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CHEMICAL SYNTHESIS OF PURE AND Gd-DOPED CaZrO₃ POWDERS

I. Erkin Gonenli and A. Cüneyt Tas *

Department of Metallurgical and Materials Engineering, Middle East Technical University, Ankara 06531, Turkey

ABSTRACT

Aqueous solutions of calcium chloride (CaCl₂·2H₂O) and zirconium oxychloride (ZrOCl₂·8H₂O), in appropriate volumetric amounts, were used as the starting chemicals in the synthesis of phase-pure CaZrO₃ powders. Gadolinium dopings (up to 25 at%) were performed by using the aqueous stock solutions of gadolinium chloride (GdCl₃). Preparation of CaZrO₃ powders were studied by using two different chemical synthesis routes: (i) self-propagating combustion synthesis, and (ii) precipitation in the presence of EDTA by the technique of acid-base titration. Sample characterization was achieved by powder XRD (X-ray diffraction) and SEM (scanning electron microscope).

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 [1-3], humidity and hydrogen [4-8]. 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.* [9] reported that undoped calcium zirconate (CaZrO₃) was a p-type semiconductor in air. When doped with oxides such as Al₂O₃, Y₂O₃ and MgO or with a small excess of ZrO₂ or CaO, it becomes predominantly an oxygen-ion conductor [1, 2, 7]. 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 [4, 5]. The protonic conduction, however, tends to diminish at higher temperatures and can be replaced by electronic conduction, especially in a dry air atmosphere [4]. CaZrO₃ has also been studied for its potential use as high-temperature thermistor material [8]. The electrical response of calcium zirconate (prepared by the solid state reactive firing of CaCO₃ and ZrO₂

* Present address: Max-Planck-Institute, Heisenbergstrasse 5, D-70569, Stuttgart, Germany

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powders at 1400°C) found to be sensitive to methane, but was practically unaffected by humidity and 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_3 a potential candidate material for hydrocarbon sensing.

The results of two different chemical powder preparation techniques for synthesis of fine powders of pure and Gd-doped (5–25 at%) CaZrO_3 were hereby reported. 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.

EXPERIMENTAL PROCEDURE

Starting chemicals used in this study were reagent-grade $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Riedel de Haen, Germany), $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Merck, Germany), Gd_2O_3 (+99.9%, Ames Laboratory, IA, USA), EDTA ($\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$, Merck, Germany), NaOH (Merck, Germany), and Urea ($\text{CH}_4\text{N}_2\text{O}$, Riedel de Haen, Germany). GdCl_3 stock solutions were prepared by reacting the oxide powders in a strong HCl solution of correct stoichiometry.

Two different synthesis techniques were employed to produce pure and Gd-doped calcium zirconate powders. In the first technique, i.e., "self-propagating combustion synthesis (SPCS)" [10, 11], appropriate amounts of Ca- and Zr-chloride salts (in the case of Gd-doping, proper aliquots of Gd-chloride solutions were also 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 preheated to $500 \pm 10^\circ\text{C}$. The combustion reaction was completed in less than 15 minutes 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°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 was added in a dropwise manner into a concentrated NaOH solution at room temperature. The formed precipitates were filtered, washed with distilled water, dried at 90°C , and later calcined at 1200°C for 17 h.

Phase characterization of the calcium zirconate powders were achieved by powder XRD (X-ray diffraction). The diffractometer (Rigaku Corp., Model: D/Max-B, Japan) was used with a monochromated $\text{Cu K}\alpha_1$ radiation tube, operated at 40 kV and 20 mA. The XRD data were collected at a step size of 0.02° and count time of 5 s. Powder morphology was investigated via the SEM (scanning electron microscopy; JEOL Corp., JSM-6400, Japan) micrographs.

The sintering behavior of phase pure and Gd-doped CaZrO_3 powders were 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 rate of $10^\circ\text{C}/\text{min}$) at 1200°C for 6 hours in a stagnant air atmosphere.

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 CaZrO_3 , as an alternative route of powder synthesis to that of conventional, solid-state reactive firing of CaO and ZrO_2 .

In the SPCS method, the weight ratio of chloride salts (i.e., of Ca and Zr) in the combustion solutions was found to strongly influence the final phase purity of the calcined (at 1200°C) powders. When the solutions were away from the proper stoichiometry, major impurity phases were found to be CaO -stabilized cubic zirconia or calcium oxide, depending on which cation being the excess in solution. Fig. 1 shows the influence of Ca-Zr-chloride weight ratio on phase purity in the SPCS method. The solutions given in this figure were all prepared by mixing 0.735 g of Ca-chloride in 50 mL of water with the corresponding amount (as indicated in the caption of Fig. 1) of Zr-oxychloride. 3 g of urea was then dissolved in these solutions just before placing them into the furnace. The XRD data given in Fig. 2 indicated that there is an upper limit to the level of Gd-doping in CaZrO_3 , and that limit was found to be in the range of 10 to 15 at%. Beyond that limit, free Gd_2O_3 and ZrO_2 phases were detected in the respective XRD charts.

In the acid-base titration method (in the presence of EDTA) used for CaZrO_3 powder synthesis, it was found that this technique was also suitable for the synthesis of phase-pure cubic zirconia (CSZ) powders, as shown in the XRD chart of Fig. 3 below, as well for the preparation of CaZrO_3 . For the production of CSZ powders of this study (having the Ca : Zr mole ratio of 0.145, as determined by EDXS analysis on powders calcined at 1200°C), 0.729 g of Zr-oxychloride, 0.333 g of Ca-chloride and 0.834 g of EDTA were first dissolved in 30 mL of de-ionized water at room temperature. This cation solution was then added dropwise (1 mL/min) into 140 mL of water which contained 24 g of NaOH dissolved in it. The resultant opaque solution was then ultrasonicated for 5 minutes with an ultrasonic disruptor (Model: XL2015, Misonix, NY, USA), prior to filtration. 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.

It was experimentally confirmed in this study that at the levels of 5 and 10 at% Gd-dopings, by using the EDTA-precipitation technique, the lanthanide cation goes into solid solution within the structure of CaZrO_3 . However, at the nominal level of 15at% Gd-doping, the XRD peaks for Gd_2O_3 and ZrO_2 were also observed.

Phase-pure CaZrO_3 powders prepared by the EDTA-precipitation technique had sub-micron particles, and possessed the lattice parameters of $a = 8.0159$, $b = 5.7516$, $c = 5.5954$ Å, with an orthorhombic (space group: $Pnma$ (62)) unit cell of the volume of 257.97 Å³. The ICDD powder file (35-790) already present for this phase reported the lattice parameters of $a = 8.0101$, $b = 5.7558$ and $c = 5.5929$ Å. A typical XRD chart of these powders was shown in Fig. 4. The insert in this figure showed the regular increase in the d-spacings of 211 planes of this orthorhombic unit cell, with increasing

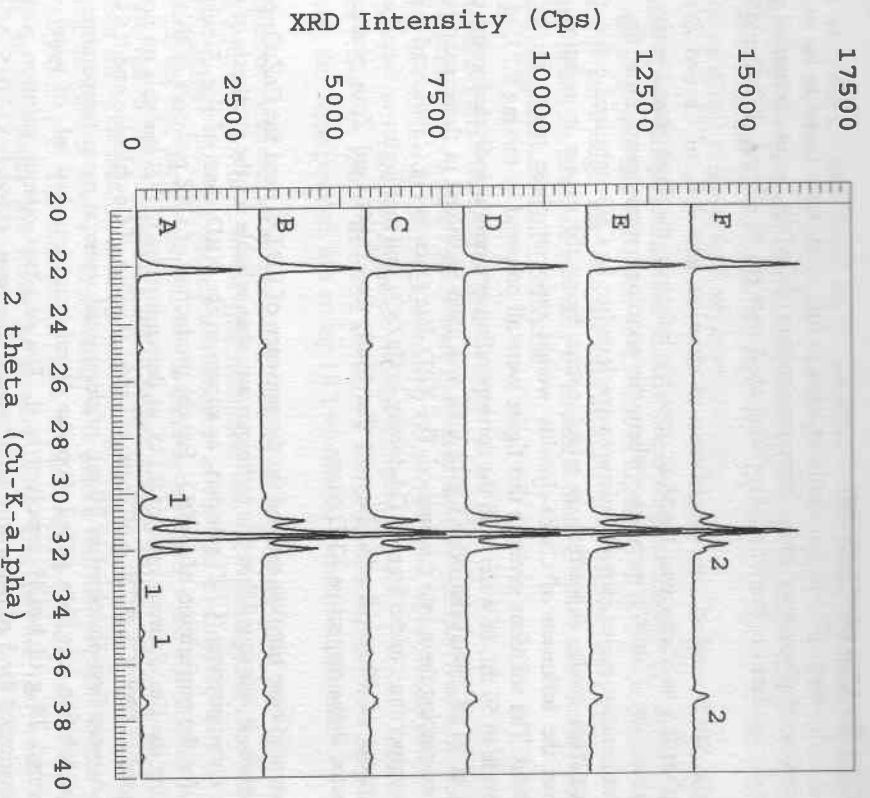


Fig. 1 XRD traces showing the effect of Ca:Zr-chloride weight ratio on the phase purity of CaZrO_3 powders produced by the SPCS method [10, 11]. (Ca:Zr-chloride weight ratios = **A** : 0.456, **B** : 0.507, **C** : 0.537, **D** : 0.553, **E** : 0.562, **F** : 0.570; (1) CSZ (ICDD PDF 26-341) and (2) CaO (ICDD PDF 37-1497)).

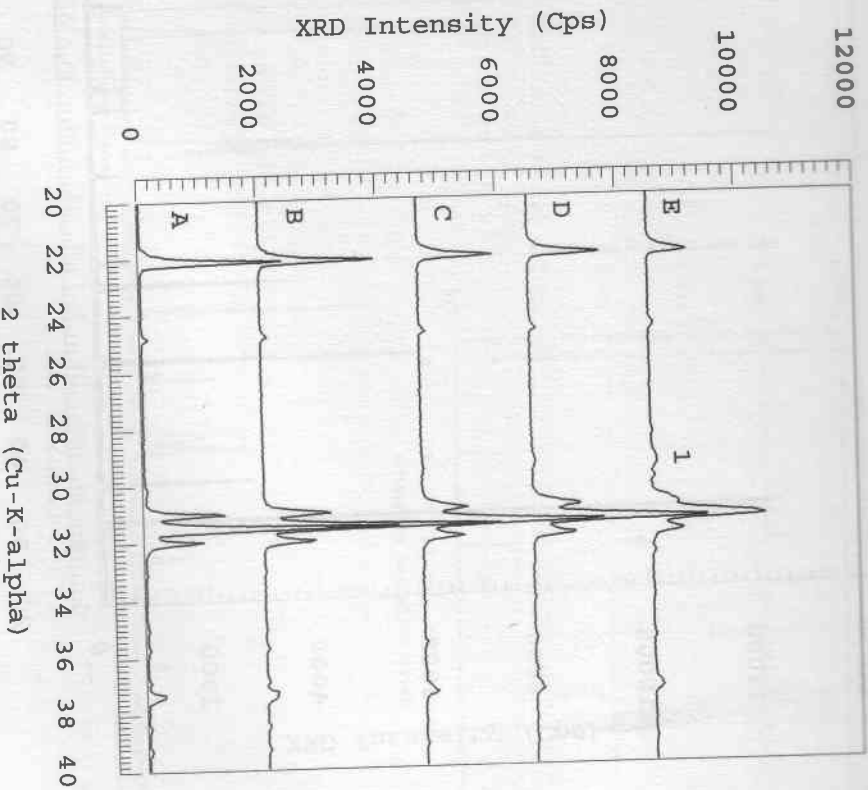


Fig. 2 XRD traces showing the effect of Gd-doping on the phase purity of CaZrO_3 powders, SPCS method (**A** = undoped, **B** = 5, **C** = 10, **D** = 15, **E** = 25 at% Gd; (1) ZrO_2 (ICDD PDF 37-31)).

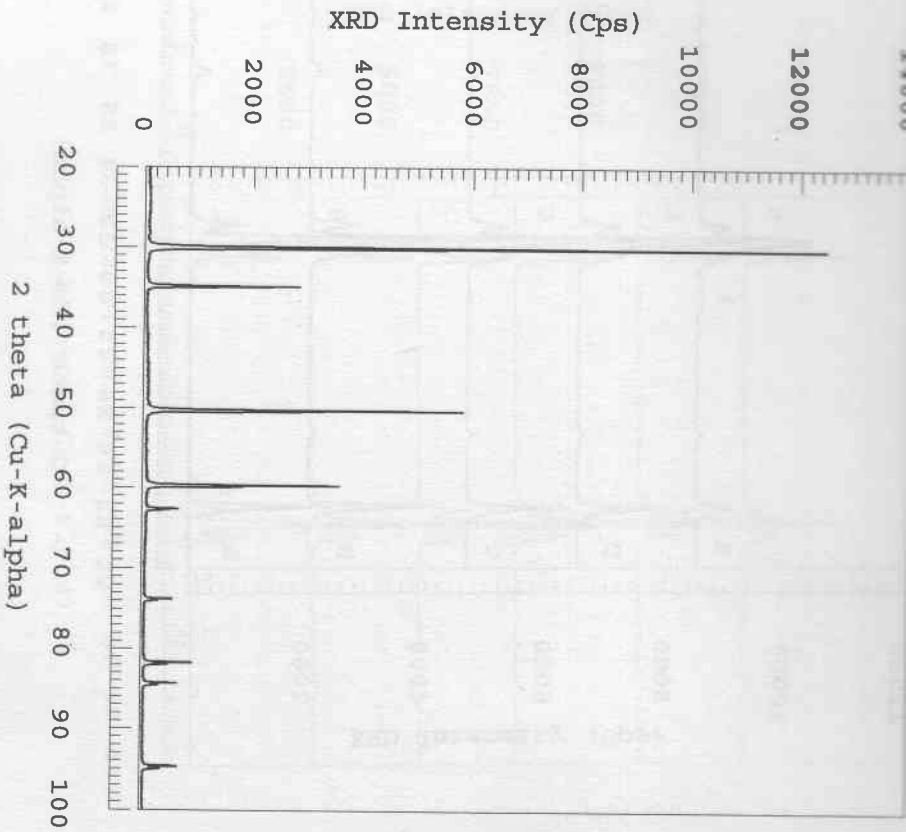


Fig. 3 A typical XRD chart of CaO-stabilized (cubic) zirconia powders synthesized by the EDTA-precipitation technique

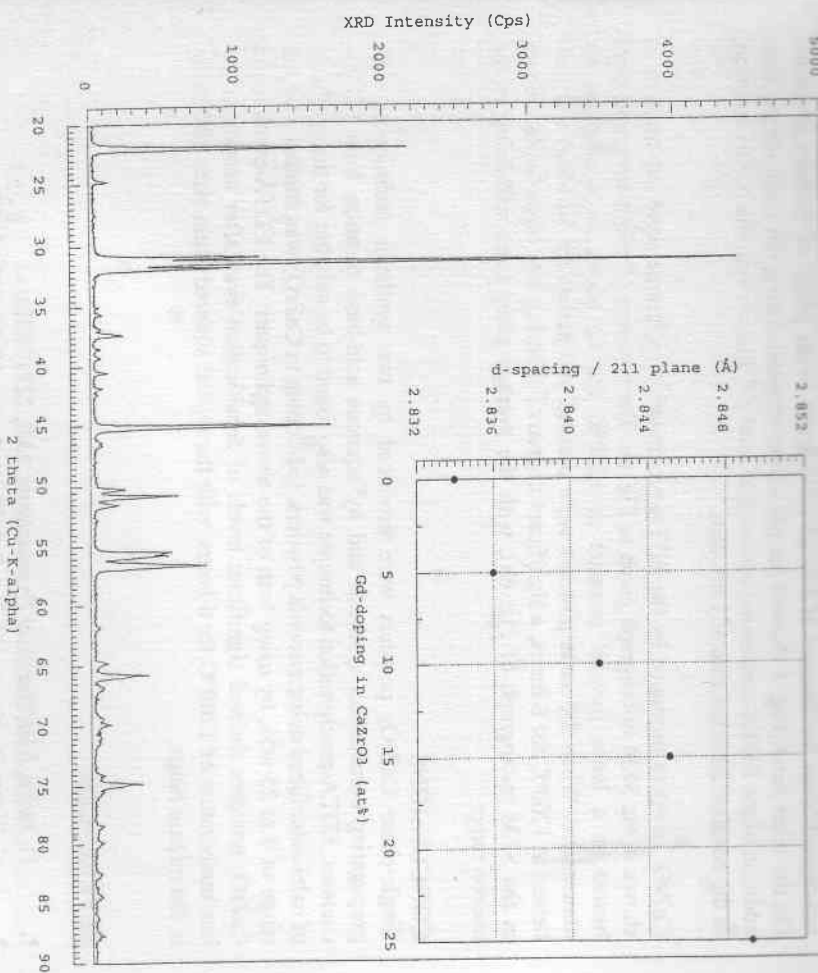


Fig. 4 A typical XRD chart of EDTA-precipitated CaZrO₃ powders (Insert: Effect of Gd-dopant concentration on the d₂₁₁ of CaZrO₃ unit cell)

Gd-dopant (over the interval of 5 to 25 at%) levels in the phase of calcium zirconate. On the other hand, Fig. 5 showed the pH values attained during the room temperature addition of the EDTA-containing cation (Ca^{2+} and Zr^{4+}) liquor into the NaOH solution, at the constant addition rate of 1 mL/min.

CaZrO_3 powders produced by the EDTA-precipitation technique were sub-micron, as shown in the SEM micrograph given in Fig. 6a. The powders of this micrograph were heated as a loose powder compact at 1200°C for 12 hours, in a stagnant air atmosphere. When the same powders were pressed into pellets (at 90 MPa) and then heated at 1200°C for 6 hours, a significant degree of sintering was observed (as shown in the SEM micrograph of Fig. 6b), with the average grain sizes still being in the micron range.

CONCLUSIONS

Single-phase CaZrO_3 powders were produced by two synthesis techniques; self-propagating combustion synthesis and by aqueous acid-base titration from EDTA-chelates. EDTA-precipitation technique was also found to be suitable for the synthesis of calcia-stabilized cubic zirconia powders. Gd-doping in CaZrO_3 was studied over the range of 5 to 25 at%, by using both of the above techniques. The EDTA-precipitated CaZrO_3 powders showed significant levels of densification even after heating at the low temperature of 1200°C for 6 hours, with the typical sintered grain sizes still being in the micron range.

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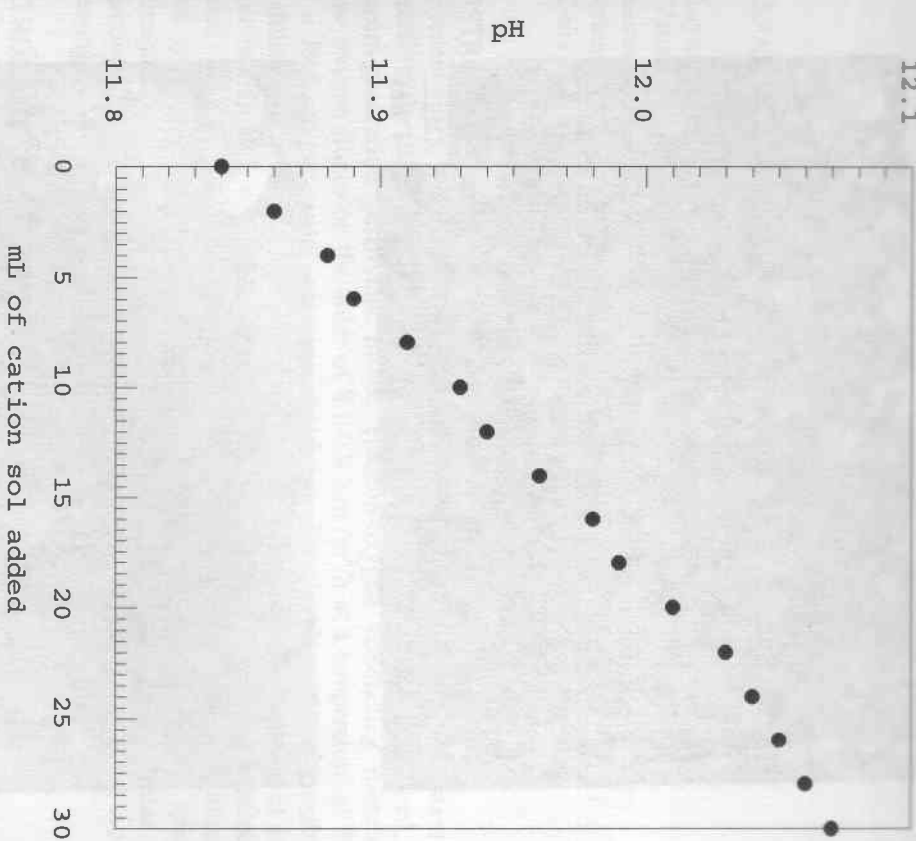


Fig. 5 pH vs mL of cation liquor added plot obtained during EDTA-precipitation of undoped CaZrO_3 powders (Base solution: 10 M NaOH, addition rate: 1 mL/min)

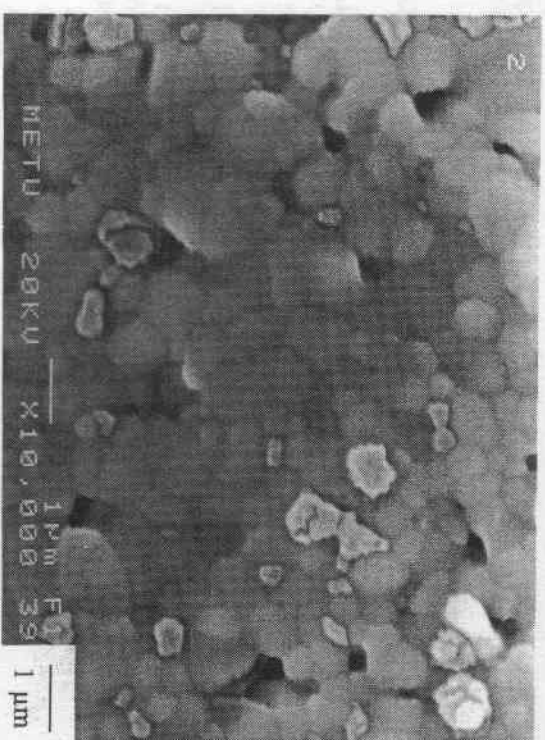
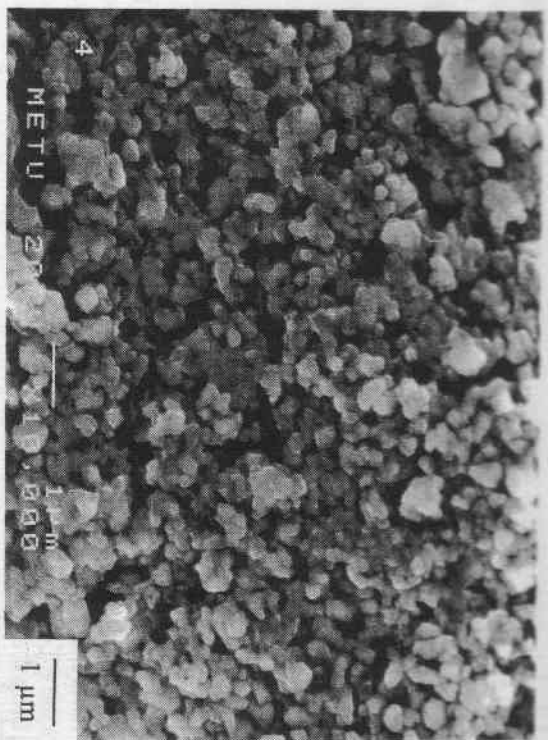


Fig. 6 SEM micrographs of EDTA-precipitated powders of CaZrO_3 : (top) 1200°C, 12 h, loose powder compact, (bottom) 1200°C, 6 h, powders pressed into a pellet.

PREPARATION OF LaSrCoFeO_{3-x} MEMBRANES

J. Luyten, A. Buekenhoudt, W. Adriansens, J. Cooymans, H. Weyten,
E. Vanswijgenhoven and R. Leysen
Vlaamse Instelling voor Technologisch Onderzoek, Materials Technology
Boerentang 200
B-2400 Mol, Belgium

ABSTRACT

In recent years, the use of oxygen in industrial processes has grown substantially. Therefore, the use of dense O_2 -conducting ceramic membranes is considered. Current-generation perovskite mixed electron-oxygen conducting membranes show oxygen fluxes on the order of 0.1-0.8 $\text{Nm}^3/\text{m}^2/\text{h}$ at a temperature of 850°C for a feed oxygen partial pressure of 0.2 bar. The development of membranes modules with a higher (membrane surface)/(module volume) ratio or of multi-layer membranes with a dense skin will allow more commercially interesting fluxes. With this in mind, dense hollow fibers and porous multi-layer substrates were synthesised. The hollow fibers were produced using a polymeric spinning technique based on phase inversion. The multi-layer porous substrates were manufactured following conventional ceramic processing routes as cold isostatic pressing and tape casting.

INTRODUCTION

In recent years, the use of oxygen in industrial processes has grown substantially [1,2]. Many oxidation processes, originally using air, have switched to oxygen because of an accompanying increase in efficiency and overall performance. More processes are expected to do so as oxygen production technology advances and the related production and delivery cost decrease.

Oxygen is produced in large-scale plants by cryogenic distillation or by vacuum or pressure swing adsorption. These production methods are cost-efficient at high production volumes. At small and intermediate capacities, for which flexibility of operation is desired, the use of oxygen permeating polymeric or ceramic membranes is economically more promising. Furthermore, on-site production with membrane technology will substantially reduce transport of oxygen from producer to user, reducing related costs and pollution. Polymeric membranes are currently used for the on-site production of oxygen with a

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