Dopant segregation in nanometric TZP ceramics

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Tetragonal zirconia (TZP) presents a large potential to be applied as solid electrolyte in IT-SOFCs (400-700°C) because of good mechanical properties (1), good ageing (2) and high ionic conductivity (3). At present, the grain boundary blocking contribution remains of great importance particularly for nanometric grain sizes.

This work is focused on the influence of the substitution of Zr⁴⁺ by oversized R³⁺ dopant (from Yb³⁺, Y³⁺, Gd³⁺ to Sm³⁺) on electrical properties and especially on the grain-boundary blocking contribution in nanometric ZrO₂ ceramics using impedance spectroscopy.

TZP ceramics have been prepared by isostatic pressing from spray pyrolysis powders (4). All ceramics are characterized by the same microstructure (high purity, 60 nm-sized grains, density of 97% of the theoretical one) and are tetragonal single-phased for a constant 3 mol. %R₂O₃ content.

The grain-boundary (gb) blocking capacitances are decreased when the dopant ionic radius is increased in the 300-500°C temperature domain (Fig. 1). From these data, gb thicknesses have been evaluated from 0.8 to 1.9 nm for Yb to Sm-doped ZrO₂. The dopant nature has been found the key parameter in the blocking contribution.

In order to put into evidence the segregation phenomenon due to the migration of R³⁺ to the gb, quenching treatments have been undertaken on as-prepared 2.5Y-TZP ceramics from different temperatures. No noticeable alteration of the structure and microstructure was detected (Fig. 2). For higher quenching temperatures from 1500°C, the blocking contribution has been reduced as expected thermodynamically (Fig. 3) and simultaneously gb thicknesses have been decreased from 1.3 to 0.9 nm for as-prepared and quenched samples, respectively.

From Fig. 4, blocking resistivity is strongly decreased due to the quenching of Sm-TZP from 1500°C. A comparison with Sc-TZP evolution allowed us to conclude that this behavior has been fully related to segregation which is strongly marked for larger dopants.

Therefore, segregation has been evidenced by impedance spectroscopy in nanometric TZP ceramics and has been also discussed on a micrometer scale. EXAFS and STEM studies are in progression on these specimens in order to assess the larger segregation phenomenon in TZP doped with larger ionic radii.

References