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Characterization of Zirconia-India Ceramics Sintered by Spark Plasma

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We present the synthesis and characterization of ZrO_2:*x* mol% In_2O_3 ceramics with *x* = 8, 10 and 12. Sintering has been achieved with spark plasma sintering which allows for higher densification (~ 97% of theoretical density). The powders were characterized by thermal analyses, scanning electron microscopy, and x-ray diffraction. The electrical properties of the sintered samples were studied by electrochemical impedance spectroscopy as a function of dopant concentration *x* and temperature. The spark plasma sintering is effective to sinter the ZrO_2–In_2O_3 nanoparticles, and samples with *x* = 8 were found to be pure ionic conductor at temperatures above ~ 300°C.

Introduction

Advanced ceramics based on zirconia (ZrO_2) are very complex materials with remarkable properties and are employed in a wide range of technological applications, more often in electrochemical devices like sensors and fuel cells. Of particular interest is the Solid Oxide Fuel Cell (SOFC), where YSZ (Yttria-Stabilized Zirconia) is often used as electrolyte, since it has high ionic conductivity properties at high temperatures (from about 700°C to 1000°C, depending on the specific material). Lowering the operating temperature range to intermediate temperatures can significantly reduce the cost and improve SOFC reliability and lifetime. Although YSZ is considered to be the most reliable electrolyte in terms of structural and thermodynamic stability, its lower ionic conductivity in intermediate temperatures restricts SOFC usage to high temperatures (1).

The versatility of zirconia ceramics, including its capability of ionic conductivity, originates from the creation of atomic defects in the zirconia crystal. If aliovalent oxides are added to ZrO_2, anion (oxygen) vacancies may charge balance these substitutional cations, thus giving rise to the ionic conductivity. These defects and their mutual interactions not only are responsible for the materials high ionic conductivity in certain conditions, but also affect structural, thermal, mechanical, and electrical properties altogether. Also, zirconia has a big band gap so electronic conductivity is low at relatively low temperatures, which makes it the best candidate for making fuel cell electrolytes.

Pure zirconia ZrO_2 is stable only for very high temperatures (> 2600 K). Below this temperature, this cubic phase transforms to a tetragonal form. A further structural change occurs on cooling below 1370 K, when the phase becomes monoclinic baddelyite-structured. It is well known that the addition of suitable divalent (Ca^{2+}, Mg^{2+}, etc) and trivalent (Y^{3+}, Sc^{3+}, Nd^{3+}, etc) cation species can stabilize the two high temperature forms under lower temperatures (2).

Also, ionic conductivity increases monotonically with dopant concentration until a maximum in some critical dopant concentration (typically 8–12 mol%) from which ionic conductivity decreases on both sides. Concerning the temperature dependence, the ionic dc conductivity may be expressed by a well-known Arrhenius relationship (3), where the parameters are a pre-exponential factor and the activation energy for oxygen diffusion *H*, such that at a constant temperature a material with maximum pre-exponential factor and minimum *H* will show the highest grain ionic conductivity.

Bogicevic *et al.* (4) studied defect ordering in aliovalently doped cubic-stabilized zirconia (with divalent and trivalent oxides) using gradient corrected density-functional calculations and were able to directly link (thermodynamic) defect ordering to (kinetic) ionic conductivity in cubic-stabilized zirconia using first-principles atomistic calculations. They showed that anion vacancies in general prefer to be closer to the smaller of the two cations between Zr or the dopant. With dopant ions similar in size to Zr^{4+}, like is the case of In^{3+}, vacancies show little preference, and thus are less likely to be bound to any specific cation sites as the vacancies traverse the material, thus increasing its conductivity. Their calculations point to In_2O_3 as a particularly promising stabilizer for high ionic conductivity. Experimentally, Gauckler and Sasaki (5,6) have investigated ionic conductivities of materials of the system ZrO_2- In_2O_3 as functions of dopant concentration, temperature and oxygen partial pressure, and found the highest ionic conductivity at 1000°C at 25 mol% $InO_{1.5}$.

In this paper we investigate the structure (XRD, SEM) and electrical conductivity of ZrO_2- In_2O_3 sintered with the technique known as SPS (Spark Plasma Sintering). As extensively described in the literature (7-9), SPS is often used to sinter materials to very near the full theoretical density. With the new insight on the zirconia based systems provided by the theoretical calculations in (4) and stimulated by the previous works of Gauckler and Sasaki (5,6), our aim is to improve ionic conduction and enable low-temperature operation of zirconia-based electrolytes.

Experimental

Nanocrystalline ZrO_2:*x* mol% In_2O_3 (with x = 8, 10 and 12) powders were prepared by co precipitation of zirconium base carbonate ($Zr(OH)_2CO_3 \cdot ZrO_2$) and indium nitrate ($In_2(NO_3)_3$). HNO_3 was added in a continuously stirred bath of the mixed solution (zirconium base carbonate and indium nitrate) for 2 hours at 100°C in the proper stoichiometry to achieve ZrO_2:*x* mol %In_2O_3 powders. Thermal analysis was performed after mixing to verify the temperature of the desired reactions (nitrates decomposition and oxide formation). The precipitates were then submitted to heat treatment at 500°C for 1 h. The powder particle size was estimated using Scanning Electron Microscopy (SEM), and the present phases were investigated using X-Ray Diffraction (XRD).

Densification of the samples was provided by Spark Plasma Sintering (SPS), at a rate of 200°C per minute, up to 1050°C with a 5 minutes dwell. Finally, electrical conductivity data was obtained for the samples (with x = 8, 10 and 12) at several temperatures, and 3 different oxygen partial pressure, using Electrochemical Impedance Spectroscopy (EIS). A schematic drawing of the experimental procedures could be found in Figure 1.

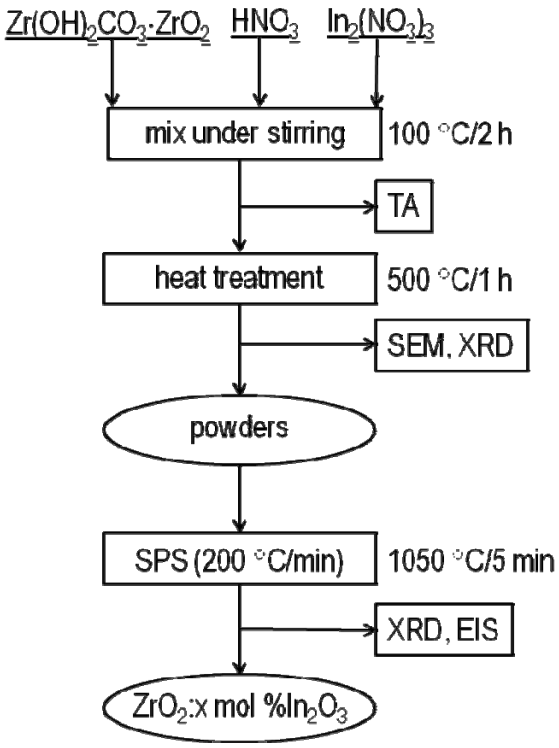

Figure 1. Schematic drawing of the experimental procedure.

Results and Discussion

Thermal analysis (Figure 2) reveals pronounced sample weight loss at about 275°C, due to the decomposition of nitrogen. Subsequent sample weight stabilization at 500°C and above was observed. All samples present similar behavior. Figure 3 shows the SEM analysis of the powders and reveals nanoparticles with size of about 50 nm.

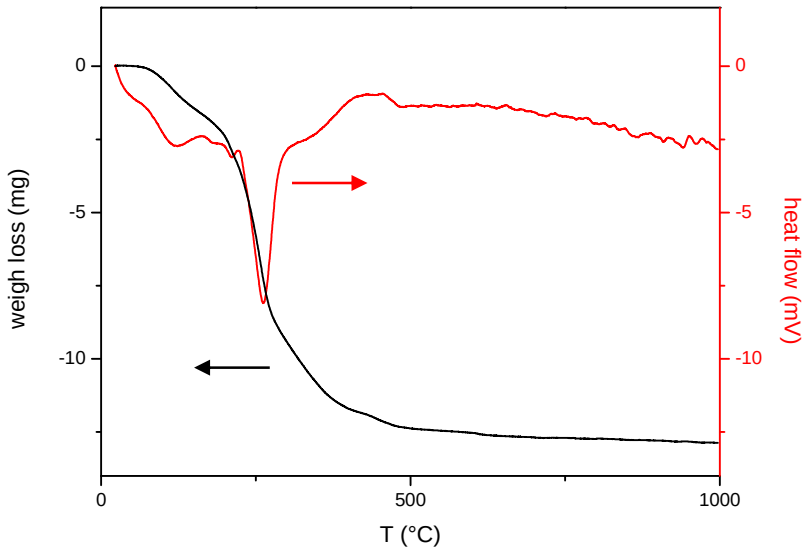

Figure 2. Thermogravimetry (left) and Differential Thermal Analysis (right) of the ZrO_2:12 mol% In_2O_3 sample powder.

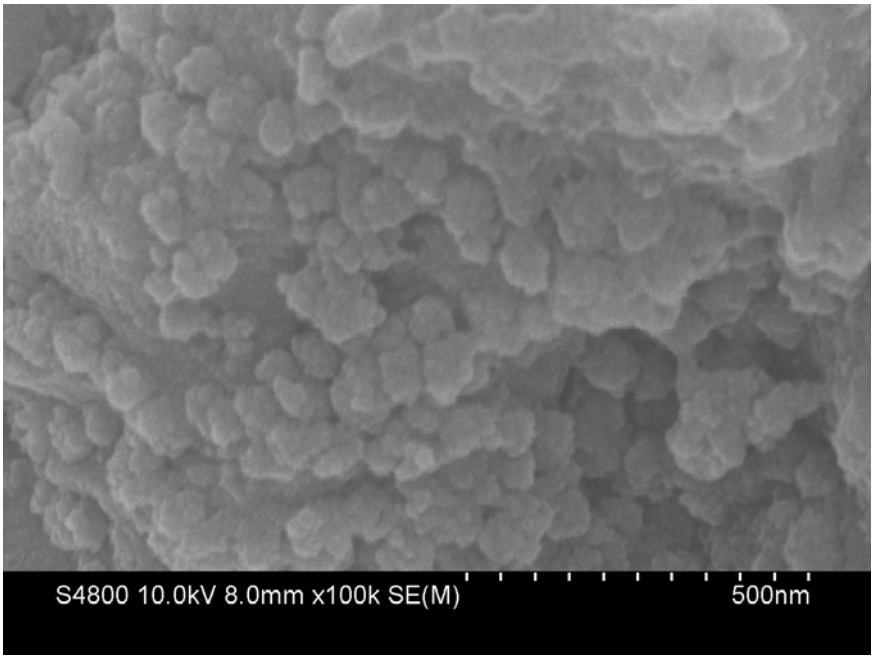

Figure 3. SEM image of the ZrO_2:8 mol %In_2O_3, revealing that the powder is constituted of nanoparticles of approximately 50 nm.

Surprisingly, the XRD results for all samples reveal the stabilization of the cubic phase just after a simple heat treatment at 500 C/1 h. In Figure 4 we show an example of this feature using the ZrO_2:10 mol %In_2O_3 sample.

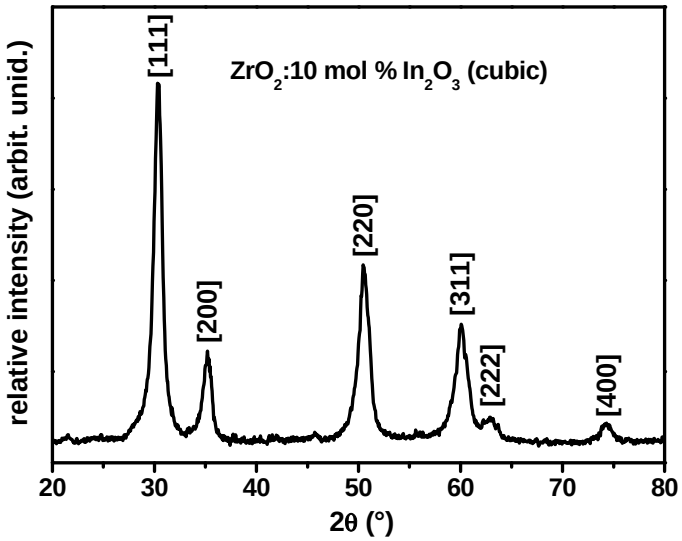

Figure 4. XRD pattern of the ZrO_2:10 mol% In_2O_3, the Miller indexes referred to the cubic phase of zirconia.

The linear retraction measured during SPS experiments show that samples achieve 97% of the theoretical density after 300 s at 1050°C.

The Arrhenius plot (Figure 5) shows dc conductivity for the samples (with x = 8, 10 and 12) at several temperatures and their activation energies. At high temperatures the samples with x = 10 and 12 present activation energy compatible with mixed, ionic and

electronic, conduction. However, the sample with x = 8 present activation energy of a pure oxygen conductor, this result were preliminary confirmed by impedance measurements under different partial oxygen pressures (not showed).

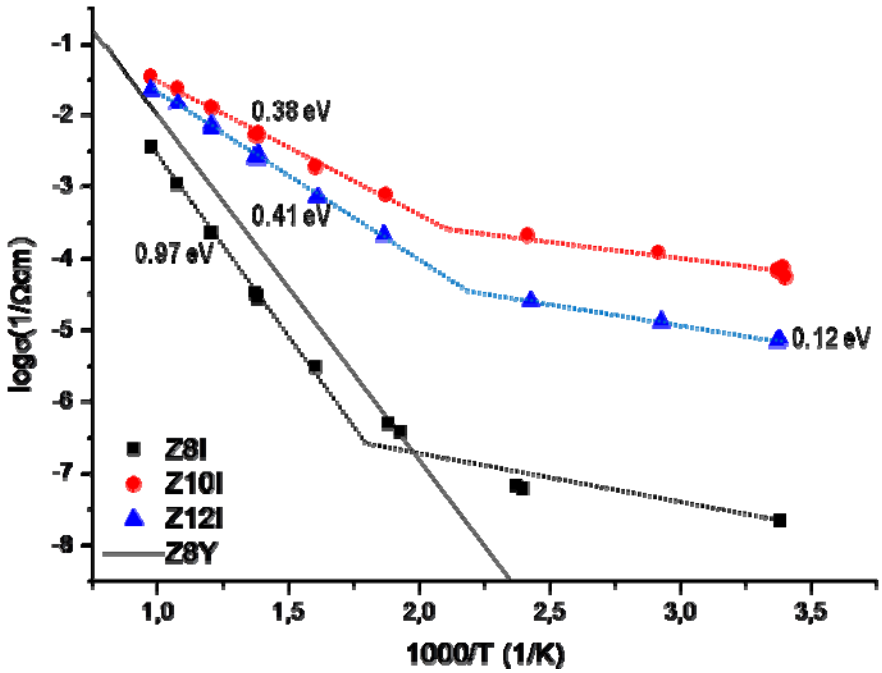

Figure 5. Arrhenius plots of the ZrO_2: x mol% In_2O_3 (x = 8, 10 and 12) samples.

Conclusions

We have synthesized ZrO_2:x mol% In_2O_3 ceramics with x = 8, 10 and 12 via carbonate and nitrate decomposition and spark plasma sintering. The method is suitable to produce small (nano) particles and stabilize the zirconia doped india cubic phase at very low temperature. Furthermore, the sample with x = 8 looks like a pure ionic conductor at temperatures higher than ~ 300°C.

Future work plans include the production of samples co-doped with other aliovalent oxides, and more precise measurements of the structure of these samples using X-Ray Fluorescence (XRF), High-Temperature X-Ray Diffraction (HTXRD) and FEG-SEM.

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