

# Preparation and characterization of $\text{Ln}_2\text{Zr}_2\text{O}_7$ microspheres by an inorganic sol–gel route

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Free-flowing  $\text{Ln}_2\text{Zr}_2\text{O}_7$  microspheres (Ln = lanthanide) were prepared by an aqueous inorganic sol–gel route without any intermediate phase formation. The gel spheres obtained at room temperature were shown by X-ray diffraction to be amorphous but calcination to 750 °C produced fully crystalline fluorite phases. On calcination to 850 °C, pyrochlore phases were formed with suitable lanthanides. The microspheres were characterized by X-ray diffraction and scanning electron microscopy with energy dispersive analysis of X-rays to give accurate determination of structure, composition and crystallite size.

## 1. Introduction

Solid solutions of the  $\text{Ln}_2\text{O}_3$ – $\text{ZrO}_2$  system (Ln = lanthanide metal), possess the cubic fluorite structure, space group  $Fm\bar{3}m$ , over a wide range of lanthanide compositions [1–6]. This structure has a high vacancy concentration in the anionic sub-lattice and therefore possesses high anionic conductivity via movement of  $\text{O}_2^-$  ions between vacancies [1]. The position of these vacancies within the lattice is random, due to the disordered nature of the defect fluorite structure [4], and as substitution increases, vacancy clustering occurs limiting anionic conductivity. However, as substitution approaches the  $\text{Ln}_2\text{Zr}_2\text{O}_7$  formulation (Ln = La–Tb), pyrochlore structures are formed at high temperatures. Here, the vacancies from the defect fluorite lattice are converted to empty 8(b) oxygen sites and long-range vacancy ordering takes place, producing an ordered pyrochlore structure, space group  $Fd\bar{3}m$  [5]. These compounds with pyrochlore structure are good anionic conductors at high temperatures and can be used as high-temperature heating elements [7], as solid electrolytes in high-temperature fuel cells [2], and as oxygen-monitoring sensors. They can also host fluorescence centres with possible optical applications [8, 9]. These properties are very sensitive to the ordered microstructure of the material and so homogeneity of samples is extremely important. Previous research into pyrochlore synthesis has been centred around the citrate method, where the inorganic salts are converted to citrates *in situ* and a swelling agent added to produce a fluffy sinter-reactive powder [10–12]. Even so, temperatures in excess of 1500 °C have been used to produce homogeneous pyrochlore phases. Recently, the solution-sol–gel method has been applied to make homogeneous pyrochlore structures at lower temperatures [13]. Here, metal acetoacetates have been hydrolysed and fired at 810 °C to give the fluorite phase and at 1000 °C to give crystalline pyrochlore  $\text{La}_2\text{Zr}_2\text{O}_7$ . Previous work has produced low-temperature zirconia containing

ceramic compounds with nanometre crystallite sizes using a specific inorganic zirconia sol [14, 15], which is gelled by anion extraction. The present work, therefore investigated the preparation of  $\text{Ln}_2\text{Zr}_2\text{O}_7$  microspheres using this inorganic sol–gel route over a range of lanthanide elements, at the lowest reported temperatures to date.

## 2. Experimental procedure

### 2.1. Sample preparation

An inorganic polymeric zirconia sol was prepared by adding a salt of zirconium (basic carbonate or hydroxide) to a requisite quantity of concentrated mineral acid, followed by dilution and boiling to produce a transparent sol. The sol had a density of  $1.35 \text{ g cm}^{-3}$ , a concentration of  $280 \text{ g l}^{-1} \text{ ZrO}_2$ , and a counter ion/ $\text{Zr}^{\text{IV}}$  ratio of 1.0. To a fixed quantity the sol, the requisite amount of rare-earth nitrate (Aldrich chemicals 99.9%) was added as a concentrated solution. The resulting mixture was dispersed in an organic solvent/surfactant solution and the spherical sol particles gelled using an organic anion extracting agent. The spheres were then dried in an air oven at 105 °C and heat treated to various 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.

### 2.2.2. X-ray powder diffraction measurement (XRD)

X-ray powder diffraction patterns of the samples were recorded in the region of  $2\theta = 10^\circ\text{--}80^\circ$  with a scanning speed of  $1/4^\circ \text{ min}^{-1}$  on a Philips diffractometer (Model PW1710) using  $\text{CuK}_\alpha$  radiation. The Philips APD 1700 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

$$D = k\lambda/h_{1/2}\cos\theta \quad (1)$$

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

### 3. Results and discussion

Scanning electron microscopy of the gelled microspheres shows spherical particles between 40 and 70  $\mu\text{m}$  as seen in Fig. 1. Broad-beam analysis by EDX was performed to determine the composition of the spheres, and the results showed a close correlation between the achieved average bulk composition and the nominal composition  $\text{Ln}_2\text{Zr}_2\text{O}_7$ . Spot analysis was also in close agreement with expected values indicating good compositional homogeneity.

For the demonstration of XRD structure, the three lanthanide dopants, lanthanum neodymium and dysprosium, were chosen out of the series produced, because the former two were known to produce pyrochlore structures, while the latter remains fluorite. XRD patterns of the gel spheres showed an amorphous structure at room temperature (not shown). Calcination to  $750^\circ\text{C}$ , however, produced fully crystalline fluorite structures as shown in Fig. 2. This is the lowest temperature of formation of these compounds reported to date. Indexing of these patterns using the analysis software within the APD 1700 program was done to determine the lattice parameters of these fluorite structures, and the results are given in Table I. These values agree closely with those previously reported, produced at high temperature [1]. Further calcination of these fluorite phases at  $850^\circ\text{C}$  for lanthanides Tb–Er resulted in no change of crystal

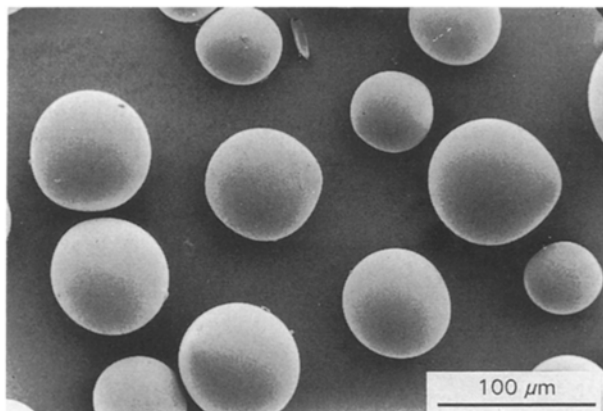


Figure 1 Typical scanning electron micrograph of  $\text{Ln}_2\text{Zr}_2\text{O}_7$  dried gel microspheres.

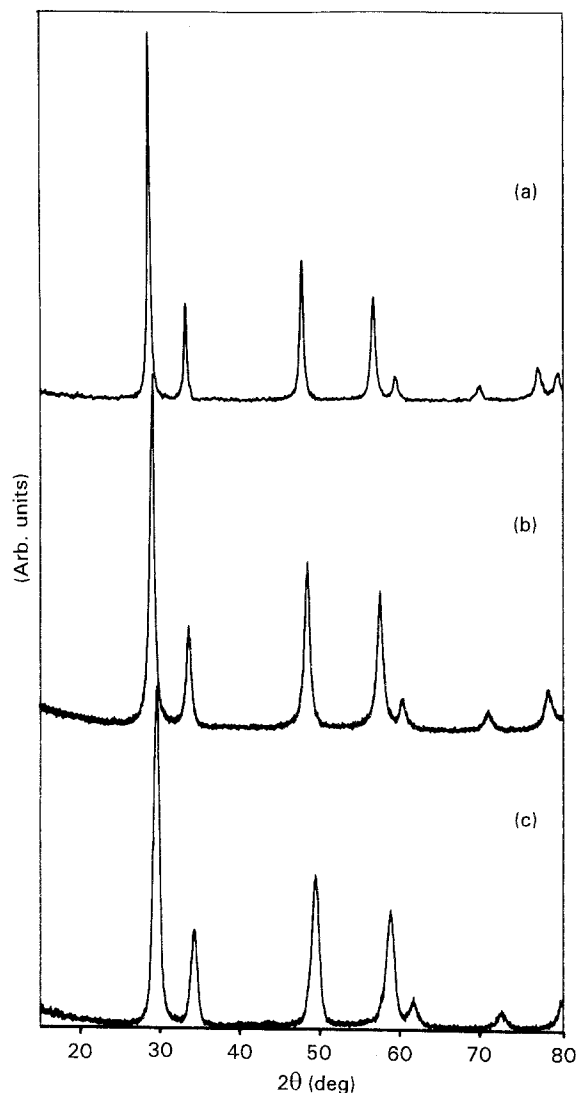


Figure 2 Powder X-ray diffraction patterns following heat treatment at  $750^\circ\text{C}$  for (a)  $\text{La}_2\text{Zr}_2\text{O}_7$ , (b)  $\text{Nd}_2\text{Zr}_2\text{O}_7$ , and (c)  $\text{Dy}_2\text{Zr}_2\text{O}_7$ .

TABLE I Structural parameters of  $\text{Ln}_2\text{Zr}_2\text{O}_7$  (Ln = La, Nd and Dy) at selected temperatures

Compound	Calcination temperature ( $^\circ\text{C}$ )	Crystallite size (nm)	Lattice parameter, $a$ (nm)	Structure
$\text{La}_2\text{Zr}_2\text{O}_7$	750	29.32	0.5397	Fluorite
	800	31.87	0.5400	Fluorite
	850	43.53	1.0811	Pyrochlore
$\text{Nd}_2\text{Zr}_2\text{O}_7$	750	20.19	0.5320	Fluorite
	900	61.18	1.0811	Pyrochlore
	900	31.44	1.0663	Pyrochlore
$\text{Dy}_2\text{Zr}_2\text{O}_7$	750	33.85	0.5201	Fluorite
	900	38.47	0.5221	Fluorite

structure. However, for lanthanides La–Eu calcined to  $850^\circ\text{C}$ , additional (1 1 1), (3 3 1) and (5 1 1) peaks developed due to ordering of the vacancies and characteristic of the ordered pyrochlore structure. Two representatives of this structure are shown in Fig. 3. These characteristic pyrochlore peaks are intrinsically of low intensity, and because these peaks are also broad, determination of the pyrochlore formation temperature by XRD is difficult. However, after

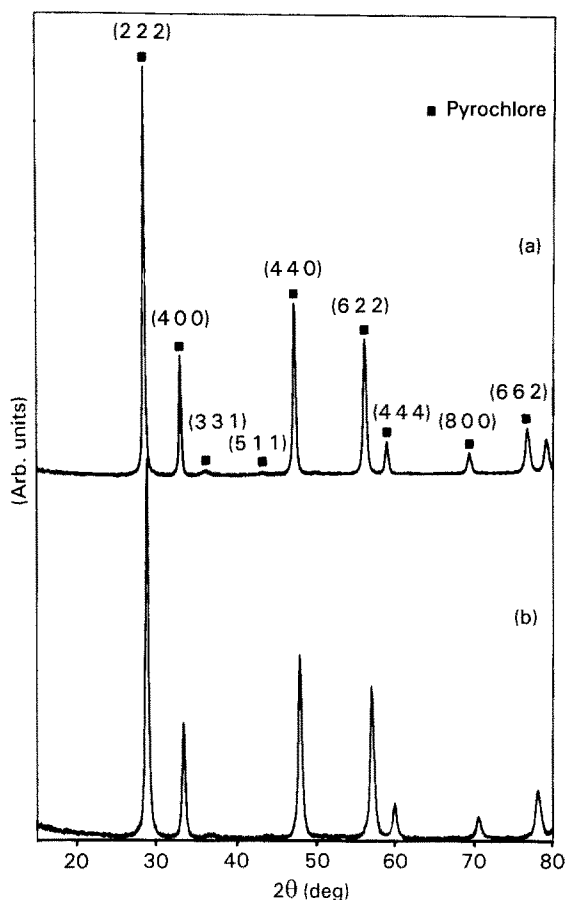


Figure 3 Powder X-ray diffraction patterns following heat treatment at 900°C for (a)  $\text{La}_2\text{Zr}_2\text{O}_7$ , and (b)  $\text{Nd}_2\text{Zr}_2\text{O}_7$ .

calcination at 850°C, both of these patterns were completely indexed as pyrochlore structures with a doubling of the fluorite cell edge. Lattice parameters again agreed closely with those previously reported [1], and are tabulated in Table I as a function of calcination temperature. This is again an improvement over the solution-sol-gel method previously mentioned [13].

The APD 1700 software was also used to calculate the average crystallite sizes of these materials using the line broadening effect of XRD peaks as a function of temperature. The results are also included in Table I. These nanometre crystallite sizes (20–30 nm at 750°C and 30–60 nm at 900°C) are responsible for the broadness of XRD peaks and, therefore, the difficulty in determination of the pyrochlore phase formation temperature. Because the smaller the crystallite size is, the larger the surface free energy, it is believed that the break-up of this inorganic polymeric zirconia sol into nanoscale homogeneous entities, is responsible for the high reactivity and, therefore, low formation temperatures experienced not only in these preparations but also those performed previously [14, 15]. Also, because gel formation via this route is an anion ex-

traction technique and not a precipitation, as in the solution-sol-gel method, the improved homogeneity associated with this may also be important in lowering formation temperatures of compounds produced by this method.

#### 4. Conclusions

The incorporation of dopant cations into the inorganic polymeric zirconia sol described in this paper, results in a doped sol which, upon anion extraction, produces nanoscale homogeneous crystallites. These zirconia crystallites, due to their high surface free energy, react readily with the incorporated dopant, producing crystalline compounds at lower temperatures than conventional methods. It is also believed that oxygen vacancy ordering is facilitated because of the ease of oxygen diffusion within these nanoscale crystallites and hence pyrochlore formation is also at a lower temperature. Further studies on the kinetic and thermodynamic effects of this phenomenon are being undertaken.

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Received 3 March  
and accepted 5 May 1994