Research Article

Understanding the High Ionic Conductivity in Nanostructured Ytterbium Stabilized Zirconia Thin Films

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Abstract

Recently, high ionic conduction has been reported in nanostructured materials. This increase in conductivity can be important in technological applications, including micro-Solid Oxide Fuel Cells, so the understanding of this phenomenon is essential. In this work, XRD, Raman spectroscopy, SEM, EDS maps, and UV-Visible spectroscopy measurements are used to have an insight into the relationship between structural and electrical properties in nanostructured ytterbium stabilized zirconia (YbSZ) thin films prepared by ultrasonic spray pyrolysis. Raman measurements allowed the identification of a mixture of tetragonal and cubic phases at 4% of Yb doping, which cannot be detected by XRD, while the compositional maps suggest that Yb can be located preferentially in the grain boundaries. Changes in the activation energy values in bulk and grain boundaries are related to the small grain sizes (≤10 nm). UV measurements support the ionic nature of the charge transport. These results indicate that the high conductivity is a consequence of different physical parameters in the films such as stress in the materials, different crystalline phases, impurities diffusion to the grain boundaries, and the presence or absence of electronic conduction. A model that explains the increase of conductivity in nanostructured materials must include all these aspects.

1. Introduction

The search for clean and renewable energy sources is imperative today. Solid Oxide Fuel Cell (SOFC) technology has a substantial potential for application in clean and efficient electric power generation. A SOFC is an electrochemical conversion device that produces electricity directly from oxidizing hydrogen (a zero-emission fuel) at temperatures that can be as high as 1000°C. This high temperature is essentially due to the low ionic conductivity of solid electrolytes at lower temperatures. There is significant interest in decreasing the SOFC operating temperature to an intermediate range to improve chemical and mechanical stability and reduce the cost, increasing its competitiveness [1]. Enhancing the ionic transport in the electrolyte and cathode materials is a key factor for this purpose. Recently, it has been demonstrated that nanostructured materials and nanoscale heterolayered oxides show increased transport properties, which reinforces their potential as electrolytes in SOFC [2–6]. But the physical basis of this phenomenon is not fully understood yet [7–11].

Yttrium stabilized zirconia (YSZ) has long been used as electrolyte in Solid Oxide Fuel Cells. The specific grain boundary conductivity in polycrystalline electrolytes is usually at least two orders of magnitude lower than that of the grain bulk, leading to a blocking effect of oxygen ion transport as well as lower ionic conductivities at low temperatures. In order to improve the conductivity in grain boundaries, the optimization of synthesis processes for such materials is of great importance. During the last years, considerable attention has been focused on the deposition of smooth, homogeneous, and dense nanostructured thin films of YSZ for μ-SOFC applications [1–3, 12–14]. However, it is known
that there are other rare earth dopants that can be used to stabilize zirconia with better electrical performance, in particular, Yb [15]. A lot of previous works have been devoted to studying the properties of bulk ytterbia stabilized zirconia [16–18]; however nanostructured thin films of this material have been little explored as electrolyte for applications in μ-SOFC.

Among the varieties of deposition processes available to prepare ytterbium stabilized zirconia (YbSZ) thin films, the spray pyrolysis techniques are very attractive for industrial applications since they allow the deposition of a wide variety of ceramic films over large areas with a simple process at low costs. In particular, ultrasonic spray deposition (USD) can generate a small and homogeneous droplet size which results in high quality films. Among other benefits, it also offers the possibility to dope thin films just by adding a salt containing the dopant atom to the spray solution precursor. This technique was originally used for production of nanometer-sized powders [20]. However, it can also be optimized to obtain thin films with nanometric grain size [3, 4].

In a previous work, we prepared nanostructured YbSZ thin films with high ionic conduction [5]. Since grain boundaries are the limiting factor in the conductivity of polycrystalline materials and nanostructured materials increase considerably the amount of grain boundaries, this is a contradictory result without explanation. While transport mechanisms in bulk materials are well understood, interfacial transport mechanisms in these materials are still a promising research field. In order to contribute to the understanding of the physical basis behind the increased ionic conductivity in these nanomaterials, in this work we focus on the morphology, compositional homogeneity, and optical band gap of nanostructured YbSZ thin films in order to gain insights to explain the unique electrical properties of these materials.

2. Materials and Methods

The experimental setup shown in García-Sánchez et al. [3] was used. Both (100) n-type, 200Ω⋅cm single crystalline silicon slices and Corning glass were used as substrates. The precursor solution was prepared by dissolving calculated mixtures of zirconium (IV) acetylacetonate (98%) and ytterbium acetate tetrahydrate (99.9%) from Sigma-Aldrich Chemicals in anhydrous methanol (Fisher 99.9%). Different ytterbium/zirconium molar ratios (between 0.04 and 0.12 mol percent) were used, the substrate temperature was fixed at 550°C, and the carrier and director gas flow rates were 1.5 L/min and 3.5 L/min, respectively. More details were reported in [5]. Thermal annealing at 700°C was performed to all the samples in order to improve the crystallinity and avoid the presence of organic residues from precursors.

Surface morphology and energy dispersive X-ray analyses were performed with a field-emission scanning electron microscope JEOL-7600F at 1kV and 15kV, respectively. The samples were observed in planar view without any further preparation, using low voltages to avoid surface charging. X-ray diffraction patterns were obtained with a Rigaku DMAX 2200 equipment using the CuKα wavelength, the XRD spectra were obtained for theta angles from 2° to 70° with steps of 0.020°. The unit cell parameters were calculated using the Celref3 program.

The Raman spectra were recorded using a T64000 Jobin-Yvon Horiba triple monochromator using a microscope objective ×100. The excitation source was the 514.5 nm line from an Ar+ Lexecel laser. All measurements were performed at room temperature in open air. The sample was irradiated at a power of 20 mW at the laser head. Ten accumulations with an integration time of 1 min were performed on each sample in the range 10–1200 cm⁻¹. The Raman signal was detected by a cooled CCD. Transmittance measurements were recorded in a UV-Vis spectrometer Jasco V-630 in a two-beam configuration. The optical band gap was calculated by the Tauc model from the UV-Vis transmission data.

AC conductivity was measured using a frequency-response analyzer (SOLARTRON SI 1260 with dielectric interface) in the frequency range 0.01 Hz–10 MHz to investigate the electrical properties for temperatures between 100 and 450°C. A parallel pattern of two platinum electrodes was sputtered on the film surface to be used as electrodes. Impedance diagrams were simulated, using the Zview program, by a series network of two subcircuits, each one consisting of one resistor and one Constant Phase Element (CPE) in parallel, as detailed in our previous work [5].

3. Results and Discussion

Figure 1 presents the XRD pattern for the film grown with 4% of ytterbium. In the same figure the theoretical peaks corresponding to tetragonal (JCPDS file number 017-0923) and cubic (JCPDS file number 013-0307) zirconia phases are presented [5]. It is noteworthy that the XRD signals corresponding to these two phases are overlapped. Three crystalline phases are reported in stabilized zirconia: monoclinic, tetragonal, and cubic. The cubic phase is the most stable one and it is usually assumed to be present in the XRD pattern. But other phases have been reported in nanometric zirconia thin films or for low dopant concentrations [15, 19–22]. The solid solution is substitutional where the Yb³⁺ ions occupy the Zr⁴⁺ ion sites, creating oxygen vacancies (inset of Figure 1). The presence of different crystalline structures is associated with the differences in cation sizes, along with the possible ordering of Yb³⁺ ions and, consequently, the oxygen vacancies. As the ionic conduction depends directly on the vacancies distribution, precise phase identification is important to analyze the conduction mechanisms in these materials. But this precise phase identification is very difficult by XRD.

Raman measurements were performed in order to clarify the identity of the crystalline phases in these films (Figure 2). The Raman spectra of oxide ceramics typically contain a large amount of information, extracted from the band positions, their intensities, and their shapes. The spectra of the tetragonal, cubic, and monoclinic phases of zirconia are sufficiently different to enable a qualitative analysis [23]. Each structure exhibits specific features that can be assigned to an actual spectral signature of the studied phases. In Table 1 we show all the peaks reported for the different
Figure 1: XRD pattern of the film grown with 4% of ytterbium. The theoretical reflections of the cubic (red) and tetragonal (green) phases in YbSZ are presented in the figure. The crystalline structure where the Yb positions and vacancies are presented is shown in the inset. Reprinted with permission from [5].

Figure 2: Raman spectra of samples with 4, 8, and 12% of ytterbium.

Table 1: Reported peaks for different zirconia phases (cm\(^{-1}\)) [19].

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<tr>
<th>Cubic</th>
<th>Tetragonal</th>
<th>Monoclinic</th>
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<td>142</td>
<td>178</td>
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XRD and Raman results evidenced a mixture of phases at low concentrations of ytterbium in the films. In order to relate these results with the electrical properties, the lattice parameter, grain size, activation energy, and total conductivity at 450 °C reported in our previous work [5] are presented.
in Table 2. With grain sizes between 5.3 and 10.6 nm and a lattice parameter of 0.51 nm, around 28 to 55% of the unit cells in the grain are located in the surface. Then, stress in the lattice, inferred from the Raman spectra, is a very important factor. However, the link between grain size, lattice-strain state, and ionic transport remains unclear. The presence of stress in the grains influences two important conduction processes: the migration space, quantified as the cation-cation distance that represents a bottleneck for the oxygen migration, and the bond strength between the oxygen and the nearest cation preventing the oxygen from migrating. Recent theoretical studies indicate that the macroscopic oxygen diffusivity increases exponentially in YSZ up to a critical value of biaxial tensile strain, with a more significant impact at lower temperatures [8]. In strained regions, the cationic or anionic lattice positions can be off-centred compared to the zero-strained bulk ceramics. Moreover, the electrical conductivity of polycrystalline thin films is influenced by the intrinsic space charge effect and extrinsic segregation of impurities to the grain boundaries [24]. Keppner et al. [11] developed a model where they can estimate the thickness of the strained interface due to mismatch between YSZ/Y₂O₃ thin films. The interface thickness, which determines the point at which the initial strain is relaxed to a value $\frac{1}{2}$, is between 8 and 11 nm. Even when taking into account the differences in preparation, we note that when reported interface thicknesses are in the order of the grain sizes reported in this work.

The maximum conductivity is obtained for films with 4% of Yb (Table 2), which contrasts with the results in bulk materials where the maximum of conductivity is reported at 8–10% of Yb. Moreover, the activation energy of grains increases with the ytterbium percent, while the activation energy of grain boundaries decreases [5]. Even when the presence of stress partially explains the conductivity in grains, other morphological and compositional aspects must be considered. Figure 3 shows SEM images of films with 4, 8, and 12% of ytterbium precursor. The figure shows that the morphology presents important changes with the Yb compositions at the nanometric scale. Films with 4% of Yb are dense and smooth, although some nanocracks are observed in the surface. When the Yb composition increases to 8%, a rougher surface is observed. For compositions higher than 12%, the amount and size of cracks increase. It is important to mention that the cracks cannot be observed at lower resolutions. As all samples were measured in the same conditions and the cracks are specifically located in between grains, we speculate that these changes in morphology are related to differences in the grain boundaries, in the intergrain connection, and maybe in the composition.

Figure 4 shows a compositional map of Yb, Zr, and O in the film with 4% of Yb. A homogeneous distribution of O and Zr in the film can be observed (Figures 4(a) and 4(c)). In contrast, the ytterbium distribution shows black holes (Figure 4(b)). This distribution can be due to the fact that there is only 4% of Yb in the film. On the other hand, it could also be related with a preferential location of Yb in the grain boundaries. Even though EDS analysis is not conclusive, Yb migration to the grain boundaries has an important effect in the electrical properties as discussed in the following part.

Research about elements diffusion (Si, Fe) has demonstrated that grain boundary diffusion of cations is commonly many orders of magnitude faster than bulk diffusion in metal oxides with fluorite structure [24]. The increment in conductivity and the decrease in activation energy for grain boundaries can be explained in the context of the space charge effect theory. The space charge potential can be changed by the doping or in-diffusion of aliovalent ions along the grain boundary. For example, effective negative charges can be introduced into the grain boundaries through substitution of Zr⁴⁺ by Yb³⁺, resulting in a decrease of the space charge potential. Meng et al. [24] reported an increase of 6–7 times in conductivity for YSZ columnar films after Fe diffusion into the grain boundaries. It is not possible to quantify the elemental composition in grain boundaries by EDS, but it can be a very important aspect that affects the reported increase in conductivity. There are other aspects which must be considered in the understanding of high ionic conduction in grain boundaries. If a percent of the grain boundaries block totally the ionic conduction, increasing the amount of grain boundaries also increases the percolative ways of conduction, which can be another cause for the high ionic conduction in nanocrystalline materials.

In some cases, the increase in conductivity is associated with the presence of electronic conduction in the material. Figure 5 presents the absorption coefficient for the sample with 4% of ytterbium deposited onto a Corning glass substrate. It is the sample with higher conductivity. The obtained optical gap is too high (3.7 eV) compared to the conduction activation energy reported in Table 2 [5]. This indicates that
Figure 3: SEM images of films with 4 (a), 8 (b), and 12% (c) of ytterbium.

Figure 4: EDS map of (a) oxygen, (b) ytterbium, and (c) zirconium.
the electronic conduction should not be representative in the conductivity values reported in Table 2.

4. Conclusions

In this work, Raman spectroscopy measurements allowed the identification of a mixture of zirconia tetragonal and cubic phases with 4–8% of Yb, which cannot be detected by XRD. Compositional maps suggest that Yb can be located preferentially in the grain boundaries, which can decrease the space charge potential in these regions and be one of the causes of the anomalous increase of grain boundary conductivities. Changes in the activation energy values in grain and grain boundaries are related to the small grain sizes. The fact of obtaining the maximum conductivity at 4% of ytterbium (which is lower than the one reported in bulk materials) may be related with the stress and the mixture of phases (cubic and tetragonal). However, the changes in morphology and composition have a very important influence, especially in the analysis of the grain boundaries conduction, which determines the total conduction in these materials. UV measurements show that the films have a wide electronic band gap, higher than 3.5 eV in all samples. On the other side, the conductivity activation energy is lower than 1 eV, which indicates the ionic nature of the charge transport.

These results indicate that the high conductivity in nanostructured ionic conductors is a consequence of different physical parameters in the films. Therefore, the stress in the materials, different crystalline phases, impurities diffusion to the grain boundaries, and the presence of electronic conduction can all affect the electric properties of nanostructured thin films. They are not independent variables, as the stress induces changes in the crystalline phase and can modify the electronic conduction or favours the impurities diffusion. A model that explains the increase of conductivity in nanostructured materials must include all these aspects. Divergences in the published results can be related to the fact that all these parameters change with the deposition technique, the analyzed material, and the sintering conditions.

**Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.

**Acknowledgments**

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