Available online at www.sciencedirect.com
ScienceDirect
Journal of Power Sources 160 (2006) 892–896
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Bismuth oxide doped scandia-stabilized zirconia electrolyte for the intermediate temperature solid oxide fuel cells

S. Sarat [a], N. Sammes [b], A. Smirnova [a,*]

[a] *University of Connecticut, Department of Materials Science and Engineering, USA*
[b] *University of Connecticut, Department of Mechanical Engineering, USA*

Received 22 November 2005; received in revised form 6 February 2006; accepted 6 February 2006
Available online 22 March 2006

Abstract

Electrical and structural properties of bismuth oxide doped scandia-stabilized zirconia (ScSZ) electrolyte for solid oxide fuel cells (SOFCs) have been evaluated by means of XRD, TGA, DTA, and impedance spectroscopy. The amount of Bi_2O_3 in the ScSZ was varied in the range of 0.25–2.0 mol%. The original ScSZ samples indicated a rhombohedral crystalline structure that in general has lower conductivity than the cubic phase. However, the addition of Bi_2O_3 to ScSZ electrolyte was found to stabilize the cubic crystalline phase as detected by XRD. Impedance spectroscopy measurements in the temperature range between 350 and 900 °C indicated a sharp increase in conductivity for the system containing 2 mol% of Bi_2O_3 that is attributed to the presence of the cubic phase. In addition, impedance spectroscopy measurements revealed significant decrease of both the grain bulk and grain boundary resistances with respect to the temperature change from 600 to 900 °C and concentration of Bi_2O_3 from 0.5 to 2 mol%. The electrical conductivity at 600 °C obtained for 2 mol% Bi_2O_3 doped ScSZ was 0.18 S cm^{-1}.

Keywords: Electrolyte; ScSZ; Doping; Bismuth oxide; SOFC

1. Introduction

Decreasing the operation temperature of SOFCs and SOFC stacks is one of the most significant objectives being addressed in relation to increasing system reliability, operation life, and reducing the fuel cell fabrication and balance of plant costs [1,2]. To meet these goals, alternative electrolytes with higher oxygen ion conductivity are being investigated.

Zirconia based oxides are considered the best candidates for SOFC electrolytes, and among them scandia stabilized zirconia is known to exhibit the highest conductivity, which has been attributed to the low association enthalpy of the defect reactions and the similarity between the ionic radii of Sc^{3+} and Zr^{4+} ions [3–5]. At 780 °C the conductivity values of ScSZ correspond to those of YSZ at 1000 °C [1,6].

Yamamoto [1] observed that samples with a low content of Sc_2O_3 (7–9 mol%) sintered at 1700 °C for 12 h show monoclinic and tetragonal phases. The samples with a higher content of Sc_2O_3 (10–15 mol%) demonstrate rhombohedral phase which at 600 °C transforms to cubic phase, observed to have the highest conductivity because of the open structure and enhanced mobility of charge carriers. The presence of a rhombohedral phase in the ScSZ system has been explained by the fact that the radius of the scandium cation is approximately the same as that of zirconium [7].

However, regarding stability of doped zirconia ceramics, at low concentrations of Sc_2O_3 (8 mol%) ScSZ showed significant aging effects and a decrease in conductivity at the annealing at 1000 °C, that fortunately has not been observed for 11ScSZ and 12ScSZ [7]. More recent work by Haering et al. [8] confirmed this result and indicated that ScSZ electrolyte with more than 10 mol% Sc_2O_3 did not show any decrease in conductivity by annealing at 1000 °C.

Further, 9YSZ [9] which shows a conductivity lower that of 9ScSZ [7,8] is known to possess the aging effect at temperatures of about 1000 °C that could be critical for SOFC operation. On the contrary, ScSZ electrolyte with 10 or more mol% do not show any decrease in conductivity, but undergo a cubic-rhombohedral phase transformation at a temperature of about 500 °C, and demonstrates the highest conductivity at 1000 °C.

* Corresponding author. Tel.: +1 860 428 0446; fax: +1 860 428 8378.
E-mail address: alevtina@engr.uconn.edu (A. Smirnova).

0378-7753/$ – see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.jpowsour.2006.02.007

The goal of the present study was to investigate the structure of bismuth oxide doped scandia stabilized zirconia electrolyte (10 mol% Sc_2O_3) and correlate the effect of the addition of Bi_2O_3 on the microstructure of ScSZ with the electrical properties of these systems evaluated by means of impedance spectroscopy.

2. Experimental

10ScSZ (Tosoh, Japan) and Bi_2O_3 (ASARCO, Phoenix, AZ) were sintered at different temperatures (1450, 1500, and 1550 °C) during 2 h to achieve the desired (>95%) density. The crystalline structure of the precursor and doped materials were studied using X-ray diffraction.

Bulk density measurements were performed for the sintered pellets after boiling them in distilled water for 2 h to ensure that all pores are filled with water. This procedure has been followed by Archimedes technique using a density determination kit with top-loading AB 204-S Mettler Toledo electronic balance.

The phase transitions were confirmed by differential scanning calorimetry (DSC) analysis. Differential thermal analysis (DTA) was performed on the sintered powder samples using SDT Q600V Differential Scanning Calorimeter. The heat flow and weight change were measured during a temperature scan between 20 and 1000 °C. A scan rate of 1 °C min^{-1} was used for the test.

Electrical properties of the sintered pellets were analyzed using the AC frequency response analyzer SI 1250 and electrochemical interface SI 1287. The measurements were conducted using a two-probe configuration with Ag electrodes in the temperature range of 300–700 °C with 50 °C increment. The Z-plot software from Scribner Associates Inc. was used in this study to measure and analyze the impedance spectra.

Calculation of the conductivity (σ) from the corresponding equivalent circuit for each sample was made using the following expression:

$$\sigma = \frac{L}{R_1 A} + \frac{L}{R_2 A}$$

where L is the thickness of the sample (cm); A the area of the contact between the sample pellet and the electrodes expressed (cm^2); R_1 and R_2 are the resistances (Ω) obtained from the fitting procedure.

3. Results and discussion

3.1. Characterization of crystalline structure

Modification of 10ScSZ with Bi_2O_3 has been made at 0.25, 0.5, 0.75, 1.0 and 2.0 mol%. However, the as received sample of 10ScSZ was tested before and after sintering at 1000 °C for comparison. The XRD patterns for the sintered and unsintered original 10ScSZ samples are presented in Fig. 1.

Distinct peaks of the cubic (c) and rhombohedral β-phase (β) which is the expected crystalline phase for 10ScSZ at room temperature were obtained for the powder sintered at 1000 °C. The unsintered sample showed mostly cubic crystalline structure

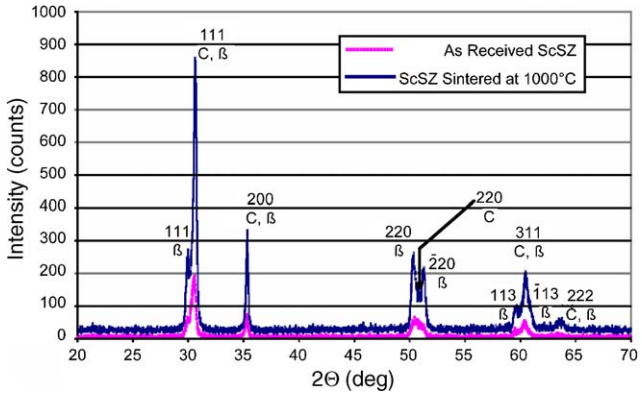

Fig. 1. XRD patterns of ScSZ taken at room temperature from the Tosoh, Japan "as received" (dashed line) powder and the same powder sintered at 1000 °C (solid line).

indexed as 1 1 1, 2 0 0, 2 2 0, 3 1 1, 2 2 2 for the cubic and 1 1 1, 2 2 0, 1 1 3, 3 1 1 and 2 2 2 for the rhombohedral phase which is in agreement with earlier studies obtained for the same 10ScSZ material [10]. The intensity of the peaks for the sintered sample was about five times greater than that for the unsintered sample which can be attributed to an increase in the size of 10ScSZ particles during the sintering process.

It is known that a sintering temperature of approximately 1300 °C is necessary for commercially available powder of 10ScSZ composition. In comparison to pure 10ScSZ, the sintering process for the Bi_2O_3 modified system can be reached at lower temperatures since Bi_2O_3 is considered to be one of the aids for sintering, e.g. the additive that decreases the sintering temperature of ceramics. However, it has been shown [11] that the electrical conductivity of 10ScSZ doped with 1 mol% Bi_2O_3 sintered at 1200 °C is higher (0.33 S cm^{-1}) at 1000 °C in comparison to the electrical conductivity of 1Bi10ScSZ sintered at 1050 °C (0.197 S cm^{-1}). The corresponding effect has been explained by a decrease of grain boundary resistance.

In this work the higher sintering temperatures, specifically 1450, 1500, and 1550 °C, were chosen for the synthesis of Bi_2O_3 doped 10ScSZ electrolyte materials. The room temperature XRD spectra obtained for the 10ScSZ doped with 0.5 mol% Bi_2O_3 and sintered at three different temperatures (Fig. 2) showed distinct peaks of the cubic and rhombohedral phases. The peak intensities increased with the increase of the sintering temperature that indicates enhance in crystallite size. Moreover, no shifts in diffraction angles were noticed with increase of the temperature indicating that the change in sintering temperature does not significantly alter the lattice spacing.

It is known that for most of the cubic and rhombohedral phases the diffraction angles are very close except for the 2 2 0 peak that imply the possibility of receiving information about the ratio of cubic and rhombohedral crystal phases. Thus, evaluation of the amount of each of the two existing phases in Bi_2O_3 doped 10ScSZ was based on the analysis of this peak located in our case at 5.07–5.08 $2\Theta^\circ$. The enlarged XRD patterns of the 2 2 0 peaks of 10ScSZ doped with different concentrations of Bi_2O_3 in the range of 0.0–2.0 mol% are presented in Fig. 3a and b. The 2 2 0 peak corresponding to the cubic phase was observed for

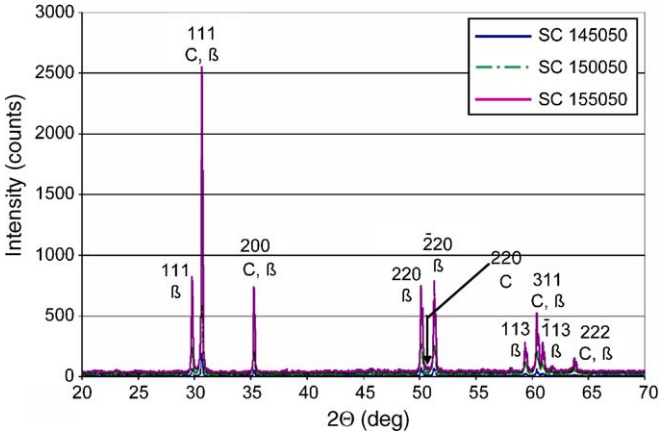

Fig. 2. XRD patterns of ScSZ with 0.5 mol% Bi_2O_3 sintered at 1450, 1500, and 1550 °C.

the concentrations of Bi_2O_3 greater than 0.5 mol%. This cubic phase cannot be seen without the presence of Bi_2O_3 and is mostly stabilized at the highest (2 mol%) of the dopant. However, the peaks corresponding to the rhombohedral phase can be seen for all compositions.

The lattice parameters calculated from the XRD data have been used for the evaluation of the spacing between the lattice planes using Bragg's law, where the cubic plane 1 1 1 was taken as a reference. The lattice parameters for three different samples sintered at 1450, 1500, and 1550 °C did not significantly change with the concentration of Bi_2O_3 and were in the range of 5.05 ± 0.01 Å which deviation can be related to the variation in measurements.

Theoretical density of all of the sintered samples was calculated using the corresponding lattice parameters. The estimated density values were higher than 95% that meets the requirement for the SOFC electrolyte material.

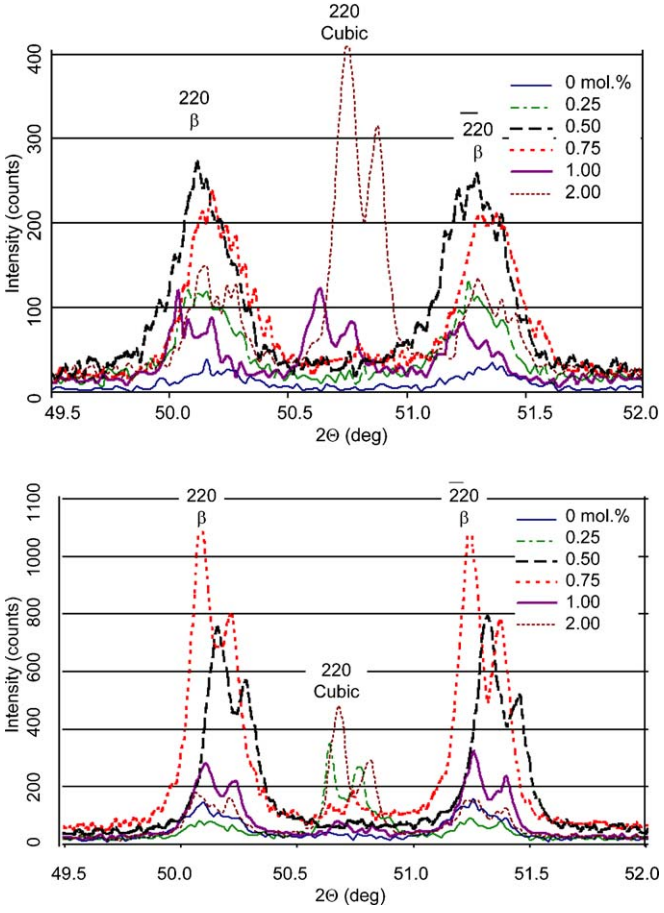

Fig. 3. XRD patterns of ScSZ with 0, 0.25, 0.5, 0.75, 1.0, and 2.0 mol% Bi_2O_3 sintered at (a) 1450 °C, and (b) 1550 °C.

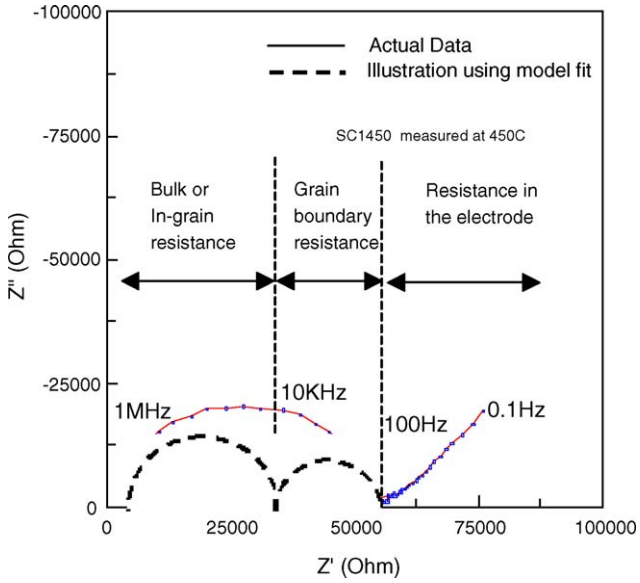

Fig. 4. Impedance spectra of 10ScSZ sintered at 1450 °C (SC1450) and measured at 450 °C (solid line – experimental data, dashed line – result of fitting procedure).

3.2. Electrical properties of 10ScSZ

The electrical conductivity measurements for 10ScSZ doped with 0.25, 0.5, 0.75, 1.0 and 2.0 mol% of Bi_2O_3 using AC

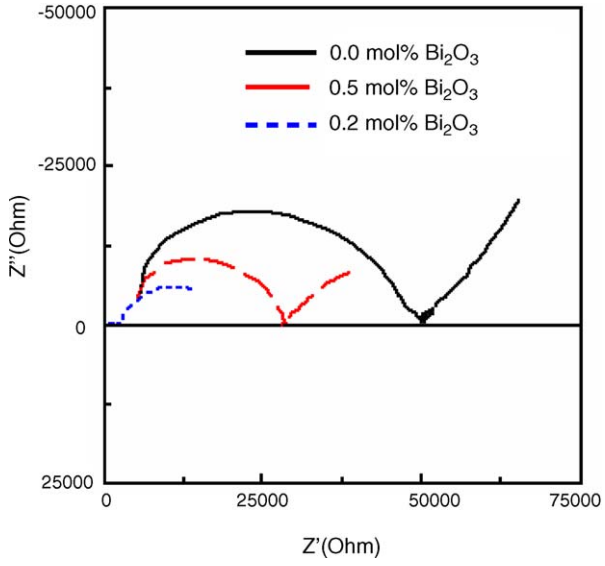

Fig. 5. Impedance plots of the 10ScSZ samples sintered at 1500 °C with #1—0, #2—0.5, and #3—2.0 mol% of Bi_2O_3 measured at 450 °C.

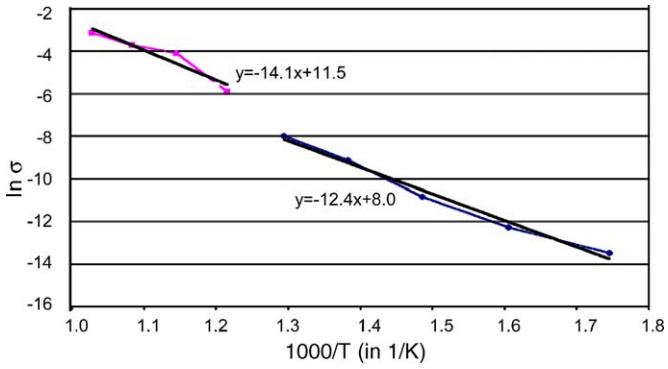

Fig. 6. Arrhenius plot for 10ScSZ sintered at 1450 °C.

impedance spectroscopy were performed in the temperature range between 350 and 1000 °C. The results of AC impedance measurements carried out at 450 °C (Fig. 4) indicate the depressed semicircle that can be attributed to the combination of grain and boundary resistances.

The equivalent circuit comprising of two RC circuits in series with electrolyte resistance [12] has been used for the interpretation of the impedance spectra and evaluation of the grain and grain boundary components contribution. The fitting result (dashed line) demonstrates two semicircles related to the bulk resistance in the high frequency range and grain boundary resistance in the range below 10 KHz. In the range of low frequencies the resistance of the electrode interfaces becomes more pronounced.

The influence of the Bi_2O_3 content in the 10ScSZ electrolyte on the grain and grain boundary conductivity (Fig. 5) indicates that significant improvement can be reached while increasing the concentration of the dopant especially in comparison to the non-modified 10ScSZ sample.

Conductivity as a function of temperature for the undoped 10ScSZ sample sintered at 1450 °C (Fig. 6) demonstrated a change in slope at about 500 °C explained by phase transformation from rhombohedral crystalline phase to a cubic phase and confirmed by the corresponding TGA/DTA data and high temperature XRD analysis (Fig. 7a and b). The TGA/DTA analysis (Fig. 7a) indicates the exothermic peak at 555 °C which is caused by a phase transition from rhombohedral to cubic phase followed by a small increase in mass probably due to the gain of non-stoichiometry oxygen. The XRD data obtained at room temperature (Fig. 1) show a predominantly rhombohedral phase, however at 600 °C (Fig. 7b) the presence of mostly cubic phase have been detected. The sharp peaks were observed for the 1 1 1,

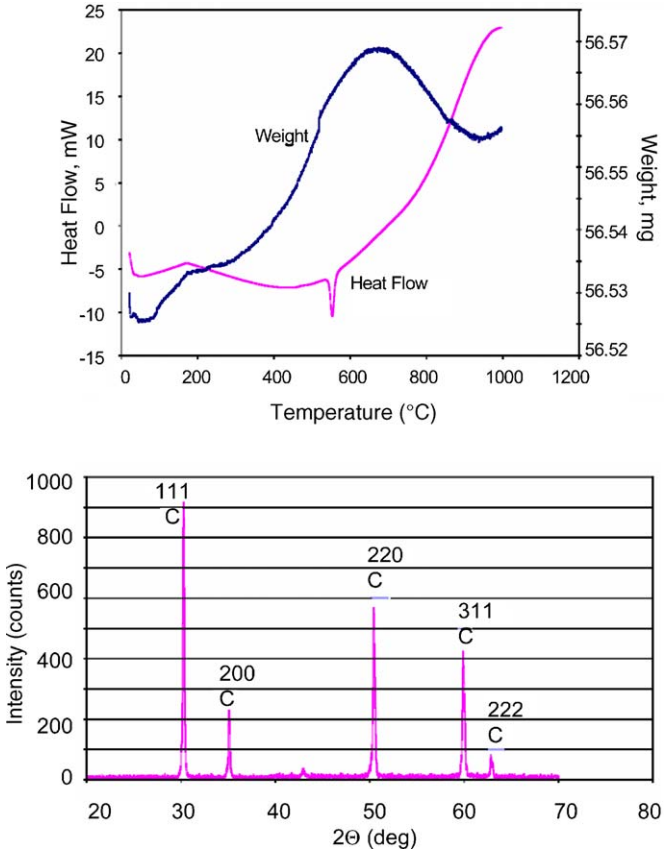

Fig. 7. (a) TGA and DTA plot for 10ScSZ sintered at 1450 °C. (b) High temperature XRD at 600 °C for 10ScSZ sintered at 1450 °C.

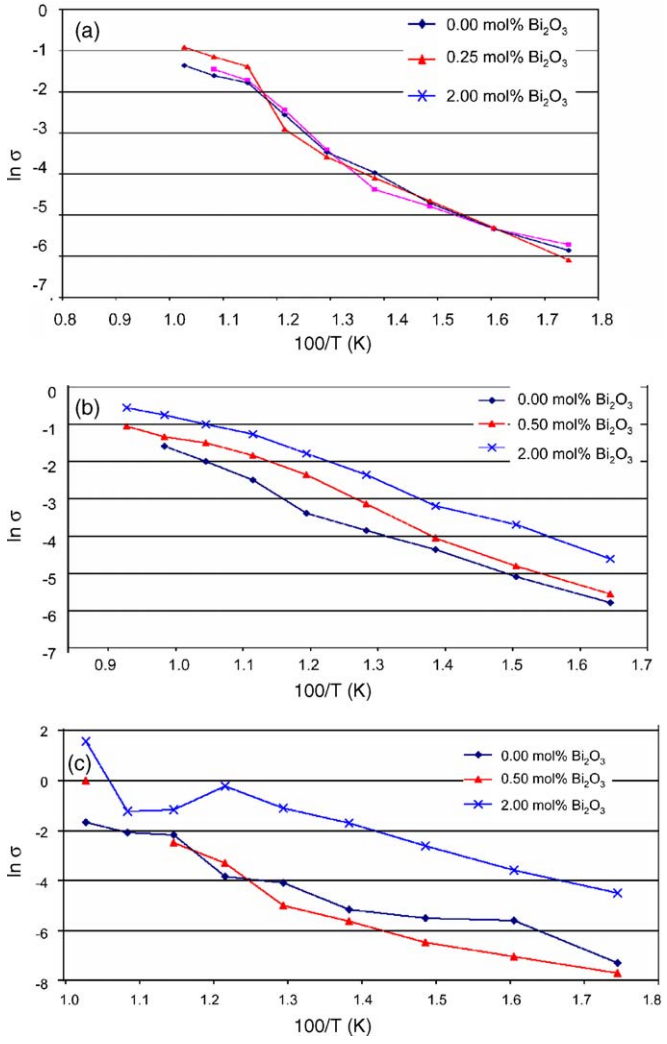

Fig. 8. (a–c) Arrhenius plots for 10ScSZ with 0.00, 0.25, and 2.00 mol% Bi_2O_3 sintered at (a) 1450 °C, (b) 1500 °C, and (c) 1550 °C.

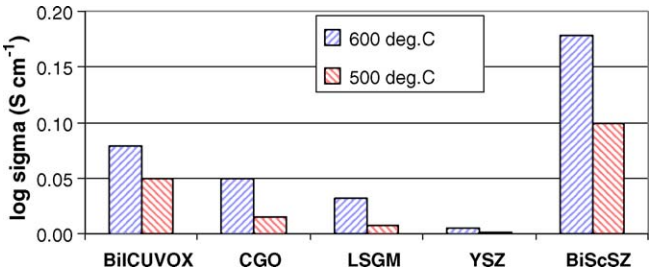

Fig. 9. Total conductivity at 600 and 500 °C of 2 mol% Bi_2O_3 doped ScSZ in air sintered at 1500 °C in comparison to other most promising oxide ion conductors [13].

2 0 0, 2 2 0, 3 1 1, and 2 2 2 diffraction planes that are characteristic of a cubic structure of 10ScSZ electrolyte.

The Arrhenius plots for doped 10ScSZ samples with 0.25 mol% and sintered at 1450 and 1500, and 1550 °C are shown in Fig. 8a–c. It can be seen that the slopes remain almost constant in the whole temperature range between 350 and 1000 °C and the values of activation energy are about 60–80 kJ mol^{-1} that correspond to the results published earlier for ScSZ system. For all sintering temperatures the electrical conductivity showed significant enhancement with increase of the bismuth oxide concentration. The highest conductivity values for the samples with 2% of Bi_2O_3 were 2.5×10^{-4} S cm^{-1} at 350 °C and 0.18 S cm^{-1} at 600 °C. In comparison to other most promising oxide ion conductors [13], such as $Bi_2V_{1.9}Cu_{0.1}O_{1.95}$ (BICUVOX), $Ce_{0.90}Gd_{0.10}O_{1.95}$ (CGO), $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ (LGSM), and $(ZrO_2)_{0.90}(Y_2O_3)_{0.10}$ (YSZ), the 2 mol% Bi_2O_3 doped ScSZ electrolyte demonstrated much higher total conductivity values in the intermediate temperature (Fig. 9). However, additional studies are needed to estimate the long-term stability and degradation rates of these materials at different temperatures in presence of oxidizing and reducing atmospheres.

4. Conclusion

The effect of Bi_2O_3 addition of on the structure and electrical properties of 10ScSZ has been studied. The undoped samples (10ScSZ) indicated a rhombohedral crystalline structure at room temperature, which has lower conductivity than the cubic phase. At higher temperatures a transformation to cubic phase occurs. A sharp increase in conductivity has been detected, that indicates that higher temperatures are required to ensure complete transformation of 10ScSZ to a cubic phase.

Addition of Bi_2O_3 was found to stabilize the cubic phase at lower temperatures that have been confirmed by room temperature XRD measurements. The highest conductivity at 600 °C (0.18 S cm^{-1}) has been observed for the samples with 2 mol% of Bi_2O_3.

These results presents a basis for the understanding of bismuth oxide doped ScSZ systems thereby enhancing design of a new generation of low temperature ionically conducting ceramic materials that can be utilized in hydrogen separation membranes, electrolyzes, and power conversion devices using a highly efficient and environmental friendly technology.

References

[1] O. Yamamoto, Solid oxide fuel cells: fundamental aspects and prospects, Electrochim. Acta 45 (15/16) (2000) 2423–2435.
[2] Y. Mizutani, M. Tamura, M. Kawai, O. Yamamoto, Development of high-performance electrolyte in SOFC, Solid State Ionics 72 (1994) 271–275.
[3] D. Lee, I. Lee, Y. Jeon, R. Song, Characterization of scandia stabilized zirconia prepared by glycine nitrate process and its performance as the electrolyte for IT-SOFC, Solid State Ionics 176 (11/12) (2005) 1021–1025.
[4] M. Okamoto, Y. Akimune, K. Furuya, M. Hatano, M. Yamanaka, M. Uchiyama, Phase transition and electrical conductivity of scandia-stabilized zirconia prepared by spark plasma sintering process, Solid State Ionics 176 (7/8) (2005) 675–680.
[5] C. Varanasi, C. Juneja, C. Chen, B. Kumar, Electrical conductivity enhancement in heterogeneously doped scandia-stabilized zirconia, J. Power Sources 147 (1/2) (2005) 128–135.
[6] Y. Mizutani, K. Hisada, K. Ukai, H. Sumi, M. Yokoyama, Y. Nakamura, O. Yamamoto, From rare earth doped zirconia to 1 kW solid oxide fuel cell system, J. Alloys Compd. (2005) (available online 11th July).
[7] O. Yamamoto, Y. Arati, Y. Takeda, N. Imanishi, Y. Mizutani, M. Kawai, Y. Nakamura, Electrical conductivity of stabilized zirconia with ytterbia and scandia, Solid State Ionics 79 (1995) 137–142.
[8] C. Haering, A. Roosen, H. Schichl, M. Schnöller, Degradation of the electrical conductivity in stabilised zirconia system. Part II. Scandia-stabilized zirconia, Solid State Ionics 176 (3/4) (2005) 261–268.
[9] C. Haering, A. Roosen, H. Schichl, M. Schnöller, Degradation of the electrical conductivity in stabilised zirconia systems. Part I. Yttria-stabilized zirconia, Solid State Ionics 176 (3/4) (2005) 253–259.
[10] M. Hirano, T. Oda, K. Ukai, Y. Mizutani, Effect of Bi_2O_3 additives in Sc stabilized zirconia electrolyte on stability of crystal phase and electrolyte properties, Solid State Ionics 158 (2003) 215–223.
[11] M. Hirano, T. Oda, K. Ukai, Y. Mizutani, Effect of Bi_2O_3 additives in Sc stabilized zirconia electrolyte on a stability of crystal phase and electrolyte properties, Solid State Ionics 158 (2003) 215–223.
[12] A. Smirnova, G. Crosbie, E. Ellwood, Application of Fourier based transforms to impedance spectra of small diameter tubular solid oxide fuel cells, JES 148 (2001) 610–615.
[13] S.J. Skinner, J.A. Kilner, Oxygen ion conductors, Mater. Today 6 (3) (2003) 30–37.