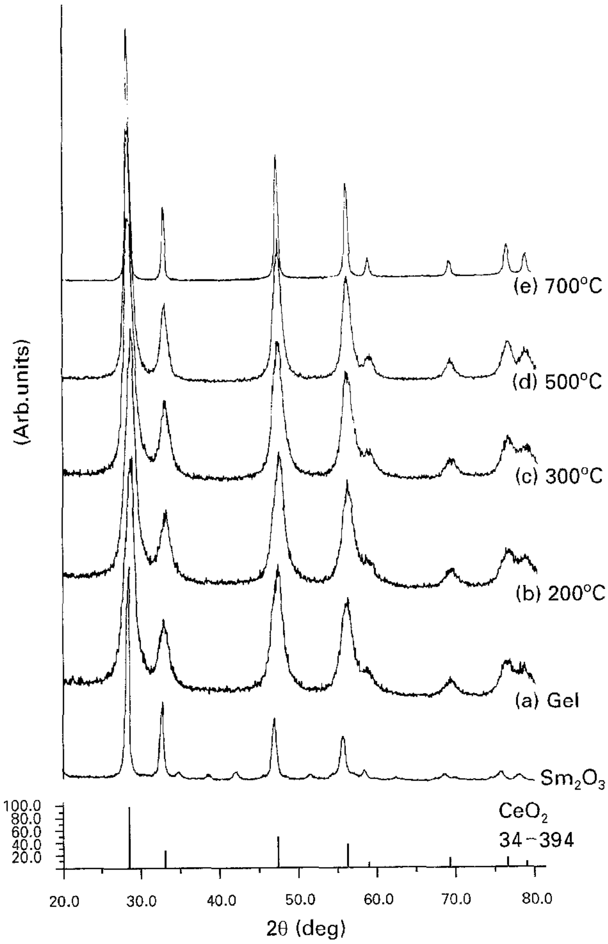

Figure 2 XRD patterns of $Ce_{1.8}Sm_{0.2}O_{2-\delta}$ calcined to various temperatures.

The trend in behaviour observed on heating the samarium-doped sample is also followed by all other doped compositions.

The XRD patterns of all doped solid solutions with $x = 0.2$ calcined to 500 °C are shown in Fig. 3. Here similar peak widths at half height indicate similar crystallite size, but the position of the (1 1 1) diffraction peak decreases linearly with increasing ionic radius of the dopant (Fig. 4).

The average size of crystallites in a sample of $Ce_{0.8}Sm_{0.2}O_{1.9}\square_{0.1}$ heat treated at various temperatures, was determined from the position and width of the (1 1 1) diffraction peak, obtained from dried gels. The results are summarized in Table II. The primary crystallite sizes of gel samples were found to be ~ 5 nm while the size for samples calcined to 500 °C was only 6 nm. These sizes are comparable to the primary crystallites of the undoped ceria starting material, and exemplify the small change seen earlier in the XRD patterns. However, crystallite growth increases markedly at 700 °C and consequently rapid densification occurs. This pattern shown here for Sm(III) as dopant, is again followed by all other doped compositions (Table III).

TABLE II Size of the crystallites in a sample of $Ce_{0.8}Sm_{0.2}O_{1.9}\square_{0.1}$ at different temperatures

Temperature (°C)	Crystallite size (nm)
105 °C dried gel	4.80
200	5.36
300	5.65
500	6.04
700	19.80

TABLE III Average crystallite size of $Ce_{0.8}Ln_{0.2}O_{1.9}\square_{0.1}$ solid solution at different temperatures

	Average crystallite size (nm)	
Sample	105 °C	500 °C
CeO_2	5.03	6.21
$Ce_{0.8}Yb_{0.2}O_{1.9}$	4.82	6.29
$Ce_{0.8}Gd_{0.2}O_{1.9}$	4.78	6.12
$Ce_{0.8}Nd_{0.2}O_{1.9}$	4.66	6.23
$Ce_{0.8}La_{0.2}O_{1.9}$	5.10	6.35

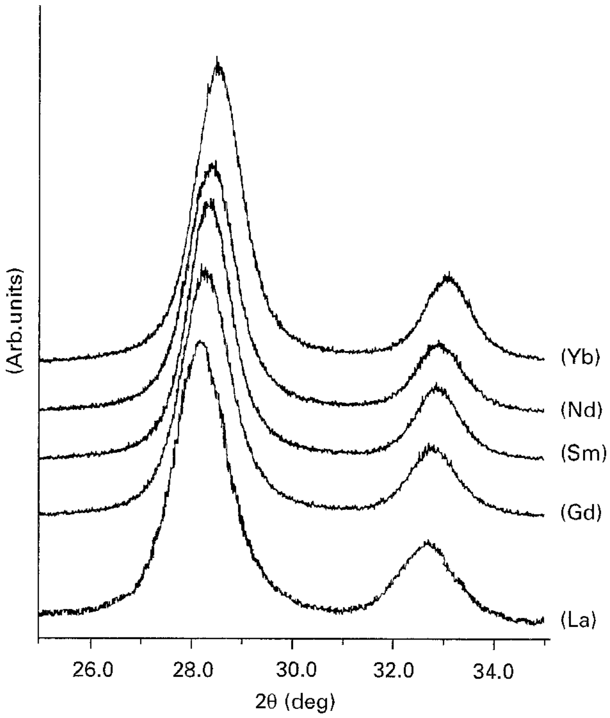

Figure 3 XRD patterns of $Ce_{1.8}Ln_{0.2}O_{2-\delta}$ calcined to 500 °C.

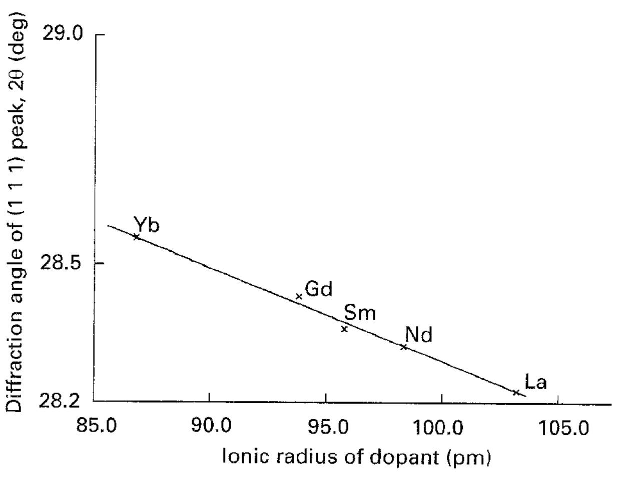

Figure 4 Position of the (1 1 1) diffraction peak versus the ionic radius of the dopant in $Ce_{1.8}Ln_{0.2}O_{2-\delta}$ calcined at 500 °C.

4. Conclusion

The novel preparative technique described in this paper was used to prepare lanthanide-doped ceria with fluorite structure at the lowest reported temperature to date.

These solid solutions were homogeneous on a nanoscale and were found to have crystallite sizes approaching 6 nm. This small crystallite size and freedom from agglomerates allow these materials to densify at 700 °C. Electron transport measurements and mechanical studies are being published separately.

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