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Microstructure and Electrical Conductivity of Yttria-Stabilized Zirconia with Lithium Addition

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Abstract. Yttria-stabilized zirconia is a singular polycrystaline ceramic with a range of technological applications. The combination of its physical properties is responsible for application as solid electrolytes in solid oxide fuel cells. High densification is required for this and other applications. The sintering of this solid electrolyte is still a matter of investigation. To reduce the sintering temperature, the introduction of additives is an effective approach. In this work, the effects of lithium addition on microstructure and electrical conductivity of 8 mol% yttria-stabilized zirconia was studied by scanning electron microscopy and impedance spectroscopy, respectively. Cylindrical pellets were prepared by pressing, followed by sintering at 1200ºC without and with 1 and 2 mol% lithium (metal basis). As precursor materials both lithium carbonate and lithium fluoride were used. The main microstructure features were correlated with the results of electrical conductivity.

Introduction

Polycrystalline ceramics based on zirconia have been extensively investigated because of their electrical, mechanical and optical properties. Zirconia containing Y_2O_3, CaO or MgO are recognized to present high values of ionic conductivity, mechanical strength e good thermal shock resistance. These properties turn these ceramic materials good candidates for a number of application in electrochemical devices, ceramic coatings, catalysts, grinding media, biomaterials, etc.

Zirconia containing yttrium oxide in contents of ~2.5-3.0 mol% exhibits high mechanical strength and fracture toughness and is currently used for structural applications. For Y_2O_3 contents of ~7.5-10 mol% its ionic conductivity attains the highest values and these ceramics are employed as solid electrolytes in solid oxide fuel cells and ceramic sensors [1,2].

One problem associated to this solid electrolyte is the relatively high sintering temperature to obtain good densification, in general higher than 1450ºC [3,4]. The main purpose of this work is to study the effect of lithium addition to the microstructure and the electrical conductivity of a commercial zirconia-8 mol% yttria. The influence of the type of precursor is also investigated by impedance spectroscopy.

Experimental

Zirconia-8 mol% yttria, 8YSZ (99.6%, Tosoh), lithium carbonate, Li_2CO_3 (99.9%, Alfa Aesar) and lithium fluoride, LiF (99.9%, Alfa Aesar) were used as starting materials. The contents of lithium were 1, 2 and 3 mol% (metal basis). The preparation of the several compositions was effected by mixing the starting precursors in an agate mortar in acetone. After drying, cylindrical pellets were prepared by pressureless sintering at 1200ºC for 2 h with 10ºC.min^{-1} heating rate.

The apparent density of the sintered pellets was determined by the immersion method. X-ray diffraction measurements were performed in a diffractometer (D8 Advance, Bruker-AXS) in the 20-80º 2θ range with 0.05º step size and 3 s time per step. Microstructural characterization was done by scanning electron microscopy, SEM, (XL30, Philips) on polished and thermally etched surface of sintered pellets. The electrical conductivity was determined by impedance spectroscopy (4192A, HP) in the 5 Hz – 13 MHz frequency range. Silver was used as electrode.

Results and discussion

Structural and microstructural characterization. Fig. 1 shows X-ray diffraction patterns of sintered pellets with 1 and 2 mol% Li prepared with lithium carbonate.

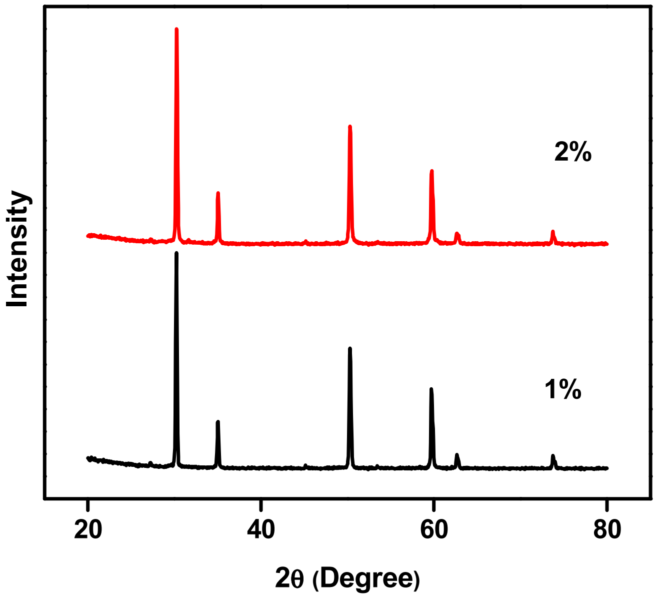


Fig. 1: X-ray diffraction patterns of 8YSZ containing 1 and 2 mol% Li prepared with lithium carbonate.

The X-ray diffraction patterns show the characteristic peaks of yttria-stabilized zirconia (JCPDS 30-1468, *Fm3m* space group) and no other feature that could be attributed to the additive. Similar results were obtained when lithium fluoride was used as precursor material.

The relative densities of pellets prepared with lithium carbonate are 95.5 (1 mol%), 93.2 (2 mol%) and 81.4% (3 mol%). At the same sintering temperature (1200ºC) the relative density of commercial powders is only ~ 71% [3]. This result shows that the additive is an effective sintering aid, allowing for obtaining high densities at relatively lower temperatures. No substantial differences were observed with lithium fluoride as precursor material. The morphology of sintered pellets is shown in the SEM micrographs, Fig. 2, for pellets containing 1 and 3 mol% Li prepared with lithium carbonate.

The pellet containing 1 mol% Li (Fig. 2 top) shows homogeneous distribution of grain sizes and few pores, mainly inside the grains, as in samples without additives. The pellets containing 2 and 3 mol% Li exhibit similar morphology. Fig. 2 bottom shows a typical SEM micrograph obtained for the pellet with 3 mol% Li as an example. It is worth noting the drastic reduction in the mean grain size, and simultaneous observation of small grains preferentially at the grain boundaries and triple grain junctions. No differences were observed when lithium fluoride was used as precursor material. These small grains are attributed to segregated Li_2O, probably due to the relatively low solubility of lithium in the zirconia matrix. This segregated secondary phase is responsible for avoiding both the grain growth and the trapping of pores inside the grains. Thus, the compositions with lithium contents higher than 1 mol% exhibit a bimodal grain size distribution and intergranular porosity.

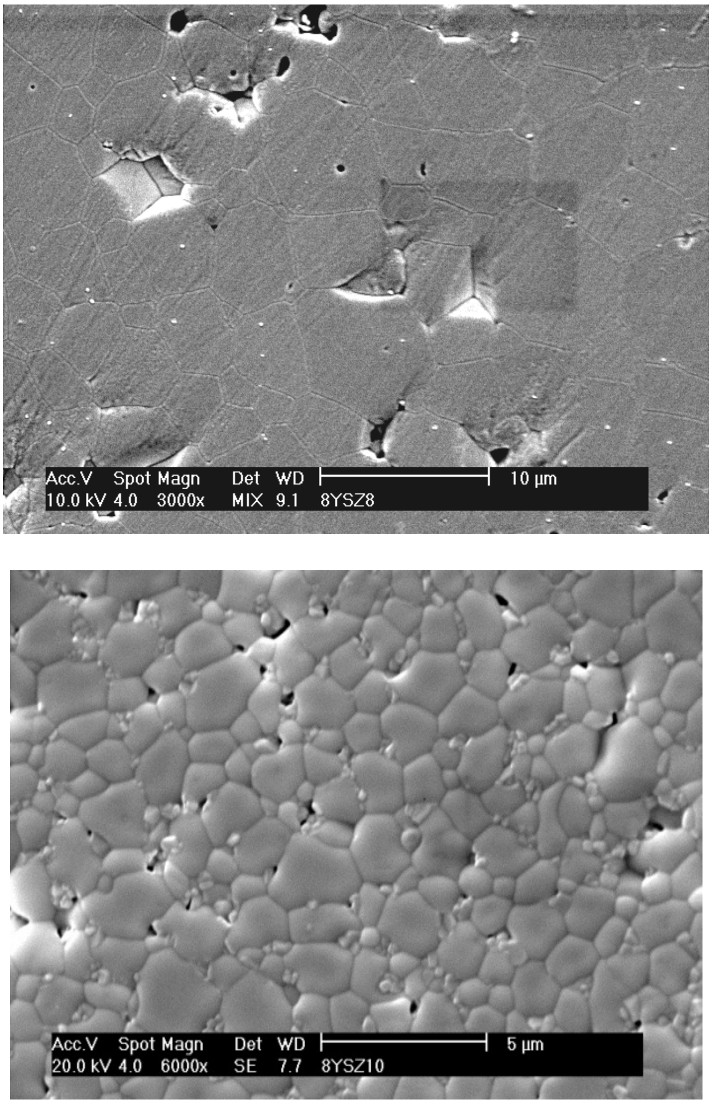
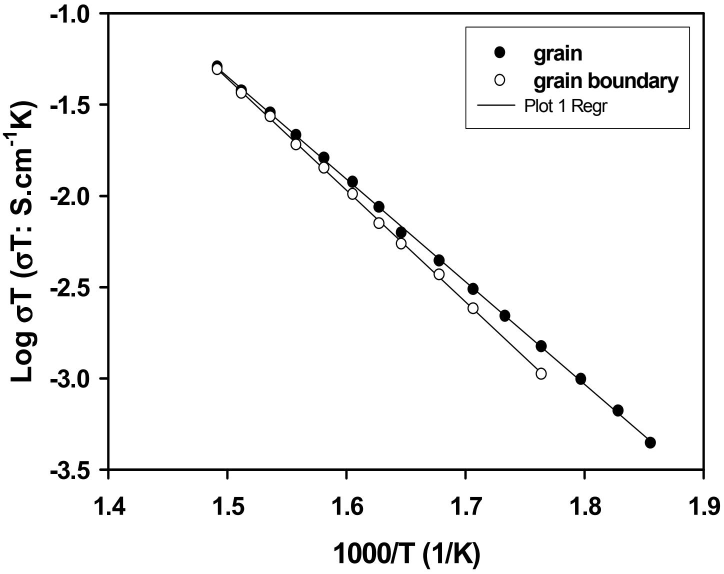


Fig. 2: SEM micrographs of 8YSZ containing 1 (top) and 3 mol% (bottom) Li prepared with lithium carbonate as precursor.

It may be concluded from the above results that the addition of lithium may carried out to improve both the sintered density and the morphology of yttria-stabilized zirconia without any significant change in the crystal structure.

The beneficial effect of lithium addition for densification of other solid electrolyte, gadolinia-doped ceria, has already been reported [5].

Electrical conductivity. In the temperature range of measurements (250-400ºC) the impedance plots show two well-resolved semicircles generally assigned to the electrolyte grain and grain boundary resistivities. Fig. 3 shows the Arrhenius plots of the electrical conductivity of pellets prepared with LiF as precursor.



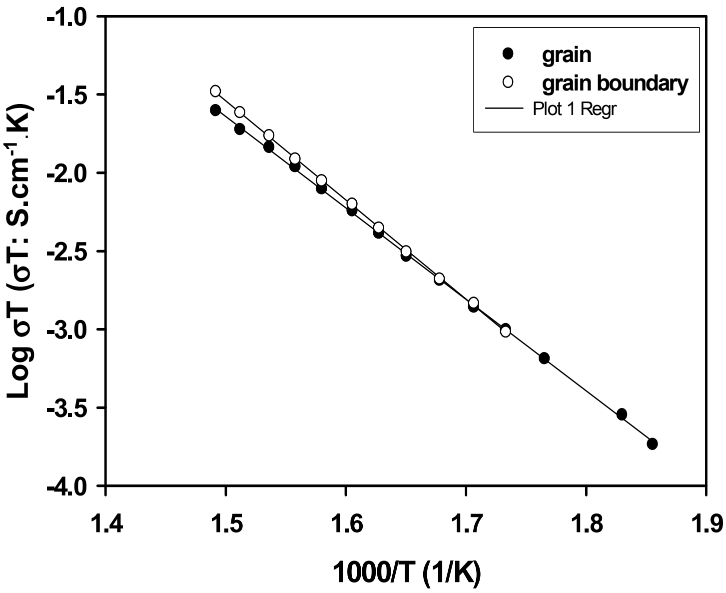
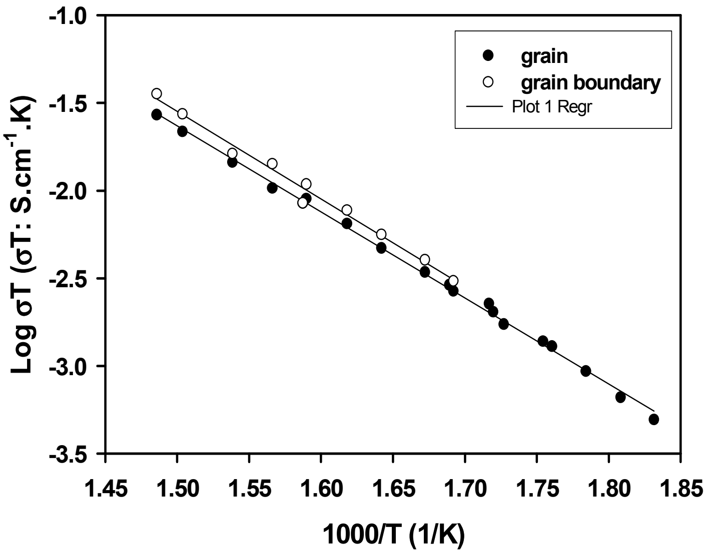


Fig. 3: Arrhenius plots of the electrical conductivity of pellets containing 1 (top) and 2 mol% (bottom) Li prepared with LiF as precursor.

The grain and the grain boundary conductivities show single straight lines in the temperature range where both components could be resolved, evidencing a single mechanism for conduction. The grain boundary activation energy for conduction is slightly higher than that of the bulk (~1 eV), as predicted for the blocking effect [6].

Fig. 4 shows the Arrhenius plots of the electrical conductivity of pellets containing 1 (top) and 2 mol% (bottom) lithium prepared from Li_2CO_3 as precursor material.



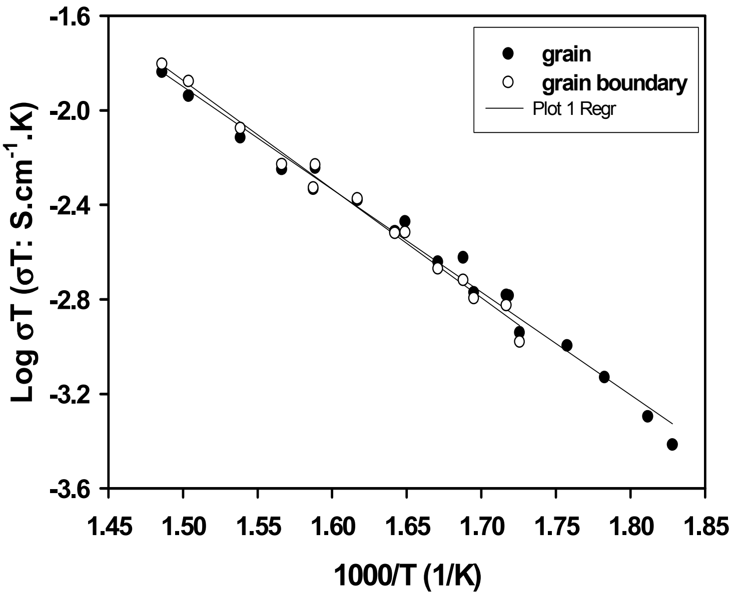


Fig. 4: Arrhenius plots of the electrical conductivity of pellets containing 1 (top) and 2 mol% (bottom) Li prepared with Li_2CO_3 as precursor.

The grain and grain boundary conductivities of the pellet with 1 mol% Li (Fig. 4 top) show approximately parallel straight lines due to the small difference between the corresponding activation energies.

The magnitudes of the electrical conductivity seem to independ on the precursor material. However, with increasing the lithium content, the magnitude of the grain and grain boundary conductivities decrease. Therefore, although the additive promotes considerable increase in the densification of 8YSZ, it degrades the ionic conductivity of the solid electrolyte, except for relatively small contents (≤ 1 mol% Li).

Conclusions

Solid electrolytes consisting of 8YSZ with additions of lithium were prepared by solid state reactions. Sintering at 1200ºC for 2 h allowed for obtaining a relative density of 96.5% for the pellet containing 1 mol% Li. For compositions with higher lithium content a secondary phase was observed to be formed along the grain boundaries. Addition of lithium up to 1 mol% improves the densification and do not influence significantly the electrical conductivity of 8YSZ.

Acknowledgements

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