

## Synthesis, sintering and conductivity behavior of ceria-doped Scandia-stabilized zirconia



Hari Prasad Dasari, Jun Sung Ahn, Kiyong Ahn, Sun-Young Park, Jongsup Hong, Hyoungchul Kim, Kyung Joong Yoon, Ji-Won Son, Hae-Weon Lee, Jong-Ho Lee\*

High-Temperature Energy Materials Center, Future Convergence Research Division, Korea Institute of Science and Technology, 39-1, Hawolgok-dong, Seongbuk-gu, Seoul 136-791, Republic of Korea

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### ABSTRACT

In this work, the effect of ceria addition on the phase formations, sinterability and electrical conductivity of 10 mol.% scandia stabilized zirconia (SSZ) is investigated. Ceria co-doped SSZ (SSZ- $x$ CeO<sub>2</sub> ( $x = 0.5, 1.0, 5.0$  mol.%)) powders were successfully synthesized by glycine-nitrate process and the electrical conductivity was measured in the temperature range of 600–900 °C. Fourier-transform infrared spectroscopy (FT-IR) analysis showed that the samples sintered at 1300 °C/3 h are free from impurities such as un-decomposed nitrates, residual water and nitrile intermediates. From the X-ray diffraction (XRD) analysis, the sintered samples results revealed that the presence of cubic and rhombohedral  $\beta$ -phases and Raman spectroscopy analysis further revealed the presence and monoclinic and tetragonal phases. From the linear shrinkage spectra, a linear shrinkage of 27% was observed at 1300 °C for SSZ and was decreased with the increase of cerium oxide content. The electrical conductivity has been decreased with the increase of ceria content and the SSZ-0.5CeO<sub>2</sub> sample displayed a higher electrical conductivity compared to others indicating that as small as 0.5 mol.% CeO<sub>2</sub> doping in SSZ is enough to ensure good conductivity results for its potential application as an electrolyte material in intermediate-temperature solid oxide fuel cells (IT-SOFCs).

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### 1. Introduction

Zirconia-based oxides were extensively investigated for applications like solid oxide fuel cells (SOFCs), solid oxide electrolysis cells (SOECs), oxygen sensors and catalysts [1–5]. Even though yttria stabilized zirconia (YSZ) has long been used as an electrolyte material in SOFCs it requires a high temperature (800–1000 °C) for adequate ionic conductivity [6,7]. Long-term exposure to such a high temperatures leads to the degradation of SOFC components [5,8]. This has led to efforts to develop new electrolyte materials which exhibit sufficient ionic conductivity in intermediate temperature (700–850 °C) range in order to reduce the operating temperature of SOFCs. Among the zirconia-based oxides, scandia stabilized zirconia (SSZ) displays high oxygen conductivity and low association enthalpy of the defect interactions [9–11]. All these superior electrolytic properties of SSZ are substantially originated from the similarity in the ionic radii of Sc<sup>3+</sup> and Zr<sup>4+</sup> ions [12,13]. Therefore this material system is a very attractive electrolyte material for intermediate temperature solid oxide fuel cells (IT-SOFCs).

The amount of Sc<sub>2</sub>O<sub>3</sub> content in SSZ plays an important role in controlling the structural phase and thus affects the conductivity of the material. The Sc<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> system with a scandia content less than 9 mol.%, exhibits

conductivity bends around 650 °C, very much like the Y<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> system. For high dopant levels (>9 mol.%), step-wise transitions accompanied by a cubic–rhombohedral transition occur in Sc<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> [14]. For the structure of low-temperature rhombohedral phase observed between 9 and 15 mol.% Sc<sub>2</sub>O<sub>3</sub>, vacancy-ordered phases are considered to be responsible for the conductivity deterioration. The presence of a rhombohedral phase in the SSZ material system has been explained by the fact that the ionic radii of Sc<sup>3+</sup> and Zr<sup>4+</sup> are very similar [15]. Hearing et al. [16] manifested that the SSZ material with more than 10 mol.% Sc<sub>2</sub>O<sub>3</sub> did not show any decrease in conductivity by annealing at 1000 °C. The Sc<sub>2</sub>O<sub>3</sub> content was fixed to 10 mol.% in the present study after noting these key observations.

The high conductive cubic phase of the SSZ material is not stable at lower temperatures (<650 °C), which has been the cause for an abrupt decrease in ionic conductivity upon cooling [17–22]. In order to overcome this problem many attempts were made to stabilize the cubic phase of SSZ even at low temperatures, which is favorable as an electrolyte material for IT-SOFCs. Many researchers have proposed various additional dopants like CeO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>, Yb<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> to reduce or prohibit such an undesirable phase transition as from a high conductive cubic phase to low conductive rhombohedral or tetragonal phases [15,21–24].

The SSZ powders were usually synthesized using techniques such as conventional ceramic method [7,25], co-precipitation [26,27], homogeneous precipitation [28], sol-gel method [29,30], urea-based hydrothermal method [31], solid-state reaction [32] and thermal-

\* Corresponding author. Tel.: +82 29585532; fax: +82 29585529.  
E-mail address: [jongho@kist.re.kr](mailto:jongho@kist.re.kr) (J.-H. Lee).

decomposition of the precursor complexes or gel combustion process/glycine-nitrate-process (GNP) [33,34]. GNP is a combustion process which is found to be the most suitable method for producing fairly fine, homogeneous and complex compositional metal oxide powders [35]. Apart from this, GNP has many other advantages such as relatively low cost, high energy efficiency, fast heating rates, short reaction times and high compositional homogeneity [36–38].

The aim of the present investigation is to characterize nano-crystalline cerium oxide doped SSZ material synthesized by GNP method. The structural properties and morphology of the powders were studied by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), Brunauer, Emmett and Teller (BET) surface area, Raman spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis. Dilatometric studies were carried out to understand the sintering behavior of the samples. Finally, effect of cerium oxide addition on the microstructure of SSZ was determined by the above said spectroscopies along with the electrical properties that were determined by DC conductivity measurement.

## 2. Experimental

### 2.1. Glycine-nitrate process

SSZ- $x$ CeO<sub>2</sub> ( $x = 0.5, 1.0, 5.0$  mol.%) nano-powders were successfully obtained by the GNP method and the synthesis procedure was reported elsewhere where CeO<sub>2</sub>-ZrO<sub>2</sub> and Gd<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> systems were prepared [39–41]. Zirconyl (IV) nitrate hydrate (Acros Chemicals), scandium (III) nitrate hydrate (Aldrich Chemicals) and cerium nitrate hexa-hydrate (Kanto Chemicals) were used as the sources of Zr, Sc and Ce, respectively. Glycine (Junsei Chemicals) was used as a combustion fuel for GNP. In this typical GNP method, for 10 mol.%SSZ-1 mol.%CeO<sub>2</sub> (SSZ-1CeO<sub>2</sub>) powders, stoichiometric amounts of zirconyl (IV) nitrate hydrate and scandium (III) nitrate hydrate and cerium nitrate hexa-hydrate were taken to obtain the (ZrO<sub>2</sub>)<sub>0.89</sub>(Sc<sub>2</sub>O<sub>3</sub>)<sub>0.10</sub>(CeO<sub>2</sub>)<sub>0.01</sub> solid-solution with a desired molar ratio of 1: 0.22472: 0.01124. These chemical compounds were dissolved in distilled water and 0.55 mole of glycine was added for each mole of nitrate. The mixture was heated on a hot plate to evaporate water present in the solution. Combustion was carried out in a large volume beaker on a hot plate being installed in a fume hood. The beaker was covered with a nickel mesh to confine the ash within the reaction chamber. The solution heated on the hot plate was thickened and ignited. The obtained powder was collected from the reaction chamber, ball milled and calcined at 600 °C for 2 h in air. Similarly, SSZ, SSZ-0.5CeO<sub>2</sub> and SSZ-5CeO<sub>2</sub> powders were also synthesized as stated above. The obtained powders were ground in an agate mortar and then pressed into pellets via cold isostatic pressing (CIP) under a pressure of 150 MPa. All the pellets were sintered at 1600 °C in air for 5 h for the characterization of microstructure and electrical properties. All the properties were measured in similar conditions.

### 2.2. Characterizations

Infrared spectra of the samples were recorded in the 400–4000 cm<sup>-1</sup> range (IR 300 Spectrometer, Thermo Mattson) by preparing KBr (Merck for spectrometry) pellets (0.5 wt.% sample). The phase analysis of the samples was carried out via X-ray diffractometer (PW 3830 X-ray generator) whereas scanning electron microscopy (XL-30 FEG ESEM) was used for the micro-structural analysis such as size, shape and morphology of the obtained powder and its agglomerates. The crystallite size was determined by means of Scherrer's equation,  $D_{XRD} = 0.9\lambda/\beta \cos \theta$ , where  $D_{XRD}$  is the crystallite size,  $\lambda$  is the wavelength of the radiation,  $\beta$  is the corrected peak width at half-maximum intensity and  $\theta$  is the peak position. Raman spectroscopy was also used to identify the existing phases, because the vibrational modes are strongly dependent on the crystal structure and composition. Raman spectra in the wave number

range of 150–800 cm<sup>-1</sup> were obtained using a Raman system (T 64000, Jobin-Yvon) with a triple spectrometer and charged-coupled device (CCD) detector. The Raman scattering was excited by an Ar<sup>+</sup> ion laser source (wave length 514 nm). The specific surface area of powders was measured by BET (Quantachrome Corporation Autosorb, U.S.A). The average equivalent particle size is calculated from the BET surface area of the powders using the equation,  $D_{BET} = 6000/(\rho \cdot S_w)$ , where  $D_{BET}$  is the average diameter of the particle,  $\rho$  is the theoretical density and  $S_w$  represents the BET surface area of the powder.

### 2.3. Sintering and conductivity measurements

Shrinkage of the green bodies was measured with a dilatometer (Netsch Dil 402C/3/G, Germany) in air, operated from 50 to 1300 °C (heating rate 3 °C min<sup>-1</sup>, flow rate 50 ml min<sup>-1</sup>). The relative density of the prepared samples was estimated by using the relation: relative density (%) = ( $d_m / d_{th}$ ) × 100, where  $d_m$  is the density of the samples measured using Archimedes method and  $d_{th}$  is the theoretical density of the SSZ sample. Conductivity measurement was performed for the samples with high relative density over 90% to avoid any disturbance from porosity. In order to get sufficient density for the conductivity measurement, all the specimens were sintered at relatively higher temperature of 1600 °C for 5 h. To measure the electrical conductivity of the samples a DC four-point probe method has been employed. The sintered specimen was cut into the shape of bars using a low speed saw (Buehler, USA) and four platinum wire electrodes were wrapped around the sample. A non-fluxed platinum paste was painted on the platinum wires to improve the contact resistance. The current source (Keithley 224, USA) was used to supply the current and the voltage drop across the probes was measured with a digital multi-meter (Keithley 2000, USA). The electrical conductivity was calculated from the slope of the  $I$ - $V$  curve and the corresponding shape factors of the samples.

## 3. Results and discussion

### 3.1. FT-IR analysis

FT-IR spectra of SSZ-1CeO<sub>2</sub> for as-prepared, calcined and sintered samples are shown in Fig. 1. The features in the IR spectra are bands in the region 1200–1700 cm<sup>-1</sup> (region I) and 3000–3500 cm<sup>-1</sup> (region II) ranges. It can be noticed from the figure that as the calcination temperature increases these bands are disappeared. The bands in

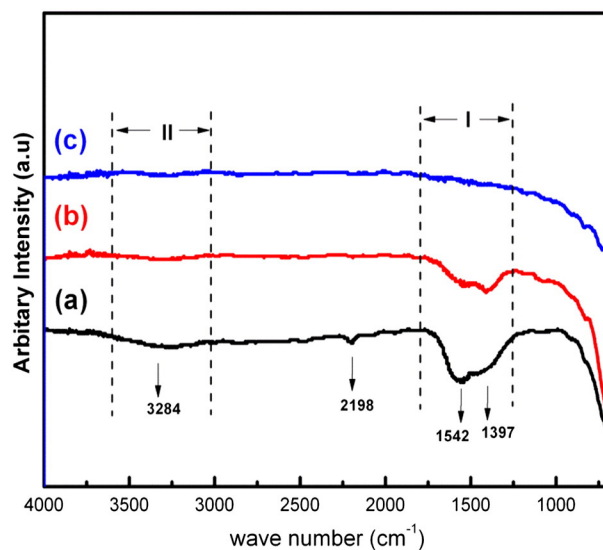


Fig. 1. FTIR spectra of SSZ-1CeO<sub>2</sub> sample. (a) As-prepared, (b) calcined at 600 °C for 2 h and (c) sintered at 1300 °C for 3 h.

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