

## Enhanced Ionic Conductivity in Heavily Doped Ceria Nanoceramics

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### 1. Introduction

Nanostructured materials are widely investigated because they have a wide functional diversity and exhibit enhanced or different properties compared to bulk materials. Particularly, in case of nanostructured ceramics, the presence of a large fraction of grain boundaries (GB) can lead to unusual or better properties. One growing area of investigation is the ionic transport in nanostructured solid electrolytes (nanoionics) with important applications, solid oxide fuel cells (SOFCs), among them, since an intense work has been conducted to find new electrolyte and electrode materials to allow the reduction of SOFCs operating temperature. Ceria-based ceramics have been regarded among the most promising electrolytes for intermediate temperature SOFCs (IT-SOFCs) since their ionic conductivity is higher than that of the traditionally used zirconia-based electrolytes. Transport properties of ceria-based electrolytes have been investigated, particularly the influence of microstructure and impurities in GB conductivity. This conductivity depends on several effects: i.e the specific GB conductivity considerably increases with decreasing grain size, for grain sizes  $< 3 \mu\text{m}$  in relatively pure  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2.8}$  ceramics<sup>[1]</sup>. The true GB conductivity,  $\sigma_{\text{GB}}^*$ , is a correction for the apparent GB conductivity,  $\sigma_{\text{GB}}$ , taking into account that only the width of the GBs perpendicular to the applied field should be considered. Therefore,  $\sigma_{\text{GB}}^*$  is related to  $\sigma_{\text{GB}}$  by the expression:  $\sigma_{\text{GB}}^* = (\delta_{\text{GB}}/d)\sigma_{\text{GB}}$ , where  $\delta_{\text{GB}}$  is the width of GBs and  $d$  is the grain size. The increasing of  $\sigma_{\text{GB}}^*$  with decreasing grain size has also been observed by other authors in calcia-stabilized zirconia<sup>[2]</sup>. In all these cases, the maximum total ionic conductivity is the grain interior (intrinsic or bulk) conductivity,  $\sigma_{\text{GL}}$ , which is independent of microstructure. Differently, a remarkable enhancement in the total ionic conductivity has been found in nanostructured  $\text{CeO}_2\text{-Gd}_2\text{O}_3$  and yttria-stabilized zirconia (YSZ) thin films, between one or two order of magnitude compared to that of polycrystals with larger grain size or single-crystals<sup>[3]</sup>. However, this behavior has not been confirmed for nanostructured heavily-doped ceria or YSZ dense pellets yet. *In the present work, the electrical properties of nanostructured  $\text{CeO}_2\text{-10 mol\% Y}_2\text{O}_3$  and  $\text{CeO}_2\text{-10 mol\% Sm}_2\text{O}_3$  ceramics have been studied as a function of grain size by electrochemical impedance spectroscopy (EIS).*

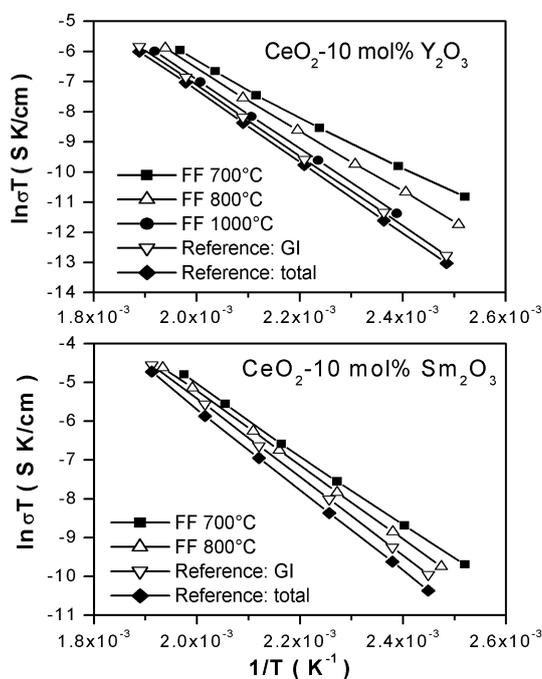
### 2. Experimental Procedure:

Commercial  $\text{CeO}_2\text{-10 mol\% Sm}_2\text{O}_3$  (CSO) and  $\text{CeO}_2\text{-10 mol\% Y}_2\text{O}_3$  (CYO) ultrafine powders (specific surface areas: 228 and 198  $\text{m}^2/\text{g}$ , respectively), were uniaxially pressed at 600 MPa into pellets (8 mm diameter) which were sintered by fast-firing process (dwell temperature: 700-1000°C and dwell time: 3 min.). Heating and cooling rates were 200°C/min. Fast-firing is a relatively non-conventional approach used to densify ceramics minimizing the grain growth during sintering. Reference specimen were

uniaxially pressed at 400 MPa into pellets (8 mm diam.) and sintered at 1300°C for 3 h. Crystalline phases and average crystallite size were evaluated by X-ray diffraction. Lattice parameters were determined by Rietveld analysis. The crystallite size was determined by the Scherrer equation. An ultracyclopometer in helium gas flow was used for density measurements. Microstructure and average grain size were studied by SEM. Ionic conductivity of samples was measured by EIS from 125 to 250°C in air.

### 3. Results and discussion

The total ionic conductivity was fitted as a function of temperature following the Arrhenius law:  $\sigma = (\sigma_0/T) \exp(-E_a/k_B T)$  where,  $E_a$ : activation energy for ionic migration,  $k_B$ : Boltzmann's constant and  $\sigma_0$ , pre-exponential factor, is a constant related to the density of charge carriers (oxide vacancies). *Figures 1a and 1b* display the Arrhenius plots for CYO and CSO ceramics, respectively.



**Figures 1a and b:** Arrhenius plots: CeO<sub>2</sub>-10 mol% Y<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>-10 mol% Sm<sub>2</sub>O<sub>3</sub> ceramics, for different grain sizes.

It can be observed that both,  $E_a$  and  $\sigma_0$  decrease with decreasing average grain size. For samples with the smallest grain sizes, a change in  $E_a$  was observed as a function of temperature. This change is observed at about 190°C in all cases. *EIS data show that, at low temperatures, the total ionic  $\sigma$  of nanostructured heavily doped ceria solid electrolytes increases by about one order of magnitude compared to that of conventional microcrystalline material. This result is attributed to the predominance of the GB conductivity in the nanostructured ceramics.* It was also found that the increase of the total ionic  $\sigma$  is associated to a reduction of the  $E_a$  probably caused by an increase of the GB ionic diffusivity with decreasing grain size. For samples with the smallest average grain size (35-50 nm), a change in the transport mechanism vs  $T$  was established, attributed to a transition from bulk-controlled (at high  $T$ ) to GB-controlled (low  $T$ ) ionic conduction.

### References

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- [3] T. Suzuki, I. Kosacki, H. U. Anderson, *Solid State Ionics* **151** (2002) 111.