

## Synthesis of ZrO<sub>2</sub>-Based Ceramics for Applications in SOFC

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**Abstract.** A process for synthesis of ZrO<sub>2</sub> based ceramics by coprecipitation, for application in solid oxide fuel cell is described. Precursors preparation, precipitate treatment by azeotropic distillation and ceramic processing are also presented. Zirconia powders containing 3 and 9 mol% of Y<sub>2</sub>O<sub>3</sub> and other additives such as TiO<sub>2</sub> were prepared, pressed by uniaxial compaction and sintered at 1500°C for one hour. The apparent densities of the pellets produced were determined by an immersion technique based on the Archimedes principles. Ceramics crystal structure was verified by X-ray diffraction, their microstructure was observed by scanning electron microscopy. The chemical composition was analyzed by energy dispersive spectroscopy. The results showed that the ceramic bodies are dense with fine grains and the titania addition causes grain growth and, above the solubility limit, a formation of a second phase.

### Introduction

Zirconia based ceramics are well known to possess excellent mechanical and electrical properties [1]. This combination of properties allows their use in a great variety of applications. When stabilized with proper amounts of additives, as 9mol% Y<sub>2</sub>O<sub>3</sub> to form a cubic fluorite structure, can be used as solid electrolyte in electrochemical devices as oxygen sensors and fuel cells. Fuel cells are a high efficiency energy conversion devices that produces electricity directly from fuels by electrochemical reactions [2] and as its component, zirconia is used in electrolytes and anodes. In this latter application, can be used in two different compounds, the YSZ-Ni composite [3] and ceramics in the system ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> that exhibits mixed ionic and electronic conduction [4].

To attain better performance in these materials, various factors, as chemical composition, grain size, microstructure, crystal phase, porosity and purity of sample, have to be controlled [5], during the ceramic powder preparation. Chemical routes using techniques as coprecipitation, sol-gel, citrates and others are suitable for this purpose, and the first was adopted in this work because it does not need expensive chemicals and are composed by simple operations [6]. The use starting solutions of common salts and yttria concentrates substituting pure yttrium salts can lower the costs of these ceramics [7].

This work presents the development of a coprecipitation process for the synthesis of ceramics of zirconia-yttria and zirconia-yttria-titania, for application in solid oxide fuel cells. The preparation of the solutions of the metal salts was done using procedures previously developed in Ipen/Brazil, for zirconia and yttria solutions and for titania solution, a process of preparation was investigated.

### Experimental procedure

Zirconium salts solutions were prepared from compounds produced in a pilot plant in our institute (IPEN). The process includes the opening of the zirconium ore (zircon), that is a zirconium orthosilicate by alkaline fusion with sodium hydroxide, and purifying by a process that includes silica elimination by gelation, basic sulphate precipitation and conversion to zirconium hydroxide or zirconium basic carbonate (99.9%  $ZrO_2 + HfO_2$ ). Two yttrium solutions were used, one from yttrium oxide (Aldrich - 99.99%  $Y_2O_3$ ), and a concentrate with 85%  $Y_2O_3$  produced in our laboratories through a solvent extraction process from a solution of heavy rare earths produced from monazite (NUCLEMON). Other elements in the concentrate are mainly Dy, Ho, Er, Yb and Tb. Titanium solutions were produced by an alkali titanate conversion process [8], from a commercial titanium oxide (99.99%  $TiO_2$ ). A schematic diagram of the processes described above is presented in fig. 1.

A coprecipitation procedure, based on chloride process was developed in our laboratories, where mixture of the solutions in the desired proportions is poured into an ammonium hydroxide solution under stirring. The pH is maintained as high as possible during the whole process to ensure the reaction of all metal ions. The precipitates formed are filtered and washed several times with water to remove the chloride ions. Washing with organic solvents and azeotropic distillation with n-butanol is then used to eliminate the remaining water that can cause a formation of hard agglomerates [9,10]. The powder is then dried at 80°C for 24 hours, calcinated at 800°C for one hour and milled with zirconia balls.

Two sets of samples were prepared, with 3mol% and 9mol% of yttria, and to these was added 5, 10, 15 and 20mol% titania. Samples were identified as  $Zy_nTi_m$  where n and m are the yttria and titania concentration, for example, ZY3T5 is a sample with 3mol% yttria and 5mol% titania. Zirconia-yttria samples were prepared both by pure (ZY3p and ZY9p) and the concentrates produced by solvent extraction (ZY3c and ZY9c).

Powders characterization was done by  $N_2$  gas adsorption for surface area measurements (BET), laser diffraction for particle size distribution, scanning electron microscopy for powder observation and X-ray diffraction for crystal structure observations. The powders were uniaxially pressed at 100MPa to cylindrical pellets and sintered at 1500°C for 1 hour. Ceramic bodies densities were determined by an immersion technique based on the Archimedes principle, fractured and thermally etched surfaces of the ceramics were observed by scanning electron microscopy and chemical composition of the observed phases was analyzed by energy dispersive spectroscopy.

### Results

Particle size measurements showed that the powders have a mean size of about 1.5  $\mu m$  and BET analysis resulted in surface area between 46.9 and 70.1  $m^2 \cdot g^{-1}$ . Fig. 2 shows the observed X-ray patterns of a series of samples containing 3mol% yttria varying titania content where tetragonal/cubic phase are predominant and ZY3 sample shows low intensity peaks of monoclinic phase. The influence of titania addition is not clear in the patterns and similar behavior are presented by samples with 9mol% yttria.

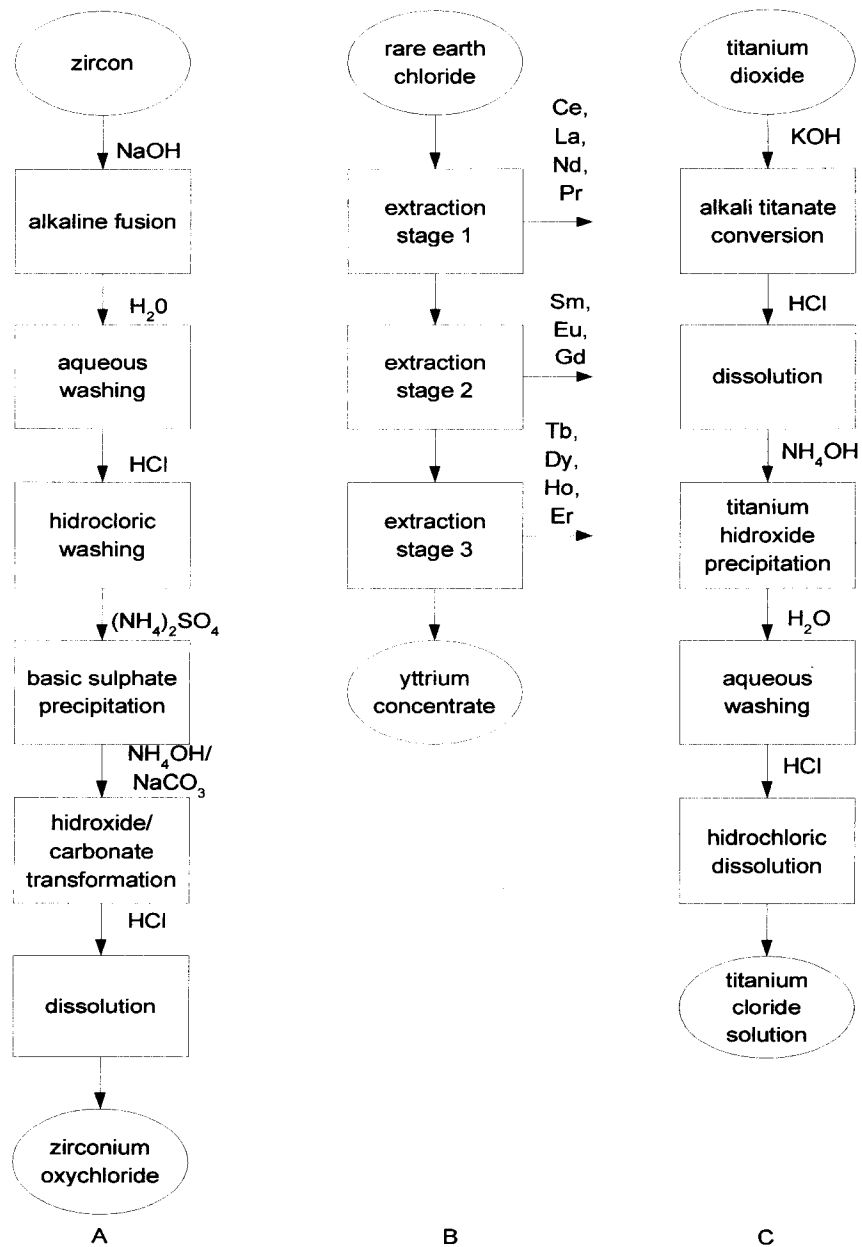


Fig. 1. Schematic diagram for the preparations of zirconium oxychloride solutions, (A), yttrium chloride solutions (B) and titanium chloride solution (C).

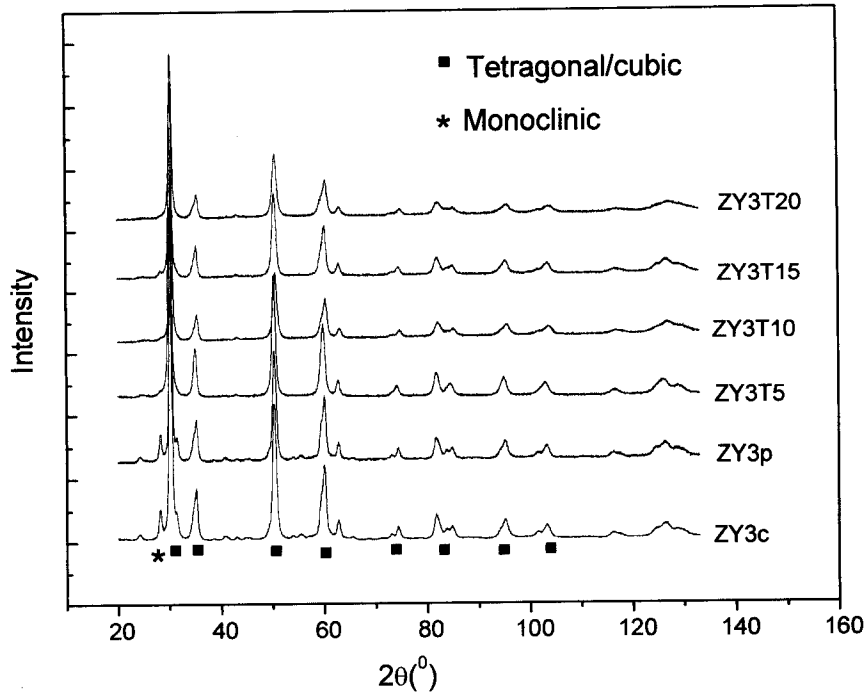


Fig. 2. X-ray diffraction patterns of samples containing 3 mol%  $Y_2O_3$ .

Fig. 3 presents SEM micrographs of samples ZY3T5 (a) and ZY3c (b). Small particles show strong tendency to group each other forming agglomerates. The presence of additives or the impurities contained in yttria concentrates does not seem to cause significant alteration on the powder morphology.

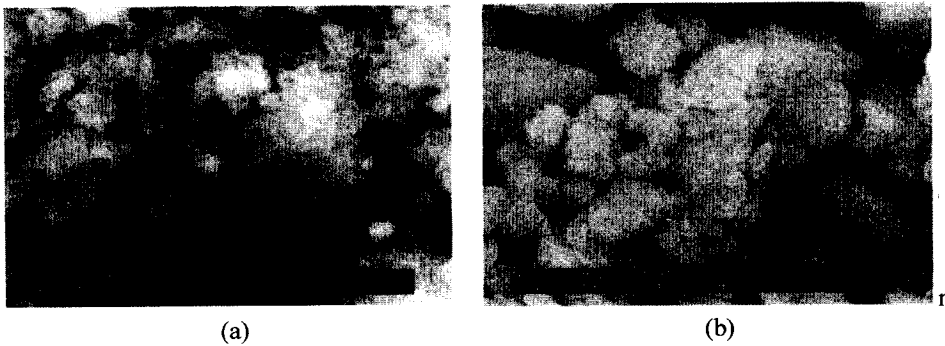


Fig. 3. SEM micrographs of the powders ZY3T5 (a) and ZY3c (b).

Density values of sintered pellets are between 5,60 and 5,97 g.cm<sup>-3</sup>. The results indicate that density has a tendency to decrease with increasing of titania content.

The microstructure of the ceramics changes with the increasing titania concentration. In samples containing 3mol% Y<sub>2</sub>O<sub>3</sub>, the grain size and intragranular fracture increases, while with 9mol% Y<sub>2</sub>O<sub>3</sub>, grains size decrease and fracture mode turns to be similar to 3mol% Y<sub>2</sub>O<sub>3</sub> with titania. Fig. 4 presents the fracture surface of ZY3 sample (a) with small grains and intergranular fracture and ZY3T10 sample (b) with larger grains exhibiting the two fracture modes.

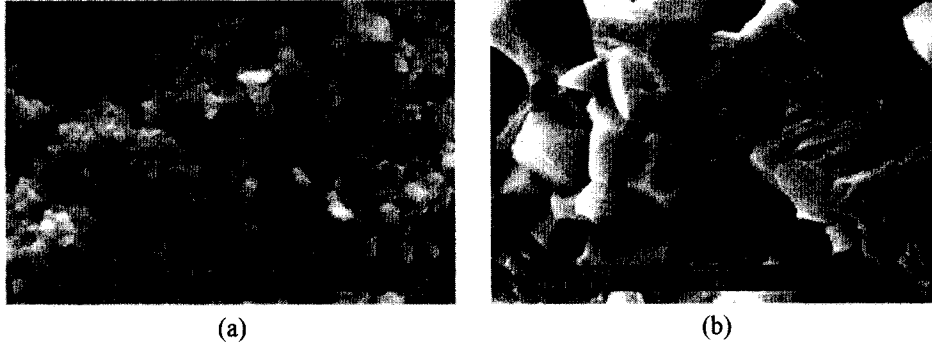


Fig. 04. Sem micrographs of fracture surfaces of samples ZY3(a) and ZY3T10(b).

SEM micrographs of polished and thermally etched ceramic surfaces confirm the microstructure change and show the formation of a new phase when the titania solubility limit is surpassed. Fig. 05 presents an example of a usual ZY3 ceramic surface with small grains (a) and a ZY9T20 sample with larger grains (b) where the second phase can be seen. Both samples present low porosity

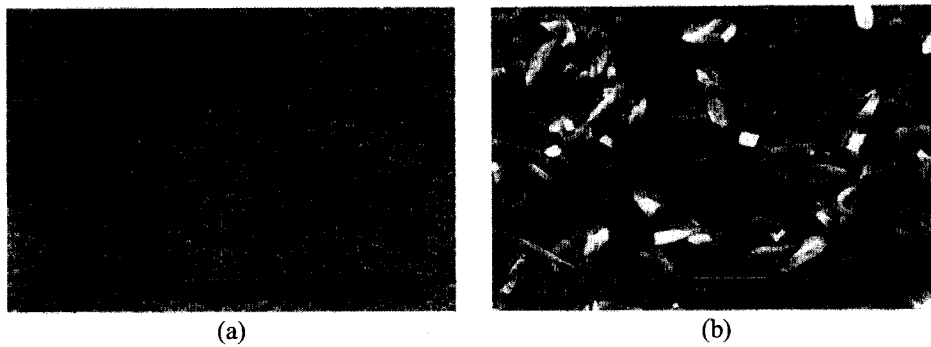


Fig. 05. SEM micrographs of surfaces of polished and thermally etched ZY3(a) and ZY9T20(b) samples.

Chemical composition analysis of the samples with second phase showed that this phase is a compound of titanium and zirconium that has a titanium concentration higher than in the continuous phase.

### Conclusion

Preparation methods of starting materials and the coprecipitation route were established. Zirconium and titanium solutions can be produced using simple laboratory apparatus, but the production yttrium concentrates needs much more complex procedures. The preparation process adopted in this paper results in yttria doped zirconia ceramics of high density and a microstructure showing small grains and low porosity. Titania addition on the zirconia-yttria causes change in microstructure and a formation of a second phase of zirconia with titania concentration higher than in the continuous phase. The use of yttria concentrates instead of pure oxides to lower the starting materials cost does not results in ceramics with significantly different properties

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## **Synthesis of ZrO<sub>2</sub>-Based Ceramics for Applications in SOFC**

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