

Ionic Conductivity of Zirconia-Scandia-Dysprosia Solid Electrolyte

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The effects of small additions of dysprosia (1, 1.5 and 2 mol%) to zirconia-10 mol% scandia were investigated by spectroscopic techniques. The main purpose of this work was to study the influence of the rare earth additive on the structural and electrical properties of the zirconia-scandia solid electrolyte. The compositions were prepared by solid state synthesis and the characterization techniques comprise X-ray diffraction, Raman spectroscopy and impedance spectroscopy. Fully stabilization of the cubic structure occurred for 2 mol% dysprosia addition. For lower additive contents the cubic reflections coexist with those of the β -rhombohedral phase. The additive was also found to inhibit the densification of the zirconia-scandia solid electrolyte. The activation energy for oxide ion conduction is 1.31 eV.

Introduction

Zirconia-based solid electrolytes are the preferred materials for high-temperature applications due to the combination of their electrical and mechanical properties. Zirconia containing scandia exhibits higher values of ionic conductivity at temperatures above 600 °C, lower electronic conductivity and higher chemical stability than other zirconia solid solutions (1). One of the main concerns related to this system is the complex nature of its phase composition. This structural characteristic depends on dopant content. For compositions containing less than 9-10 mol% scandia, thermal degradation of the crystalline phase occurs, whereas for higher scandia contents, the cubic phase readily decomposes giving rise to a rhombohedral phase with relatively low ionic conductivity (2).

One approach to overcome the cubic phase decomposition is by introducing a second additive. In this context, it has been shown that rare earth oxides such as ceria, gadolinia, holmia, samaria, ytterbia and yttria are good candidates for phase stabilization in the zirconia-scandia system (3-8). However, these additives influence the ionic conductivity. In general, all of them decrease the total conductivity of zirconia-scandia. A recent evaluation of the effect of the ionic radius of rare earths on the ionic conductivity of zirconia-scandia based solid electrolytes evidenced an increase of the total ionic conductivity with increasing the ionic radius up to 0.9-1.0 Å (7).

In this work, the effects of small additions of dysprosium on phase composition and ionic conductivity of zirconia-10 mol% scandia were investigated by X-ray diffraction and impedance spectroscopy.

Experimental

ZrO₂-10 mol% Sc₂O₃, 10ScSZ (Daiichi Kigenso Kagaku Kogyo, Jpn) and Dy₂O₃ (Alfa Aesar) were used as starting materials. The studied compositions, 1, 1.5 and 2 mol% Dy₂O₃, were prepared by the conventional method of mixing of oxides. Stoichiometric amounts of the starting materials were mixed together in alcoholic medium in an agate mortar followed by drying in an oven at 40 °C.

Dic-shaped specimens were prepared by uniaxial (50 MPa) and isostatic pressing (100 MPa) followed by sintering at 1500 °C for 5 h with heating rate of 5 °C.min⁻¹ and cooling down to room temperature by turning off the furnace.

Apparent density values were determined by the geometric and the immersion methods and compared to theoretical densities calculated from the lattice parameters of the several compositions. Structural characterization was performed by X-ray diffraction, XRD (D8 Advance, Bruker-AXS) using Ni-filtered Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$) in the 20-80° 2 θ range, with 0.05° step size. Indexing of the XRD patterns were done by comparison of the experimental profile with those of JCPDS 89-5483 and 51-1604 files for cubic and rhombohedral phases, respectively. Additional structural characterization was performed by Raman spectroscopy (InVia Raman Microscope, Renishaw) with excitation of a He-Ne laser with wavelength of 633 nm in the 200-800 cm⁻¹ spectral range. Microstructure characterization was carried out by scanning electron microscopy, SEM (Inspect F50, FEI). The ionic conductivity was determined by impedance spectroscopy measurements (4192A, HP) in the frequency range 5 Hz to 13 MHz and ac applied voltage 100 mV. For these measurements platinum was applied onto the large surfaces of the specimens and fired at 800 °C for 1 h to act as electrode.

Results and Discussion

Figure 1 shows XRD patterns of the studied compositions. The Miller indexes correspond to those of the cubic phase. The angular positions of the main rhombohedral peaks are indicated in the bottom of the figure.

As can be seen in those patterns, partial stabilization of the cubic phase was obtained for dysprosia additions of 1 and 1.5 mol%. Total stabilization of the cubic phase was attained in this case for dysprosia contents of at least 2 mol%. The minimum co-dopant content able to stabilize the cubic phase in the zirconia-scandia matrix may be reduced whenever the preparation of the solid solution is carried out by wet chemical methods.

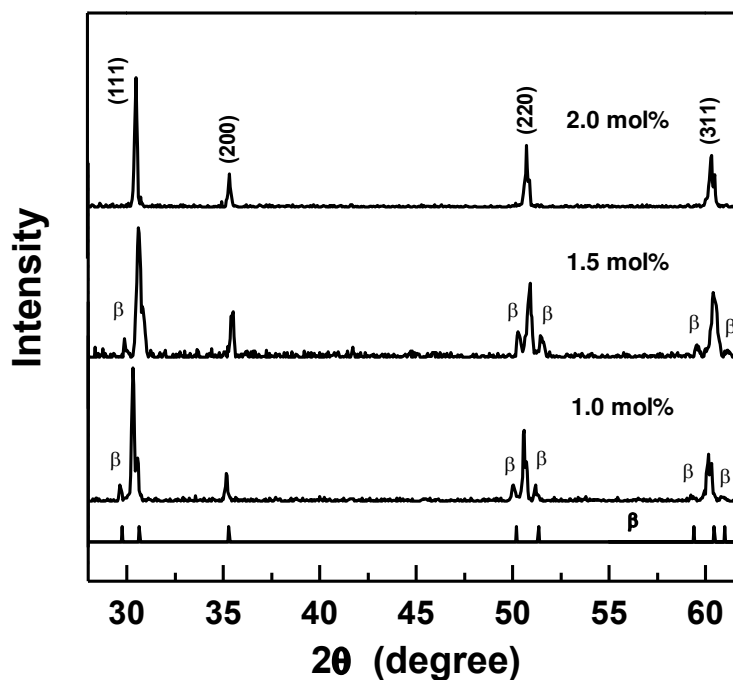


Figure 1. XRD patterns of zirconia-10 mol% scandia specimens with 1, 1.5 and 2 mol% of Dy_2O_3 .

The Raman spectrum of the specimen containing 2 mol% dysprosia is shown in Figure 2.

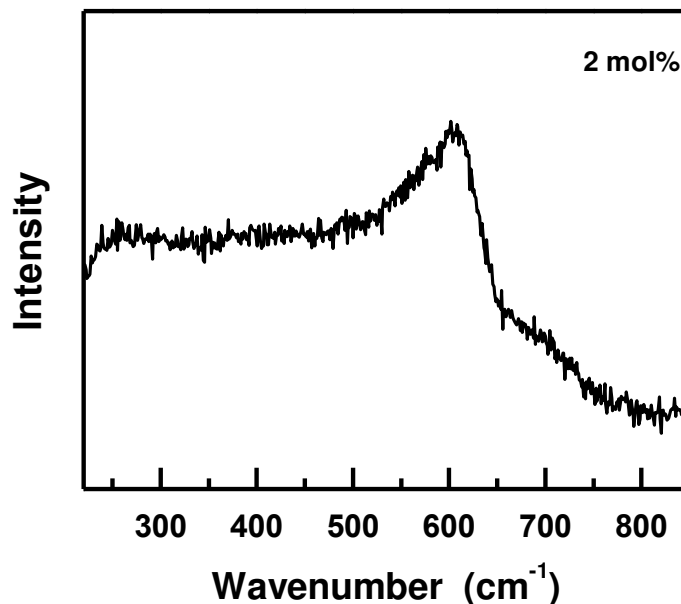


Figure 2. Raman spectrum of zirconia-10 mol% scandia-2 mol% dysprosia.

The Raman spectrum of the cubic fluorite-type phase of zirconia-scandia consists of a single F_{2g} mode centered at 620 cm^{-1} (9). No other bands are observed in that spectrum which could be attributed to other crystallographic phases, such as tetragonal with a characteristic Raman band at 480 cm^{-1} (10). This result corroborates that of XRD (Figure 1) evidencing that 2 mol% of the additive resulted in fully stabilization of the cubic phase in zirconia-scandia.

Values of sintered density are listed in Table I.

Table I. Values of relative density (ρ_R) as a function of the dysprosia content (x).

x (mol%)	ρ_R (%)
1.0	95.6 \pm 0.5
1.5	95.5 \pm 0.1
2.0	92.3 \pm 0.4

The relative density of specimens sintered at 1500 °C for 5 h are in the 92-95.5% range. Increasing the additive content resulted in decrease of the sintered density. It is remarkable the role of the sintering conditions for densification of the solid electrolyte. According to results, not shown here, the increase of the sintering temperature is relevant for increase densification before the fully stabilization of the cubic phase occurs. For example, for specimens with 1 mol% dysprosia, sintering at 1400 °C and 1500 °C for 2 h fixed time increases the relative density from 85 to 94%. In contrast, once the fully stabilization is attained (dysprosia content of at least 2 mol%), the variation of the sintering temperature and time do not impart a significant change in the relative density (\sim 92%). These results reveal that introduction of dysprosia into the zirconia-scandia crystal lattice inhibits its densification.

Figure 3 shows a fracture surface of the specimen containing 2 mol% dysprosia.

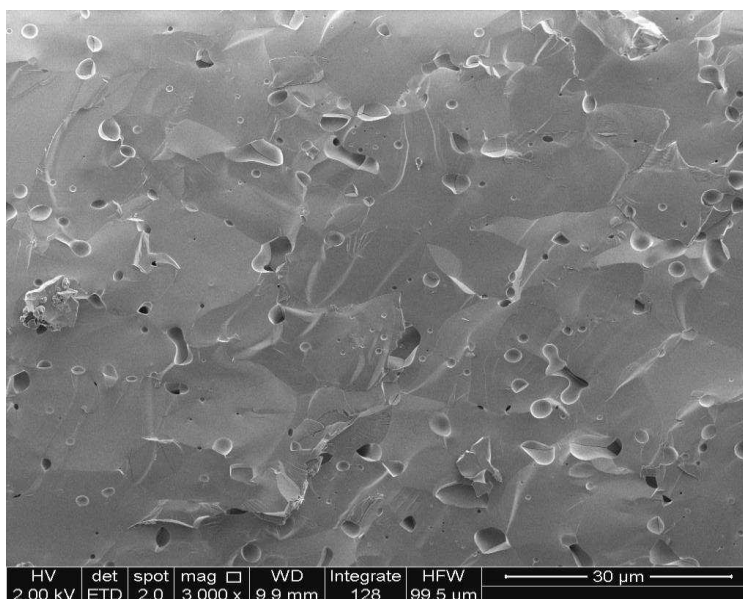


Figure 3. SEM micrograph of zirconia-10 mol% scandia-2 mol% dysprosia.

Observations of sintered specimens in a scanning electron microscope revealed that the predominant fracture mode is transgranular, the grain vary in size, but most of them are relatively large ($>$ 5 μ m), and the average size depends on sintering temperature and time.

The ionic conductivity of zirconia-10 mol% scandia containing 2 mol% dysprosia was investigated by impedance spectroscopy in the 450-800 °C range. For oxide-ion conductors, the ionic conductivity is represented in the complex plane by two semicircles attributed to the bulk (or grain) conductivity and the blocking (or grain boundary) contribution, as shown in Figure 4a for the measuring temperature of 600 °C. At high temperatures, the grain and the grain boundary contributions to the total conductivity could not be resolved. Then, only the total conductivity could be analyzed. The Arrhenius plot of total ionic conductivity is shown in Figure 4b. The behavior of the total conductivity may be represented by a single straight line.

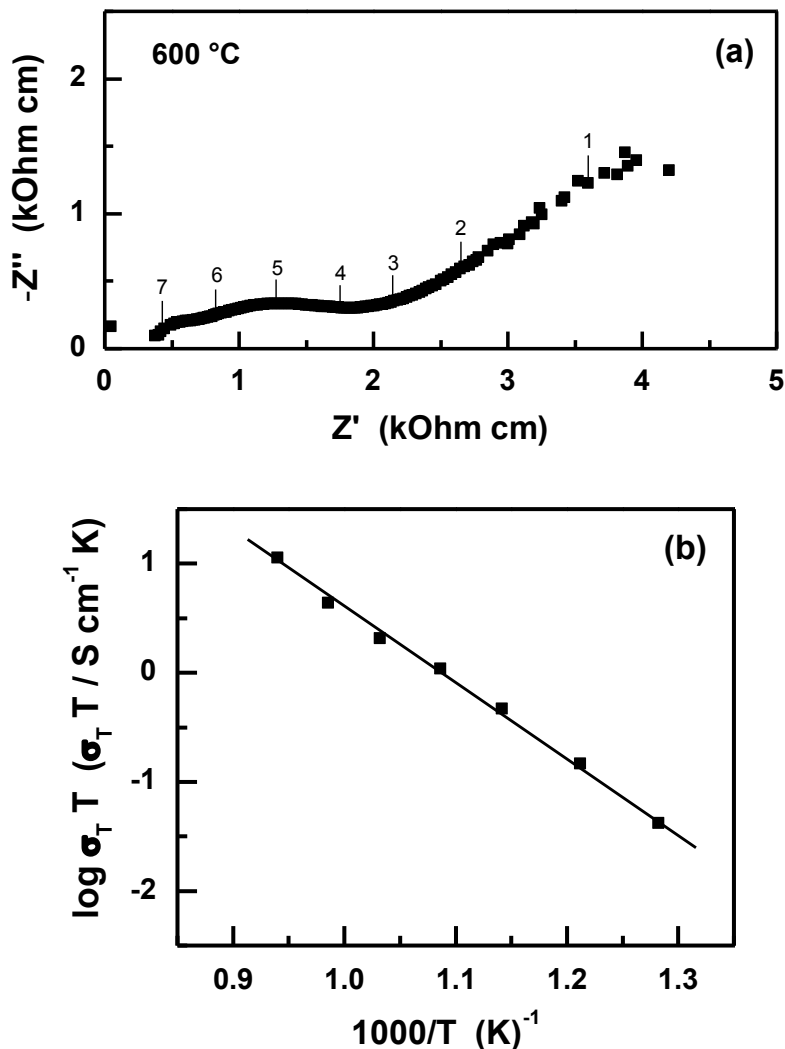


Figure 4. (a) Impedance spectroscopy diagram at 600 °C. (b) Arrhenius plot of the total ionic conductivity of zirconia-10 mol% scandia-2 mol% dysprosia.

The activation energy for conduction (1.31 eV) obtained from the slope of the straight line is similar to those of other zirconia-scandia systems containing rare earths (6-8). The ionic conductivity at 650 °C amounts 1.2 mS cm^{-1} . This value seems to be lower than those for other rare earth containing zirconia-scandia (7). However, it can be further improved by increasing the sintered density.

Conclusion

Addition of dysprosia to zirconia-10 mol% scandia leads to an increase of the cubic phase content. For dysprosia additions of at least 2 mol%, full stabilization of the cubic structure was obtained as revealed by X-ray diffraction and Raman spectroscopy results. The preferential fracture mode of sintered specimens is transgranular evidencing a good mechanical strength of the solid electrolyte. The activation energy for the total ionic conductivity is 1.31 eV.

Acknowledgments

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