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Single Cubic Phase Scandia-Stabilized Zirconia: Stabilization and Aging at 600°C

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ZrO_2:10 mol% Sc_2O_3 was mixed with MnO_2 to evaluate its effect on cubic phase stabilization, oxide ion conductivity and aging at 600°C. Pressed ceramic pellets of zirconia stabilized with 10 mol% scandia with addition of 1.0, 2.0 and 2.5 mol% MnO_2 were sintered at 1500°C/2 h. In situ high temperature X-ray diffraction data were collected to follow the rhombohedral-to-cubic transition. Polished and thermally etched surfaces of the sintered pellets were observed in scanning electron microscope. Impedance spectroscopy measurements were carried out. The single cubic structure is achieved for the specimen with 2 mol% MnO_2 nominal addition. The electrical conductivity of this specimen was monitored at 600°C for 100 days. The ionic conductivity value remained constant, suggesting its use as solid electrolyte in SOFCs operating at that temperature.

Introduction

Polycrystalline yttria-stabilized zirconia (YSZ) is a suitable solid electrolyte for solid oxide fuel cells (SOFC) due to its high oxide ion conductivity in the 900-1000°C range [1]. Solid electrolytes with higher oxide ion conductivity than YSZ would enable the design of SOFCs operating at lower temperatures, avoiding thermal expansion coefficient mismatch with the ceramic electrodes and eventual crack failure during thermal cycling, which occurs upon power failure. ZrO_2:3 mol% Y_2O_3, ZrO_2:8 mol% Y_2O_3, ZrO_2:10 mol% Y_2O_3, ZrO_2:8 mol% Sc_2O_3, ZrO_2:9 mol% Sc_2O_3, $Ce_{0.7}Gd_{0.3}O_{1.85}$, and $Ce_{0.8}Sm_{0.2}O_{1.9}$ present, respectively, the following values of oxide ion conductivity: 0.058, 0.178, 0.136, 0.31, 0.34, 0.25 and 0.25 S/cm [2]. The phase diagram of ScSZ has been described by Thornber *et al.* [3] and Ruth *et al.* [4]. Even though scandia-stabilized zirconia (ScSZ) is the best candidate for replacing YSZ, its crystallographic rhombohedral ↔ cubic phase transition near 600°C causes a departure from the single Arrhenius behavior of the ionic conductivity [5].

It has been recognized that improvement of the ionic conductivity of zirconia-based solid electrolytes may be realized by introducing a liquid phase in the grain boundaries during sintering [6]. Some additives were tried to promote single phase ScSZ: Mn_2O_3 [7], Al_2O_3 [8-10], Bi_2O_3 [11], and Y_2O_3 [12]. Porous and dense composite ScSZ solid electrolytes synthesized with 1 mol% MnO_2 addition were sintered at 1400°C/10 h and tested in a single cell at 800°C [13]. Detailed thermodynamic data for the manganese-oxygen system have been reported [14].

In this paper, the effects of manganese oxide addition in ZrO_2:10 mol% Sc_2O_3 on the crystallographic phase transition near 600°C, on the sintering behavior by liquid phase sintering, and on the electrical behavior upon aging at 600°C were evaluated.

Experimental

Manganese dioxide (MnO_2, Alfa Aesar 99.9%), 1.0, 2.0 and 2.5 mol%, was mixed to scandia-stabilized zirconia (ZrO_2:10 mol% Sc_2O_3, Daiichi Kigenso Kagaku Kogyo - DKKK, Japan). The mixture was pressed and sintered at 1500°C/4 h in air.

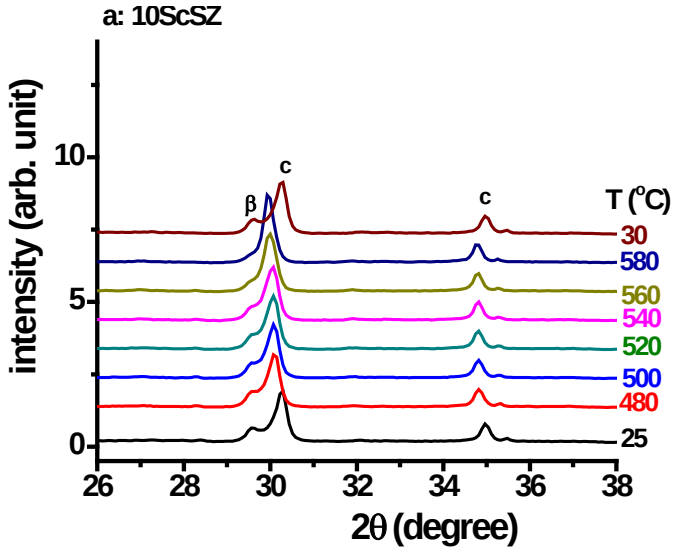
X-ray diffraction measurements were carried out in in a Bruker-AXS D8 Advance X-ray diffractometer with Cukα radiation (λ = 1.54060 Å) operating at 40 kV and 40 mA, 0.05° 2θ step size, 5 s per step. High temperature X-ray diffraction data were collected in a Bruker-AXS D8 Advance X-ray diffractometer equipped with an Anton Paar HT1400 sample chamber and a Braun position sensitive detector. ICDD files were used as reference for phase identification.

The linear shrinkage of the green pellets were evaluated in a 1161 Anter vertical dilatometer in the room temperature-1500°C range.

Impedance spectroscopy measurements were carried out in a 4192A Hewlett Packard impedance analyzer connected to a 360 series HP controller running on a special software [15] to collect and analyze the [-Z''(f) x Z'(f)] data in the 5 Hz - 13 MHz frequency (f) range, input signal 200 mV, in the 300-500°C temperature range. Electrical measurements were also carried out at 600°C up to 100 h with a ScSZ sintered pellet inserted in a programmable Lindberg tubular furnace.

Results and Discussion

Figure 1 shows X-ray diffraction patterns of 10ScSZ + x mol% MnO_2 (x=0, 1, 2 and 2.5) powders from room temperature to 580°C. For x up to 2 mol% MnO_2 both cubic and rhombohedral phases are apparent. For x = 2.5 mol% there is no rhombohedral phase for temperatures higher than 540°C. Melting manganese dioxide apparently promotes diffusion of Mn^{2+} into the ScSZ lattice with the substitution of Mn^{2+} (ionic radius 81 pm) for Zr^{4+} (86 pm). The confirmation of this assumption came out with the impedance spectroscopy results (see below).



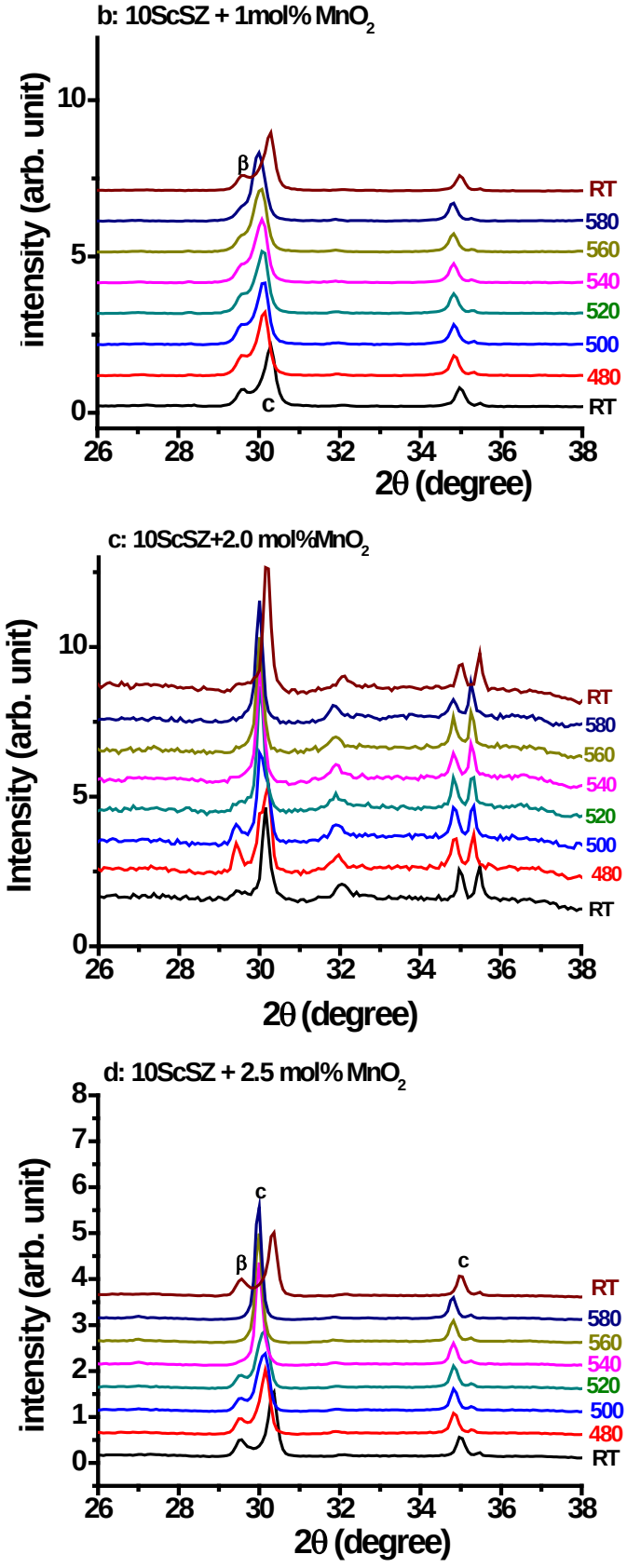


Figure 1. X-ray diffraction patterns of 10ScSZ: x mol% MnO_2 (x = 0, 1.0, 2.0 and 2.5) powders measured at room temperature and from 480 to 580°C; c: cubic phase, β: rhombohedral phase.

Near 540°C the manganese ion enters into solid solution into the ScSZ lattice enhancing the oxide ion vacancy concentration and promoting the rhombohedral-to-cubic phase transition. A consequence of the probable mechanism will be verified later in the electrical measurements with the substantial increase in the oxide ion conductivity.

Figure 2 shows the dilatometric curves of ZrO_2:10 mol% Sc_2O_3 + x mol% MnO_2 for x = 0, 1.5 and 2.5. The main effect of the addition is a decrease of the temperature of maximum shrinkage rate: 0, 1.5 and 2.5 correspond to 1170°C, 1060°C and 1050°C, respectively. The beneficial effect of manganese dioxide is probably due to liquid phase sintering (the melting point of manganese dioxide is 535°C).

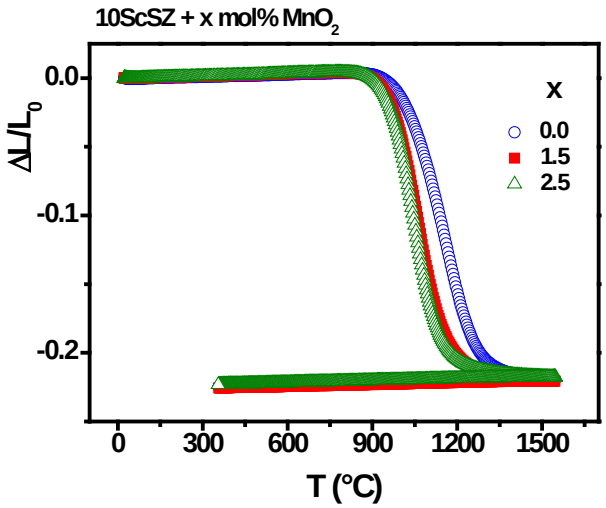
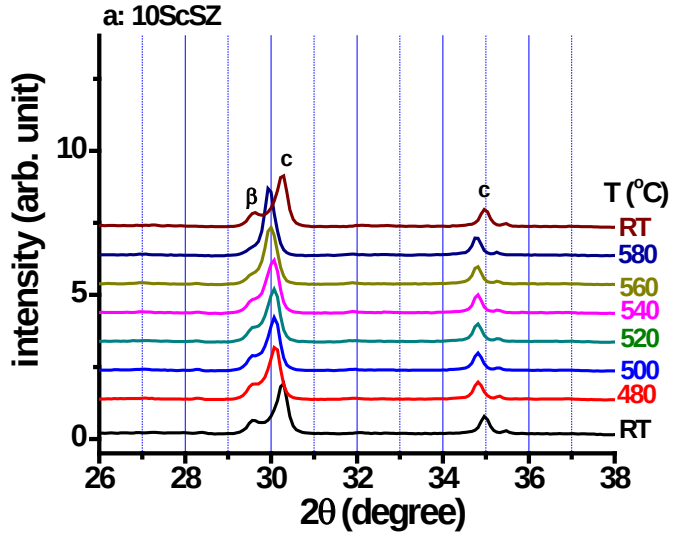


Figure 2. Dilatometric curves of green pellets of mixtures of ZrO_2:10 mol% Sc_2O_3 with x mol% MnO_2, x = 0, 1.5 and 2.

After studying the ScSZ powders with manganese dioxide additions and their sintering behavior, the powders were pressed, sintered at 1500°C, and analyzed by high temperature X-ray diffraction to evaluate the effect of the additive on the crystallographic phase. Figures 3a, b, c and d show the X-ray diffraction patterns, from bottom to top, measured from room temperature to 580°C at temperature steps of 20°C, and again at RT.



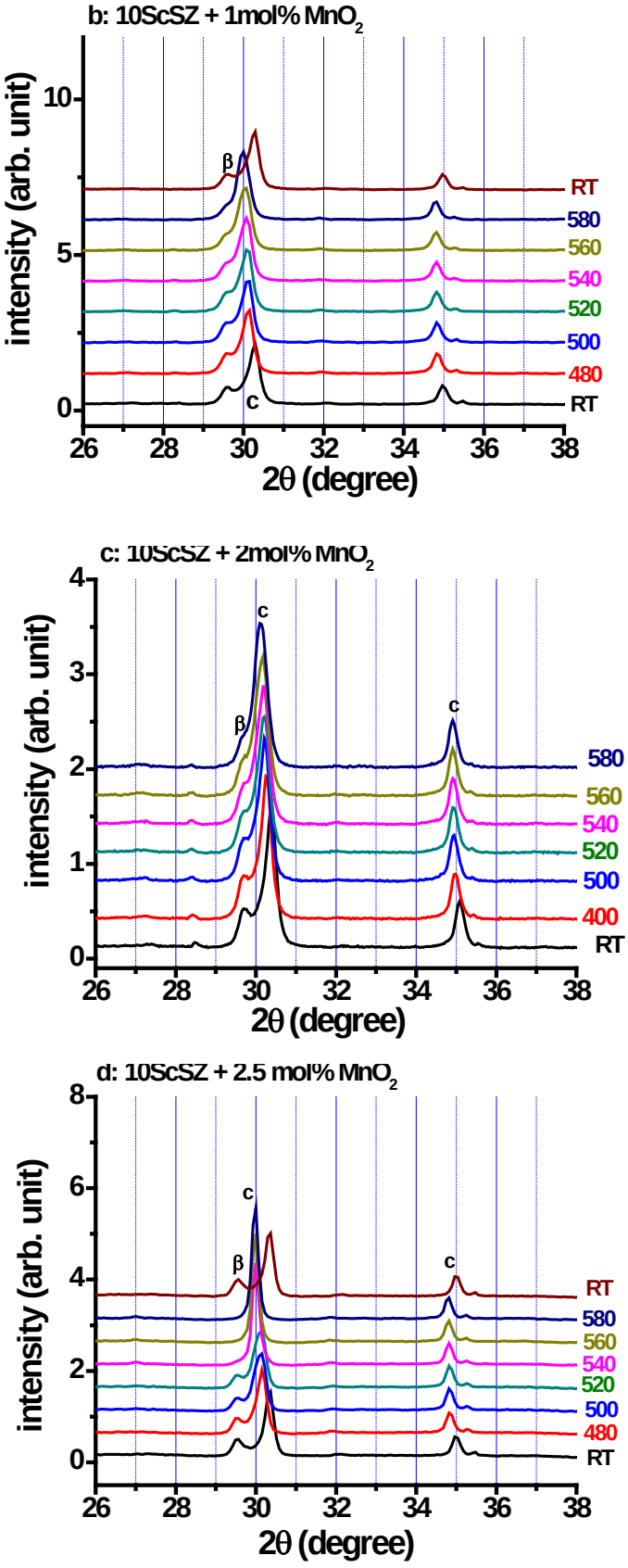


Figure 3. X-ray diffraction patterns of 10ScSZ: x mol% MnO_2 (x = 0, 1.0, 2.0 and 2.5) pellets sintered at 1500°C, measured at room temperature and from 480 to 580°C.

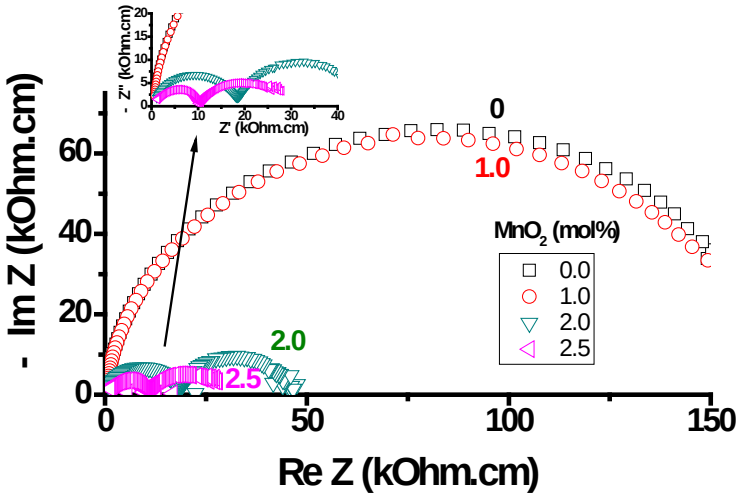


Figure 4. Impedance plots measured at 450°C of 10ScSZ: x mol% MnO_2 (x = 0, 1.0, 2.0 and 2.5) pellets sintered at 1500°C. Inset: zoom of the high frequency region.

A drastic reduction in the total electrical resistivity at 450°C is obtained in zirconia-10% scandia sintered with 2.0 and 2.5 mol% manganese dioxide addition (Figure 4). The value for the undoped ScSZ is 165 kOhm.cm while for 2.0 and 2.5 mol% MnO_2 doping levels are 45 and 28 kOhm.cm, respectively. To be considered as adequate for use as solid electrolyte in a solid oxide fuel cell, it is necessary to follow the electrical response at the temperature the cell is expected to operate. A 100 h follow up experiment was performed, the ScSZ-2.0 mol% MnO_2 being kept inside a furnace at 600°C and impedance spectroscopy measurements being carried out at different elapsed times. The results are shown in Figure 5. Even though longer aging times are required to be sure the solid electrolyte is stable from the electrical point of view to propose it to be used in Solid Oxide Fuel Cells, no appreciable decrease of the electrical conductivity is detected. An initial decrease in the total conductivity of zirconia-8 mol% scandia has been reported to depend on the aging temperature, becoming more severe for higher temperatures [5].

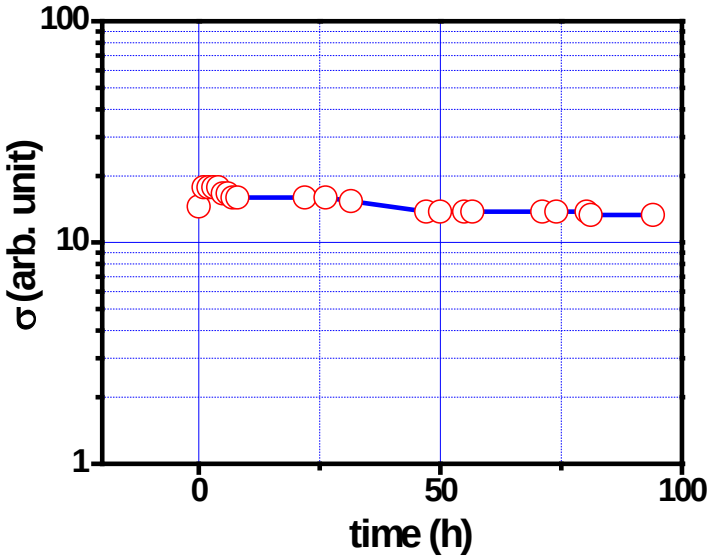


Figure 5. Values of the total electrical conductivity of ZrO_2:10 mol% Sc_2O_3 sintered at 1500°C with 2.0 mol% MnO_2 addition, measured by the impedance spectroscopy technique, as a function of the stored time at 600°C.

Conclusions

Analysis of the electrical behavior of solid electrolyte pellets of ZrO_2:10 mol% Sc_2O_3 (10ScSZ) sintered at 1500^{o}C/4 h with addition of MnO_2 shows that 2.0 mol% addition produces pellets with cubic single phase and with enhanced oxide ion conductivity in comparison to 10ScSZ. Moreover, no degradation of the total electrical conductivity is detected during ageing at 600^{o}C for 100 hours. Additional experiments are necessary on the compatibility with ceramic anode and cathode, and evaluation of the open circuit voltage during operation of the cell at that temperature for longer times.

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