

## Influence of additives on phase stabilization of scandia-doped zirconia

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### ABSTRACT

The effects of small additions of tin, zinc, calcium and boron oxides on phase composition and electrical conductivity of zirconia-10 mol% scandia were investigated. Compounds containing 1 mol% zinc, tin and calcium oxides and 1, 3 and 5 wt.% boron oxide were prepared by solid state reaction and characterized by X-ray diffraction, density measurements, scanning electron microscopy and impedance spectroscopy. Full stabilization of the cubic structure at room temperature was obtained with additions of 1 mol% calcium oxide and 2 wt.% boron oxide. Partially stabilized compounds exhibit herringbone structure, characteristic of the  $\beta$ -rhombohedral phase. Specimens with calcium as additive show total conductivity of  $23.8 \text{ mS}\cdot\text{cm}^{-1}$  at  $750^\circ\text{C}$  with activation energy of 1.13 eV. Liquid phase sintering by boron oxide addition is effective to enhance the densification of the solid electrolyte.

**Keywords:** scandia-doped zirconia, phase stabilizer, sintering aid, ionic conductivity.

### 1. INTRODUCTION

The combination of high ionic conductivity, wide electrolytic domain and low electronic conductivity turns the scandia stabilized zirconia, ScSZ, solid electrolyte a promising candidate for replacing yttria stabilized zirconia for application in solid oxide fuel cells operating at intermediate temperatures, typically  $800^\circ\text{C}$  [1-3]. The higher ionic conductivity of ScSZ is found for scandia contents of 8-10 mol% [3]. Nevertheless, the phase diagram of this solid electrolyte reveals a thermal degradation of the cubic phase for scandia contents up to 9-10 mol% giving rise to the tetragonal polymorph. Moreover, for higher scandium contents, the cubic to  $\beta$ -rhombohedral phase transition readily occurs. Both, tetragonal and rhombohedral phases exhibit lower ionic conductivity than that of the high symmetry cubic structure [2,3].

Then, up to date, one of the main goals has been to stabilize the cubic phase at room temperature. One approach to accomplish that is by the introduction of a second additive. In this context, continuing efforts have been made to find a suitable additive allowing for phase stabilization without excessive deterioration of the ionic conductivity. The additives investigated include those oxides with relatively high solubility such as rare earths [4-8] and other oxides [9-12].

So far, the higher ionic conductivity, amounting  $\sim 18 \text{ mS}\cdot\text{cm}^{-1}$  at  $600^\circ\text{C}$ , was found for the system zirconia-10 mol% scandia-1 mol% ceria [10]. However, it was found that the cubic phase transforms on the surface of the solid electrolyte to monoclinic via tetragonal phase during operation at  $900^\circ\text{C}$  of a tubular-type SOFC [13]. Conductivity degradation of this electrolyte was also observed at  $600^\circ\text{C}$  during long-term operation in humidified mixture of  $\text{H}_2/\text{N}_2$  and humidified  $\text{H}_2$  [14].

In this work, small amounts of tin, zinc and calcium oxides as phase stabilizer, and boron oxide as sintering aid were added to zirconia-10 mol% scandia and their effects on structure, microstructure and ionic conductivity were investigated.

### 2. MATERIALS AND METHODS

#### 2.1 Materials preparation

Zirconia-10 mol% scandia, ScSZ (Daiichi Kigenso Kagaku Kogyo, Japan), SnO (Alfa Aesar, 99.9%), CaCO<sub>3</sub> (Vetec, 99%), zinc stearate (Zn(C<sub>18</sub>H<sub>35</sub>O<sub>2</sub>)<sub>2</sub>) and boron oxide (B<sub>2</sub>O<sub>3</sub>, Alfa Aesar 99.9%) were the starting materials. The investigated composition was ZrO<sub>2</sub>-10 mol% Sc<sub>2</sub>O<sub>3</sub>-1 mol% A (A=Zn, Sn, Ca) and 1, 3 and 5 wt.% B<sub>2</sub>O<sub>3</sub>.

The starting materials were weighted in the stoichiometric proportion and mixed together in alcoholic medium followed by drying at 40°C for 1 h. Cylindrical specimens were prepared by uniaxial (50 MPa) followed by isostatic (100 MPa) pressing. The sintering of the green compacts was carried out at 1500°C for 5 h in a resistive furnace (Lindberg BlueM, 51524) with heating and cooling rates of 5 and 30 °C.min<sup>-1</sup>, respectively. Specimens containing calcium and zinc were first heated up to 800°C for 1 h for precursor decomposition. Specimens with boron oxide addition were sintered at 1500°C for 4 h. Sintered specimens are named 10Sc1ASZ standing for zirconia-10 mol% scandia-x mol% additive. The experimental procedure for boron oxide was similar to that of other additives. In this case the prepared compositions were zirconia-10 mol% scandia-y wt.% B<sub>2</sub>O<sub>3</sub> with y=1, 2, 3 and 5.

## 2.2 Characterization methods

The apparent density of sintered specimens was determined by measuring sample dimensions and mass and compared to the theoretical value calculated from the lattice parameters of the several compositions. Phase characterization was performed by room temperature X-ray diffraction, XRD (Bruker-AXS, D8 Advance) in the 20-80° 2θ range with Ni filtered Cu K<sub>α</sub> radiation (λ=1.5405 Å). Indexing of diffraction profiles was performed by comparison of XRD patterns with those of JCPDF 89-5483 and 511604 files for cubic and rhombohedral phases, respectively. The microstructure of sintered specimens was observed by field emission scanning electron microscopy, FEG-SEM (FEI, Inspect F50) on polished and thermally etched surfaces. The ionic conductivity was measured by two-probe electrochemical impedance spectroscopy (HP4192A), with 100 mV of applied signal in the 13 MHz-5 Hz frequency range. Silver and platinum were used as electrode materials for electrical measurements in the low (< 600°C) and high (≥ 600°C) temperature ranges, respectively. Special software was used for data collecting and analysis [15].

## 3. RESULTS AND DISCUSSION

### 3.1 Zirconia-10 mol% scandia-1 mol% SnO<sub>2</sub>, ZnO and CaO

Figure 1a shows XRD patterns of zirconia-10 mol% scandia-1 mol% A (A=SnO<sub>2</sub>, ZnO, CaO) specimens sintered at 1500°C for 5 h. Addition of calcium promoted fully stabilization of the cubic phase at room temperature. Specimens containing zinc oxide exhibit only reflections of the rhombohedral phase, whereas partial stabilization of the cubic structure is found for tin oxide addition. The angular region of 2θ between 48 and 53° is highlighted in Fig. 1b evidencing the phase composition for these specimens.

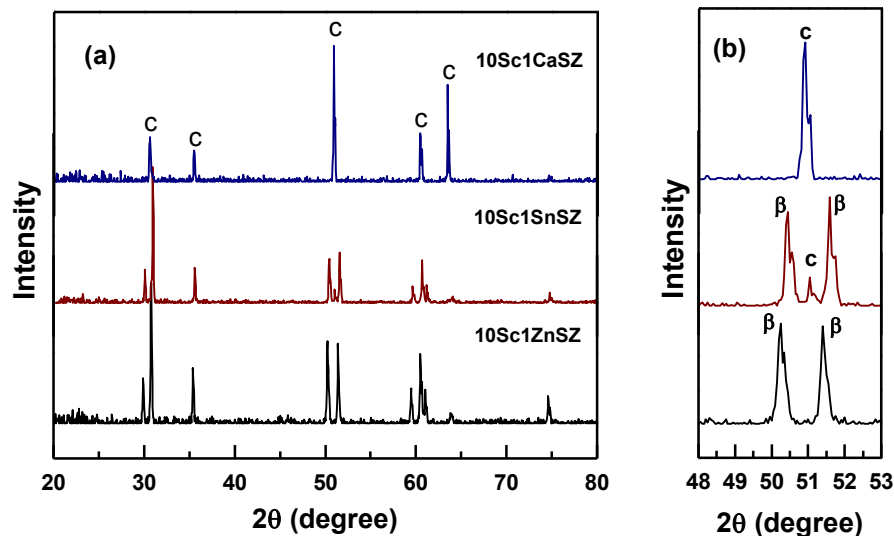


Figure 1: XRD patterns of ZrO<sub>2</sub>: 10 mol% Sc<sub>2</sub>O<sub>3</sub>-1 mol% A (A=SnO<sub>2</sub>, ZnO, CaO) specimens sintered at 1500°C for 5 h,

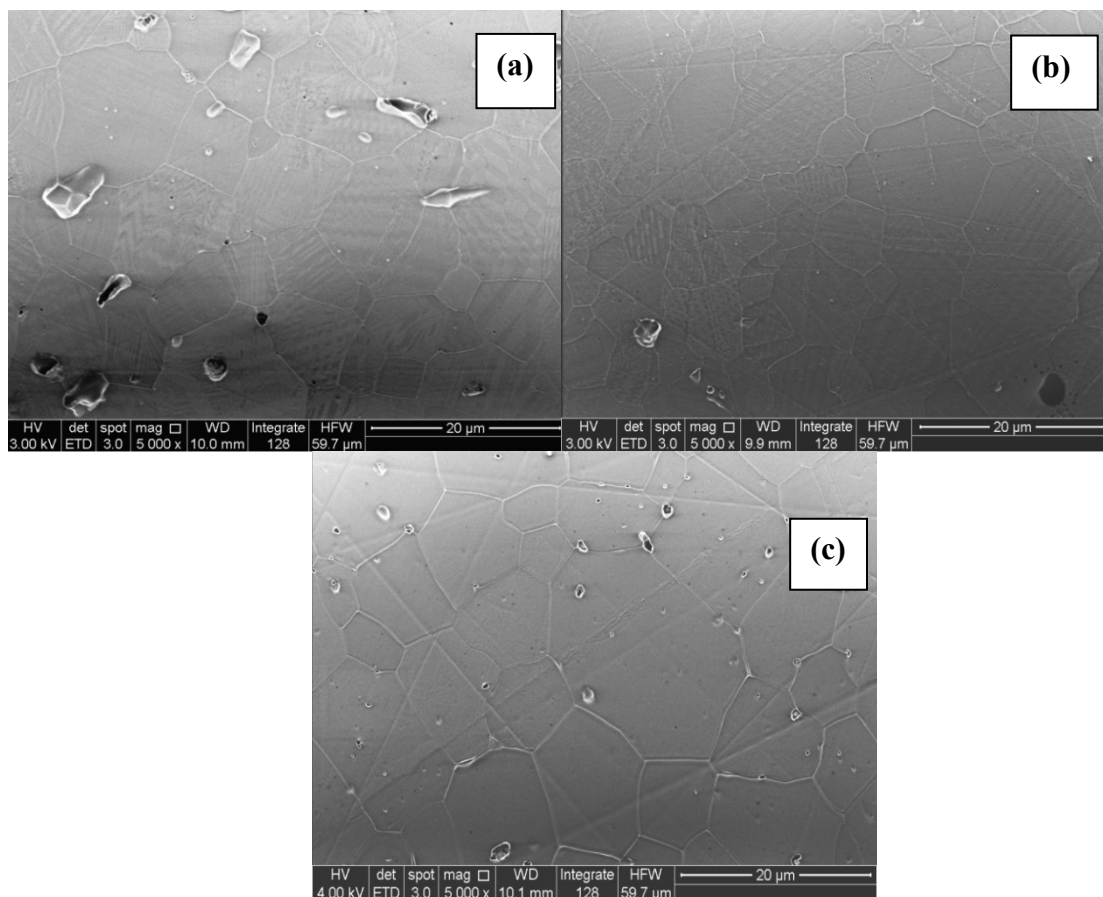
in the (a) 20-80° and (b) 48-53° 2θ ranges; c and β stand for the cubic and rhombohedral phases, respectively.

Table 1 lists values of relative density (in %) and phase composition (c=cubic, β=rhombohedral) of sintered specimens. It is remarkable the effect of the additive on microstructure. Zinc oxide does not promote phase stabilization and decreases the sintered density. Addition of calcium oxide is effective for the cubic phase stabilization at room temperature. Tin oxide promotes partial stabilization of the cubic phase with good densification.

**Table 1:** Values of relative density and phase composition (c=cubic, β=rhombohedral) of 10Sc1ASZ (A=Sn, Zn, Ca) sintered specimens.

SPECIMEN	RELATIVE DENSITY (%)	PHASE COMPOSITION	MEAN GRAIN SIZE (μm)
10Sc1SnSZ	97	β + c	10.0
10Sc1ZnSZ	89	β	11.4
10Sc1CaSZ	97	C	12.5

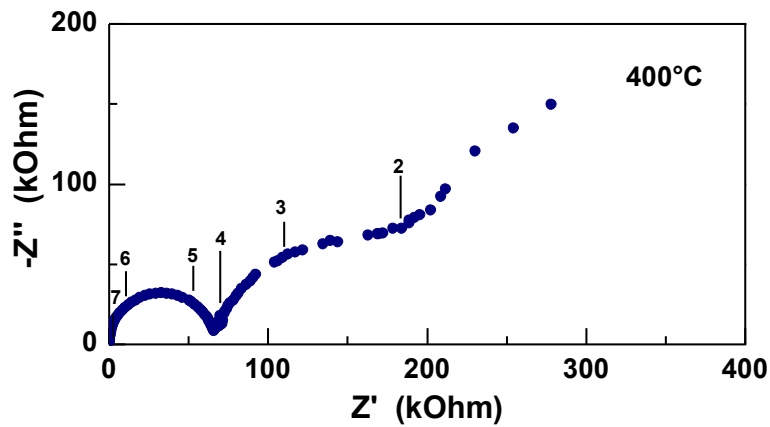
Figure 2 shows FEG-SEM micrographs of sintered specimens of 10Sc1ASZ (A=Sn, Zn and Ca). The microstructure of sintered specimens consists of micrometer sized grains (Table 1). The herringbone structure, characteristic of the cubic-to-rhombohedral phase transition, is seen in the micrographs of specimens containing zinc and tin oxides, Figures 2a and 2b, respectively.



**Figure 2:** FEG-SEM micrographs of 10Sc1ASZ. A: (a) Zn, (b) Sn, and (c) Ca.

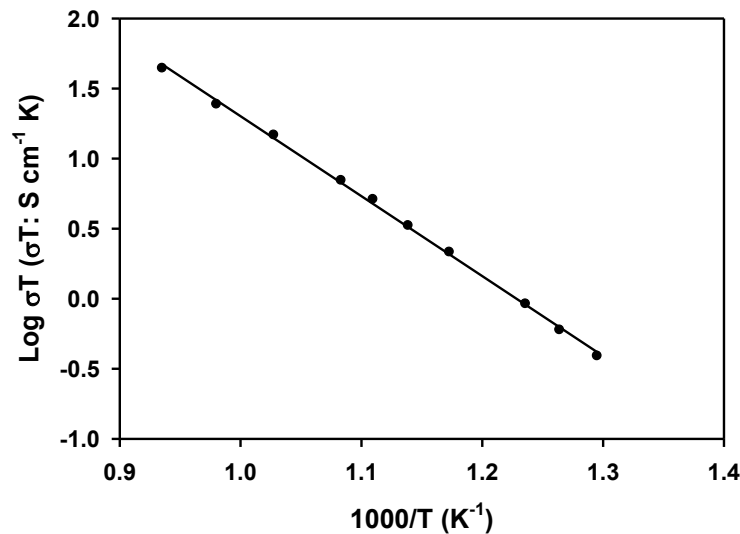
These results indicate that calcium is a suitable phase stabilizer for zirconia-scandia electrolyte. Then, we investigated the electrical conductivity of this ternary system by impedance spectroscopy measurements. Figure 3 shows typical impedance diagram for 10Sc1CaSZ collected at 400°C, consisting of bulk (high frequency) and grain boundary (intermediate frequency) components of the electrolyte resistivity. In this figure,

the original data was normalized for specimen dimensions. Then, the diameter of the high frequencies semi-circle stands for the electric resistivity of the bulk (or grains), and that at intermediate frequencies the inter-grain resistivity.



**Figure 3:** Impedance spectroscopy diagram of 10 Sc1CaSZ at 400°C.

The Arrhenius plot of the total ionic conductivity of 10Sc1CaSZ is shown in Figure 4. In the low temperature range, the total conductivity  $\sigma$  is higher than that of zirconia-10 mol% scandia, whereas the opposite trend is verified in the high temperature range. For example, at 600°C,  $\sigma$  amounts 3.8 (10Sc1CaSZ) and 0.51 (ScSZ)  $\text{mS}\cdot\text{cm}^{-1}$ , and at 750°C,  $\sigma$  is equal to 23.8 (10Sc1CaSZ) and 37.9 (ScSZ)  $\text{mS}\cdot\text{cm}^{-1}$ .

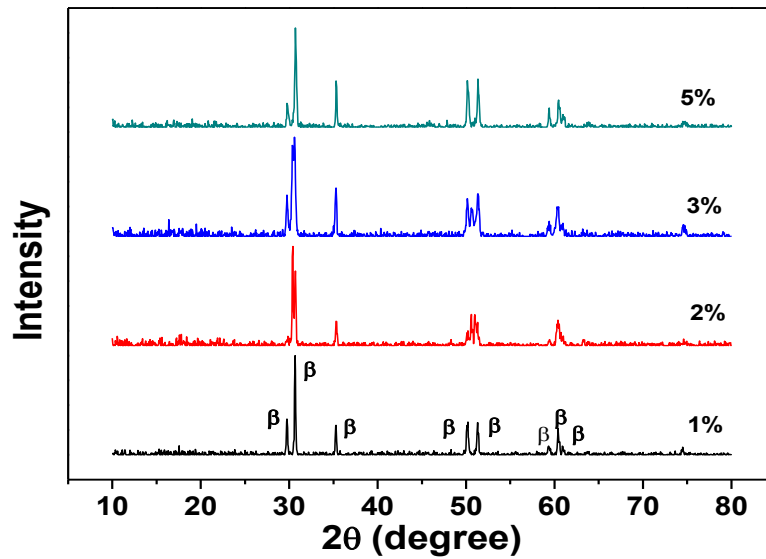


**Figure 4:** Arrhenius plots of total ionic conductivity of 10Sc1CaSZ.

In the whole temperature range of measurements, a single activation energy value for conduction was determined for 10Sc1CaSZ, 1.13 eV.

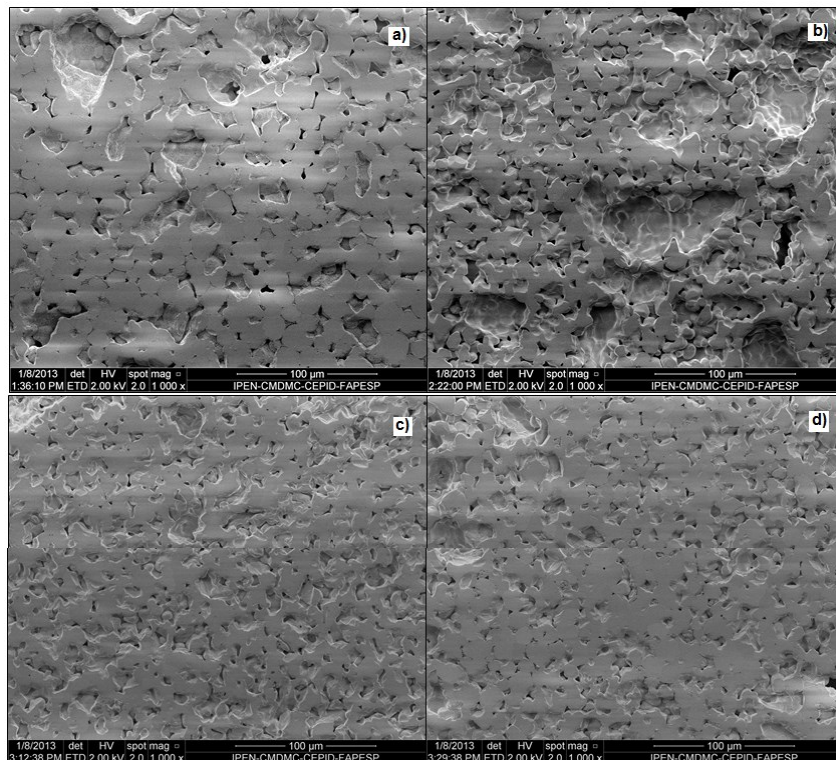
### 3.1 Zirconia-10 mol% scandia-1-5 wt.% B<sub>2</sub>O<sub>3</sub>

Figure 5 shows XRD patterns of zirconia-10 mol% scandia-1 to 5 wt.% B<sub>2</sub>O<sub>3</sub> specimens sintered at 1500°C for 4 h. Addition of 2 wt.% boron oxide promoted fully stabilization of the cubic phase at room temperature.



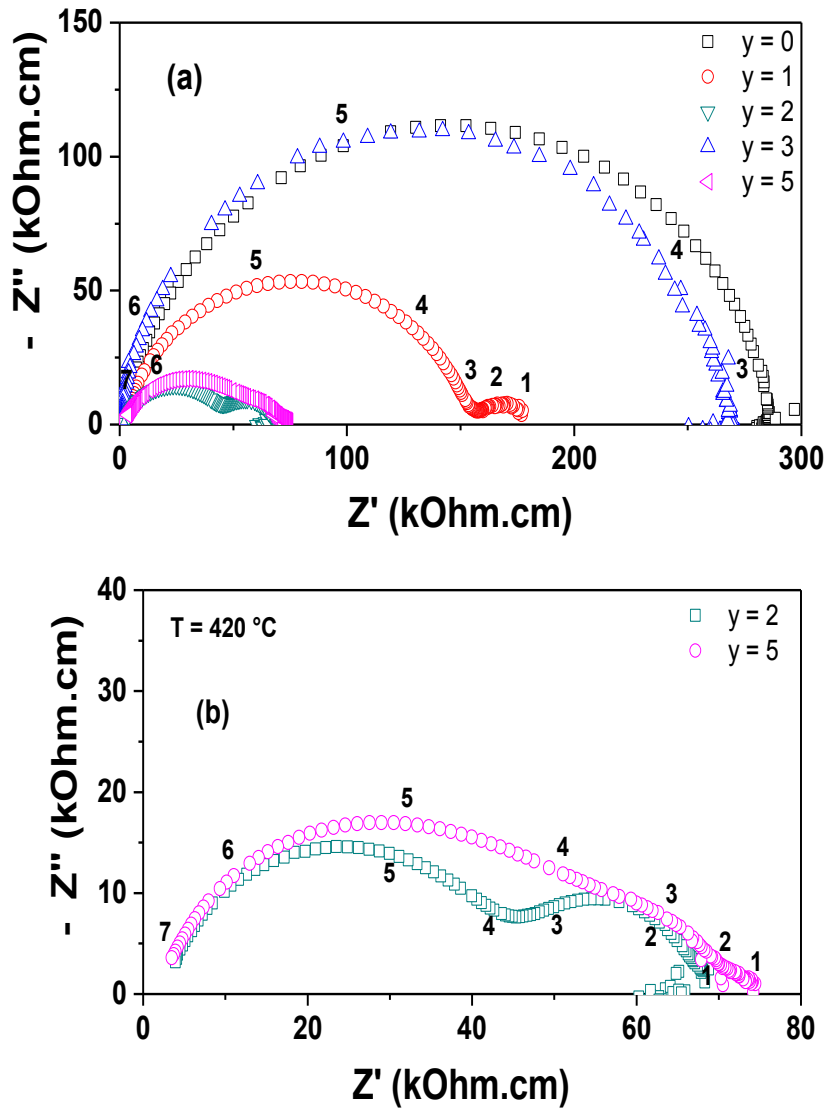
**Figure 5:** XRD patterns of  $ZrO_2$ : 10 mol%  $Sc_2O_3$ -1 to 5 wt.%  $B_2O_3$  specimens sintered at  $1500^\circ C$  for 4 h;  $\beta$  stands for the rhombohedral phase.

Figure 6 shows FEG-SEM micrographs of sintered specimens of 10ScSZ sintered with addition of 1, 2, 3 and 5 wt.%  $B_2O_3$ . The microstructure of sintered specimens consists of micrometer sized grains. Boron oxide promoted densification via liquid phase sintering and porosity due to the capillary evolution of liquid boron oxide towards the pellet surface.



**Figure 6:** FEG-SEM micrographs of 10ScSZ + y wt.%  $B_2O_3$ , y = 1 (a), 2 (b), 3 (c) e 5 (d), sintered at  $1500^\circ C/4$  h.

Figure 7 shows impedance diagrams of specimens containing boron oxide measured at  $420^\circ C$  consisting of bulk and grain boundary components of the electrolyte resistivity.



**Figure 7:** Impedance diagrams of  $(ZrO_2: 10 \text{ mol}\% Sc_2O_3) + y \text{ wt.}\% B_2O_3$  ( $x = 0, 1, 2, 3$  and  $5$ ) sintered at  $1500^\circ C/4 \text{ h}$ ; (b) is a zoom of the  $Z' < 80 \text{ kOhm.cm}$  region. Numbers stand for  $\log f$  ( $f$ : Hz).

The addition of boron oxide leads to a decrease of the electrical resistivity of 10ScSZ. This might be due to the effect of liquid phase sintering, i.e., the wetting of the grain surfaces with enhanced densification. 2 wt.%  $B_2O_3$  seems to be an optimum content to promote fairly dense specimens (Cf. Fig. 6) and enhanced ionic conductivity. Higher values of the additive (5 wt.%) does not improve the ionic conductivity, probably by the occurrence of residual amorphous non conducting  $B_2O_3$ -related phases.

#### 4. CONCLUSIONS

Scandia-stabilized zirconia, which has the higher oxide ion conductivity among the stabilized zirconias, was produced in single cubic phase or with partial stabilization of the cubic structure by adding aliovalent ions (Ca, Sn, Zn and B) prior to sintering. Improvement in the sintered density as well as in the ionic conductivity was achieved.

#### 5. ACKNOWLEDGEMENTS

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