

# Chemical Synthesis of Pure and Gd-doped CaZrO<sub>3</sub> Powders

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## Abstract

*Aqueous solutions of calcium chloride (CaCl<sub>2</sub>·2H<sub>2</sub>O) and zirconium oxychloride (ZrOCl<sub>2</sub>·8H<sub>2</sub>O), in appropriate volumetric amounts, were used as the starting chemicals in the synthesis of phase-pure CaZrO<sub>3</sub> powders. Rare earth element dopings (up to 25 at%) were performed by using the aqueous chloride solutions of gadolinium (Gd). Formation of CaZrO<sub>3</sub> powders were achieved by two different chemical synthesis techniques: (i) self-propagating combustion synthesis, and (ii) precipitation in the presence of EDTA by the technique of acid-base titration. Sample characterization was performed by powder XRD (X-ray diffraction) and SEM (scanning electron microscope). © 1999 Elsevier Science Ltd. All rights reserved.*

**Keywords:** CaZrO<sub>3</sub>, powders-chemical preparation, X-ray methods, perovskites.

## 1. Introduction

There is a growing interest in calcium zirconate-based oxides for potential sensor/device applications at elevated temperatures. In particular, several studies have been reported on the use of calcium zirconate-based systems for monitoring oxygen,<sup>1–3</sup> humidity and hydrogen.<sup>4–8</sup> In these studies, sintered polycrystalline samples were used to characterize carrier types and the concentrations of ionic (proton or oxygen) and electronic charge carriers as a function of temperature, impurity distribution, and oxygen and/or water vapor partial pressures. Pretis *et al.*<sup>9</sup> reported that undoped calcium zirconate (CaZrO<sub>3</sub>) is a p-type semiconductor in air. When doped with oxides such as Al<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub> and MgO or with a small excess of ZrO<sub>2</sub> or CaO, it becomes pre-

dominantly an oxygen-ion conductor.<sup>1,2,7</sup> For a sample doped with trivalent cations such as indium, scandium and gallium, it may become predominantly a proton conductor when exposed to a hydrogen-containing atmosphere (steam) at temperatures ranging from 600 to 1000°C.<sup>4,5</sup> The protonic conduction, however, tends to diminish at higher temperatures and can be replaced by electronic (hole) conduction, especially in a dry air atmosphere.<sup>4</sup>

CaZrO<sub>3</sub> has also been studied for its potential use as a high-temperature thermistor material.<sup>8</sup> The electrical response of calcium zirconate (prepared by the solid state reactive firing of CaCO<sub>3</sub> and ZrO<sub>2</sub> powders at 1400°C) was found to be sensitive to methane, but was practically unaffected by humidity and carbon monoxide. The use of a calcium zirconate-based thermistor is, therefore, limited to atmospheres without methane and/or possibly other hydrocarbon gases. The dramatic response to methane, however, makes CaZrO<sub>3</sub> a potential candidate material for hydrocarbon sensing.

In this paper, we report results of two different chemical powder preparation techniques for synthesis of fine powders of pure and Gd-doped (5–15 at%) CaZrO<sub>3</sub>. This study, to our knowledge, has been the first attempt in the relevant literature for the synthesis of calcium zirconate powders by chemical means, rather than conventional solid state firing and calcination practices.

## 2. Experimental Procedure

Starting chemicals used in this study were reagent-grade CaCl<sub>2</sub>·2H<sub>2</sub>O (Riedel de Haen), ZrOCl<sub>2</sub>·8H<sub>2</sub>O (Merck), Gd<sub>2</sub>O<sub>3</sub> (+99.9%, Ames Laboratory, IA, USA), EDTA (C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>Na<sub>2</sub>O<sub>8</sub>·2H<sub>2</sub>O, Merck), NaOH (Merck), and Urea (CH<sub>4</sub>N<sub>2</sub>O, Riedel de Haen). GdCl<sub>3</sub> stock solutions were prepared by reacting the oxide powders in an HCl solution of correct stoichiometry. Two different synthesis techniques were employed to produce pure and Gd-doped calcium zirconate powders.

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In the *first technique*, i.e., ‘self-propagating combustion synthesis (SPCS)’,<sup>10–11</sup> appropriate amounts of Ca- and Zr-chloride salts (in the case of Gd-doping, proper aliquots of Gd-chloride solutions were added) were first dissolved in distilled water. Urea of proper amount (which serves as the fuel / oxidant in the combustion reaction) was then added to this solution. The solution, following its transfer into a Pyrex beaker, was placed into an electric furnace pre-heated to  $500 \pm 10^\circ\text{C}$ . The combustion reaction was completed in less than 15 min yielding an amorphous and foam-like powder body. This powder body was then ground, and calcined for crystallization in a stagnant air atmosphere in 17 h at  $1200^\circ\text{C}$ .

In the *second technique* used, again, appropriate amounts of Ca-, Zr- and/or Gd-chloride salts/solution were dissolved in distilled water. EDTA was used as a chelating agent. The cation solution at room temperature was added in a drop-wise manner into a concentrated (10 M) NaOH solution. The formed precipitates were filtered, washed with distilled water, dried at  $90^\circ\text{C}$ , and later calcined at  $1200^\circ$  for 17 h.

Phase characterization of the calcium zirconate powders was achieved by powder XRD (X-ray diffraction). The diffractometer (Rigaku Corp., Model: D/Max-B, Japan) was used with a monochromated  $\text{CuK}\alpha$  radiation tube operated at 40 kV and 20 mA. The XRD data were collected at a step size of  $0.05^\circ$  and count time of 1 s. Powder morphology was investigated via SEM (scanning electron microscopy; JEOL Corp., JSM-6400, Japan) micrographs.

The sintering behavior of phase pure and Gd-doped  $\text{CaZrO}_3$  powders was studied on the pellets (1 cm diameter, 3 mm thick) uniaxially pressed in hardened steel dies at a pressure of 90 MPa. The green pellets were then heated (at the ramp rates of  $10^\circ\text{C min}^{-1}$ ) at  $1200^\circ\text{C}$  for 6 h in a stagnant air atmosphere.

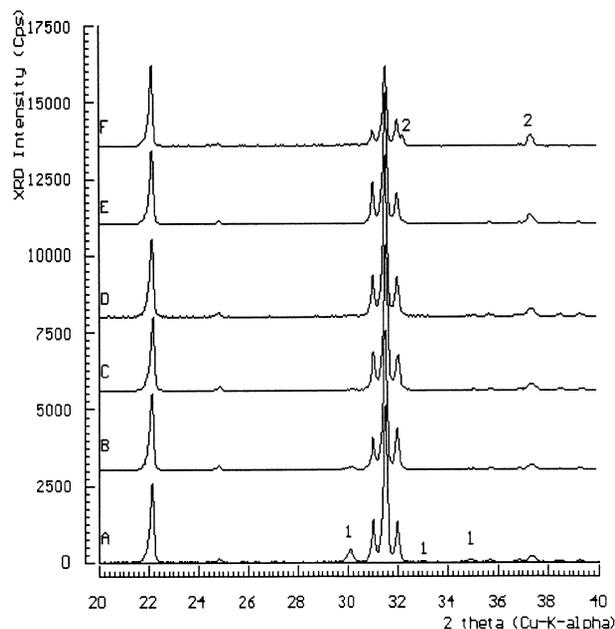
### 3 Results and Discussion

Both techniques of chemical synthesis used in this study were found to be successful in producing phase-pure and sub-micron powders of  $\text{CaZrO}_3$ , as an alternative route of powder synthesis to that of more conventional solid-state reactive firing of CaO and  $\text{ZrO}_2$ .

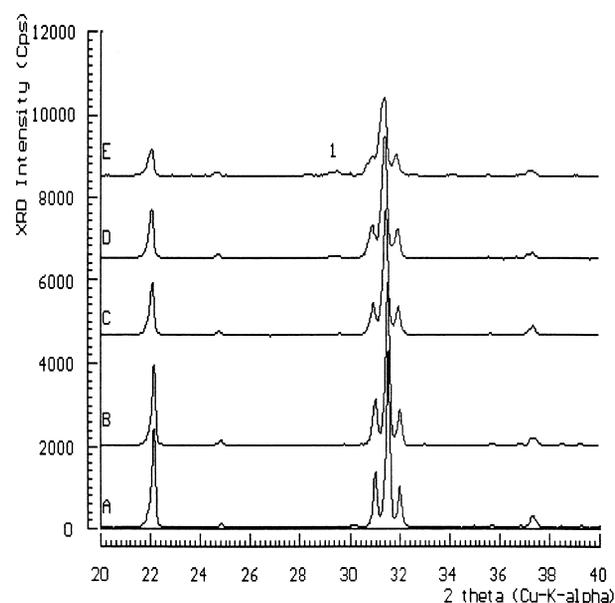
In the SPCS method, the weight ratio of chloride salts (i.e., Ca and Zr) in the combustion solutions was found to influence the phase purity of the calcined (at  $1200^\circ\text{C}$ ) powder bodies. When the solutions were away from the proper stoichiometry, major impurity phases were CaO-stabilized cubic zirconia and calcium oxide, depending on which cation was excess in solution. Figure 1 shows the influence of

Ca:Zr-chloride weight ratio on phase purity in the SPCS method. The XRD data given in Fig. 2 indicated that there is an upper limit to the level of Gd-doping in  $\text{CaZrO}_3$ , and that limit was found to be in the range of 10–15 at%. Beyond that limit, free  $\text{Gd}_2\text{O}_3$  and  $\text{ZrO}_2$  phases were detected in the respective XRD charts.

In the acid-base titration method (in the presence of EDTA) used for  $\text{CaZrO}_3$  powder synthesis, it was found that this technique was also suitable for the synthesis of phase-pure cubic zirconia (CSZ)



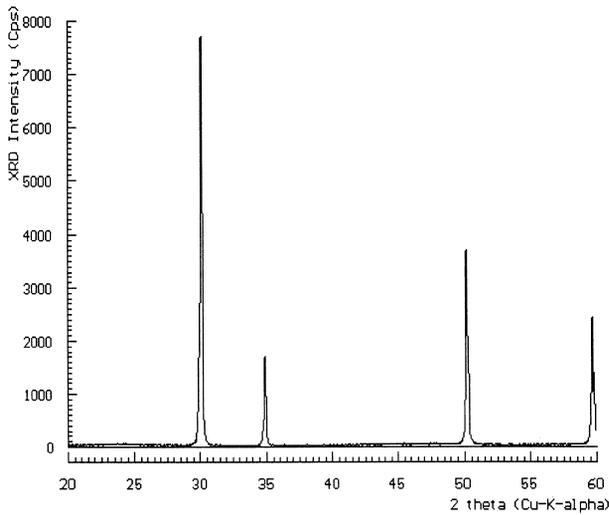
**Fig. 1.** XRD traces showing the influence of Ca:Zr-chloride weight ratio on the phase purity of  $\text{CaZrO}_3$  powders produced by the SPCS method.<sup>10,11</sup> [Ca:Zr-chloride weight ratios: A = 0.456, B = 0.507, C = 0.537, D = 0.553, E = 0.562, F = 0.570; (1) CSZ (ICDD PDF 26-341) and (2) CaO (ICDD P13F 37-1497)].



**Fig. 2.** XRD traces showing the effect of Gd-doping on the phase purity of  $\text{CaZrO}_3$  powders, SPCS method [A = pure, B = 5%, C = 10%, D = 15, E = 25 at%; (1)  $\text{ZrO}_2$  (ICDD PDF 37-31)].

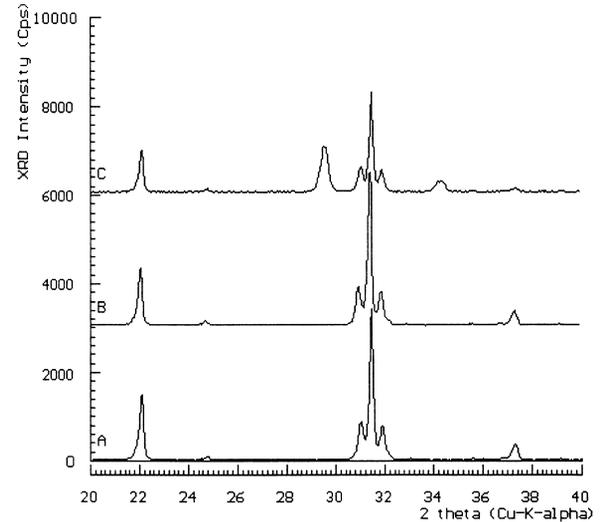
powders, as shown in the XRD chart of Fig. 3, as well as for the manufacture of  $\text{CaZrO}_3$ .

Calcium ions will be chelated with EDTA when an aqueous solution of calcium chloride is added with EDTA in excess of the stoichiometric quantity and then with an aqueous solution of zirconium oxychloride. We attempted the precipitation reactions of the mixed hydroxide precursors of Ca and Zr with calcium ions supplied slowly by oxidizing / decomposing the EDTA-calcium chelates.

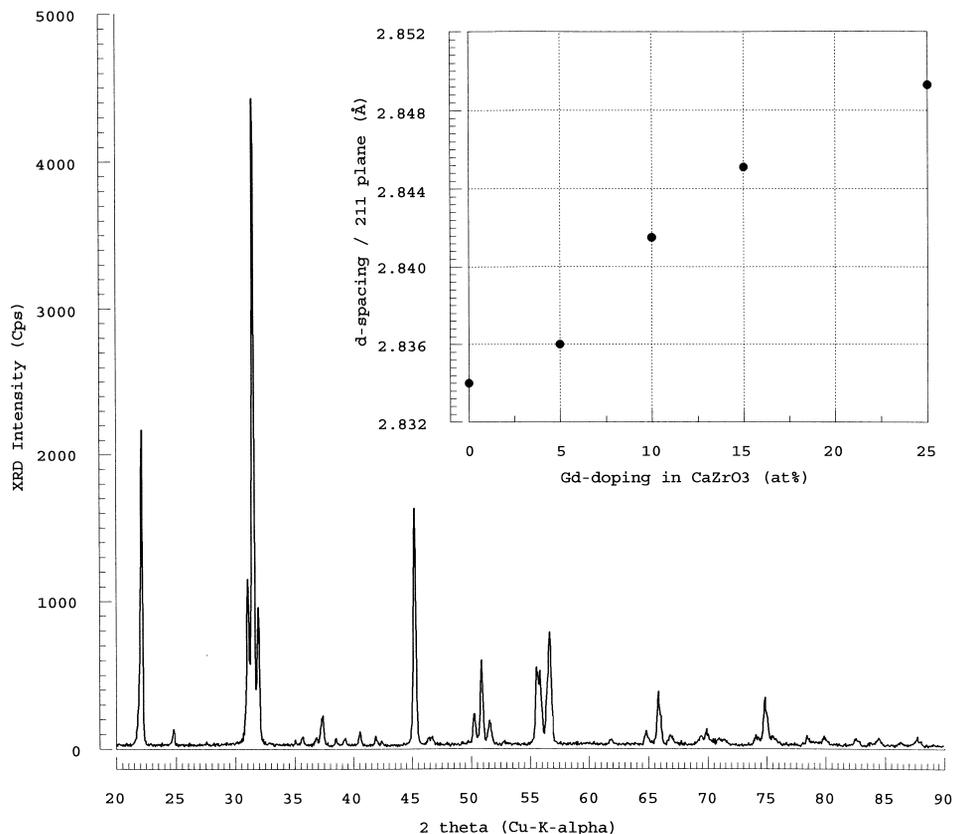


**Fig. 3.** A typical XRD chart of CaO-stabilized (cubic) zirconia powders synthesized by the EDTA-precipitation technique.

The XRD data given in Fig. 4 display the influence of Gd-doping, over the dopant concentration range of 5–15 at%, on the phase-purity of  $\text{CaZrO}_3$  produced by the EDTA method. It was found by this study that 5 and 10% dopings of Gd may easily be performed, and at such levels Gd goes into a solid solution within the structure of  $\text{CaZrO}_3$ . However, beyond 10 at% (i.e., 15 at%) the  $\text{ZrO}_2$  peaks appeared in the XRD data of Fig. 4.



**Fig. 4.** XRD traces showing the effect of Gd-doping in EDTA-precipitation process (A = 5, B = 10, C = 15 at%;  $\text{ZrO}_2$  peaks are visible in trace C at  $29.5$  and  $34.4^\circ 2\theta$ ).



**Fig. 5.** A typical XRD chart of EDTA-precipitated  $\text{CaZrO}_3$  powders (Insert: effect of Gd-dopant concentration on the  $d_{211}$  of  $\text{CaZrO}_3$  unit cell).

Phase-pure  $\text{CaZrO}_3$  powders produced by the EDTA-precipitation technique had sub-micron particles, and possessed the lattice parameters of

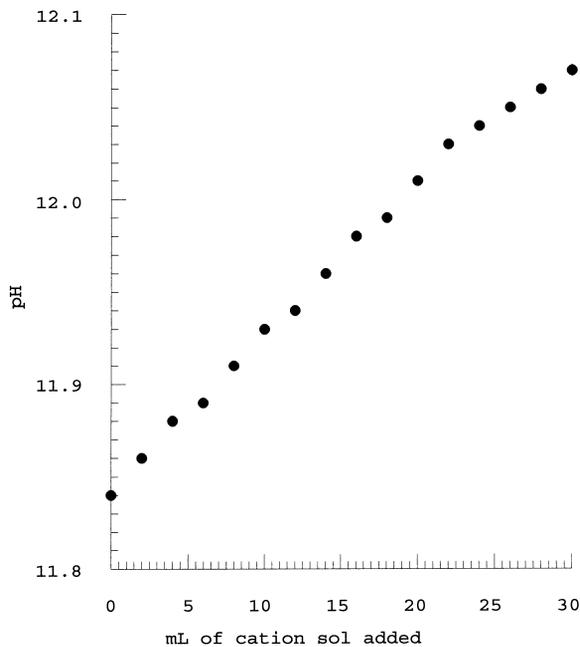
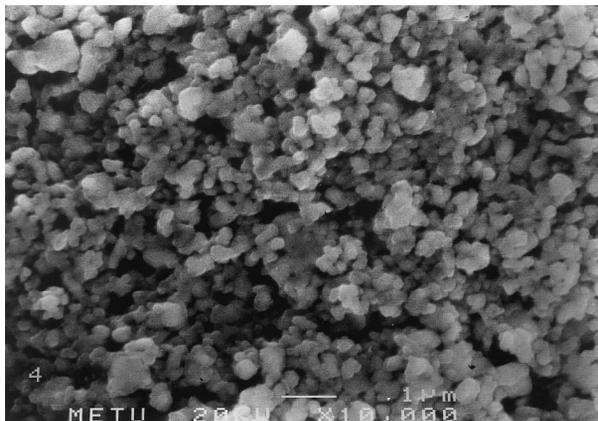
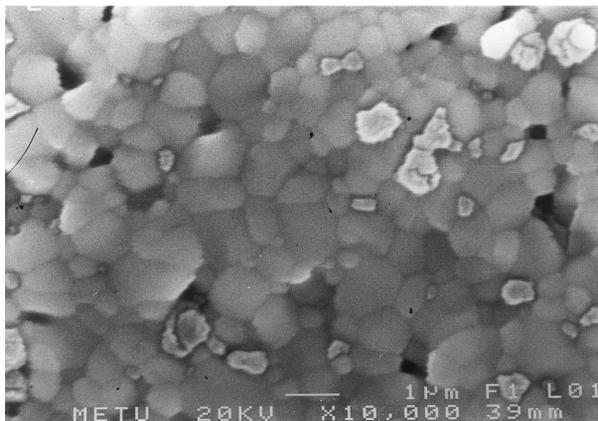


Fig. 6. 'pH' vs 'mL of cation liquor added' plot obtained during EDTA-precipitation of undoped  $\text{CaZrO}_3$  powders (Base solution: 10 M NaOH, addition rate:  $2 \text{ ml min}^{-1}$ )



(a)



(b)

Fig. 7. SEM micrographs of EDTA-precipitated powders of  $\text{CaZrO}_3$ ; (a)  $1200^\circ\text{C}$ , 12 h, loose powder compact, (b)  $1200^\circ\text{C}$ , 6 h, powders pressed into a pellet.

$a=8.0159$ ,  $b=5.7516$ ,  $c=5.5954\text{\AA}$ , with an orthorhombic [space group:  $\text{Pnma}$  (62)] unit cell of the volume of  $257.97 \text{ \AA}^3$ . A typical XRD chart of these powders is shown in Fig. 5. The insert in this figure shows the regular increase in the d-spacings of 211 planes of this orthorhombic unit cell, with increasing Gd-dopant (over the interval of 5–25 at%) levels in the phase of calcium zirconate. On the other hand, Fig. 6. shows the pH values attained during the room temperature addition of the EDTA-containing, cation ( $\text{Ca}^{2+}$  and  $\text{Zr}^{4+}$ ) liquor into the NaOH solution, at the constant addition rate of  $2 \text{ ml min}^{-1}$ .

$\text{CaZrO}_3$  powders produced by the EDTA-precipitation technique were sub-micron, as shown in the SEM micrograph given in Fig. 7a, The powders of this micrograph were heated as a loose powder compact at  $1200^\circ\text{C}$  for 12 h, in a stagnant air atmosphere. When the same powders were pressed into pellets (at 90 MPa) and then heated at  $1200^\circ\text{C}$  for 6 h, a significant degree of sintering was observed (as shown in the SEM micrograph of Fig. 7(b), with the average grain sizes still being in the micron range.

#### 4 Summary

Single-phase  $\text{CaZrO}_3$  powders were produced by two synthesis techniques. self-propagating combustion synthesis and by aqueous acid-base titration from EDTA-chelates. The EDTA-precipitation technique was also found to be suitable for the synthesis of calcia-stabilized cubic zirconia powders. Gd-doping in  $\text{CaZrO}_3$  was studied over the range of 5–25 at%, by using both of the above techniques. The EDTA-precipitated  $\text{CaZrO}_3$  powders showed significant levels of densification even after heating at the low temperature of  $1200^\circ\text{C}$  for 6 h, with the typical sintered grain sizes still being in the micron range.

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