Journal of Power Sources 195 (2010) 2301–2309

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Temperature and stress induced changes of the vibrational response of cubic and rhombohedral 10 mol%Sc_2O_3–1 mol%CeO_2–ZrO_2 ceramics

Svetlana Lukich, Cassandra Carpenter, Nina Orlovskaya*

Department of Mechanical, Material and Aerospace Engineering, University of Central Florida, 4000 Central Florida Blvd., Orlando, FL 32816, United States

ARTICLE INFO

Article history:
Received 13 September 2009
Received in revised form 17 October 2009
Accepted 19 October 2009
Available online 11 November 2009

Keywords:
Micro-Raman spectroscopy
Cubic phase
Rhombohedral phase
Zirconia
Vickers indentation
Stress

ABSTRACT

The vibration response of cubic and rhombohedral (β) 10 mol%Sc_2O_3–1 mol%CeO_2–ZrO_2 ($Sc_{0.1}Ce_{0.01}ZrO_2$) both at room and high-temperatures is reported. The in situ heating experiments and ex situ indentation experiments were performed to characterize the vibrational behavior of these important materials. A temperature and stress-assisted phase transition from cubic to rhombohedral phase was detected during in situ Raman spectroscopy experiments. While heating and indentation experiments performed separately did not cause the transition of the cubic phase into the rhombohedral structure under the performed experimental conditions and only broadened or strained peaks of the cubic phase could be detected, the heating of the indented (strained) surface leaded to the formation of the rhombohedral $Sc_{0.1}Ce_{0.01}ZrO_2$. Both temperature range and strained zone were estimated by in situ heating and 2D mapping, where a formation of rhombohedral or retention of cubic phase has been promoted.

1. Introduction

Sc_2O_3 doped ZrO_2 ($ScZrO_2$) ceramics have recently attracted a significant interest as a novel promising electrolyte material for lower temperature SOFCs due to its excellent ionic conductivity [1–3]. There have been numerous reports on the high ionic conductivity of $ScZrO_2$ ceramics [4,5] which was reported to be near twice as high as other ZrO_2 based electrolytes [6]. Most of the studies of $ScZrO_2$ ceramics were performed on the materials with 8–12 mol% doping level of Sc_2O_3, where a cubic phase is a main single phase at 700–800 °C operating temperatures. The drawback of $ScZrO_2$ has been also reported as an ordering of vacancies over time, called the aging phenomenon, accompanied by a phase transition to a lower symmetry rhombohedral phase, resulting in decreased conductivity [6]. The highly conductive cubic phase is not stable below 650 °C causing the abrupt decrease in ionic conductivity during cooling in the $ScZrO_2$ [7,8]. It is known that in 11 mol% Sc_2O_3–89 mol% ZrO_2, a cubic to rhombohedral phase transition occurs when the temperature decrease below 600 °C [9,10]. It was reported [11,12] that when ZrO_2 is stabilized with a small amount of CeO_2 along with Sc_2O_3, it no longer exhibits an unfavorable phase transition, making this material a very promising option for intermediate temperature electrolytes.

In [11], the commercially available 10 mol% Sc_2O_3–1 mol% CeO_2–ZrO_2 further referred as $Sc_{0.1}Ce_{0.01}ZrO_2$, manufactured by Daiichi Kigenso Kagaku Kogyo (DKKK, Japan) has been reported to have a stable cubic phase, superior electrical properties and excellent high temperature long-term operating characteristics of single cells using $Sc_{0.1}Ce_{0.01}ZrO_2$ as an electrolyte material. Contrary, the reversible very slow cubic to rhombohedral and rhombohedral to cubic phase transitions at 300–500 °C has been reported upon heating of $Sc_{0.1}Ce_{0.01}ZrO_2$ ceramics using X-ray diffraction [13], which were probably overlooked in other studies due to extremely slow kinetics of cubic to rhombohedral phase transition upon heating. Thus, it was recently shown that the high temperature cubic $Sc_{0.1}Ce_{0.01}ZrO_2$ is a metastable phase at room temperature and could be easily transformed to the thermodynamically stable rhombohedral phase upon annealing at 350–400 °C after at least 12 h of annealing. However, it is not expected that these transitions could have a significant effect on $Sc_{0.1}Ce_{0.01}ZrO_2$ electrolyte performance since they occur at lower temperatures and could simply be bypassed during heating up or cooling down cycles of the cells. It was reported that the kinetics of the phase transition is a strong function of the grain size of the $Sc_{0.1}Ce_{0.01}ZrO_2$ ceramics [13], and it was also found that the coefficient of thermal expansion of cubic $Sc_{0.1}Ce_{0.01}ZrO_2$ is very close to the Y_2O_3 stabilized ZrO_2 (YSZ) which is a good indicator that $Sc_{0.1}Ce_{0.01}ZrO_2$ ceramics are a perfect candidate for substitution of YSZ electrolyte SOFCs.

It has been recognized that while XRD patterns are determined by the arrangements of the cations (Zr, Sc, Ce) in the fluorite lattice, laser-excited Raman spectra are sensitive to the

---

* Corresponding author. Tel.: +1 4078235770; fax: +1 4078230208.
E-mail address: norlovsk@mail.ucf.edu (N. Orlovskaya).

0378-7753/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2009.10.060

change of the polarizability of cation-oxygen vibrations and can easily give important information about the crystal structure of $Sc_{0.1}Ce_{0.01}ZrO_2$. The different ZrO_2 structures (monoclinic, tetragonal, rhombohedral, and cubic) all have characteristic signatures in their spectra, which enable them to be easily distinguished. Besides, the strain/stress in the material can be detected from the shift of the certain peaks. The $Sc_{0.1}Ce_{0.01}ZrO_2$ ceramics under study have been previously characterized by XRD [13], but the goal of this paper is to study the spectra of cubic and rhombohedral phases as well as to detect temperature and stress induced deformation and phase transitions in zirconia using Raman spectroscopy.

2. Experimental details

The 10 mol% Sc_2O_2–1 mol% CeO_2–ZrO_2 ($Sc_{0.1}Ce_{0.01}ZrO_2$) powder produced by Daiichi Kigenso Kagaku Kogyo (DKKK, Japan) has been sintered at 1500 °C for 2 h with a 10 °C min^{-1} heating/cooling rate in air to almost full density. The detailed processing of the $Sc_{0.1}Ce_{0.01}ZrO_2$ as well as it selected properties, such as strength, hardness, fracture toughness, Young's modulus, as well as preliminary Raman data are presented in details elsewhere [13–16]. The XRD confirms that the material consists of the cubic phase upon cooling after sintering at 375 °C for 12 h [13]. The cubic $Sc_{0.1}Ce_{0.01}ZrO_2$ samples were grinded and polished in order to obtain the mirror surface and then they were thermally etched at 1300 °C for 1 h to reveal the grain boundaries. A portion of the thermally etched cubic $Sc_{0.1}Ce_{0.01}ZrO_2$ samples were annealed at 375 °C for 12 h in air in order to convert them to the rhombohedral phase, which is stable in 25–400 °C temperature range [13]. Both cubic and rhombohedral $Sc_{0.1}Ce_{0.01}ZrO_2$ phases were indented using Vickers hardness tester (LECO M-400) with a load of 9.8 N. The hardness and fracture toughness of the ceramics have been calculated using the length of the impression diagonals and cracks originating from the corners of the impressions, respectively. Optical micrographs were taken using an Olympus confocal microscope (LEXT OLS3000-IR).

Renishaw InVia Raman microscope was used to study the vibrational spectra of $Sc_{0.1}Ce_{0.01}ZrO_2$ ceramics. The Raman microscope system comprises a laser (532 nm line of solid Si or near infrared 785 nm) to excite the sample, a single spectrograph fitted with holographic notch filters, and an optical microscope (a Leica microscope with a motorized XYZ stage) rigidly mounted and optically coupled to the spectrograph. Before collecting spectra of $Sc_{0.1}Ce_{0.01}ZrO_2$ the spectrometer was calibrated with a Si standard using a Si band position at 520.3 cm^{-1}. The average collection time for a single spectrum was 20 s. High temperature Raman spectroscopy was performed using a TMS 600 and TMS 1500 heating stage (Linkam Scientific Instruments Ltd., UK) by heating/cooling of the samples to/from 400 and 1000 °C, respectively. For the high temperature experiments the incident and scattered beams were focused with a long working distance 50× objective, which maintained a laser spot as small as 2–3 μm. A 10 °C min^{-1} heating/cooling rate was used for high temperature experiments. Room temperature Raman spectra were collected from different points of interest on the sample surface, such as on the polished surface at different locations as well as inside or outside the Vickers impressions. For room temperature and area mapping experiments the short working distance 100× objective was used. To produce two-dimensional (2D) maps, Renishaw Wire 2.0 software with a mixed Lorentzian and Gaussian peak fitting function was used. The system's peak fitting results were plotted to create a position map with a spectral resolution better than 0.2 cm^{-1}. The total time of spectrum collection was decreased to 3 s per point in the case of 2D mapping and the total acquisition time to collect all spectra for one map never exceeded 24 h.

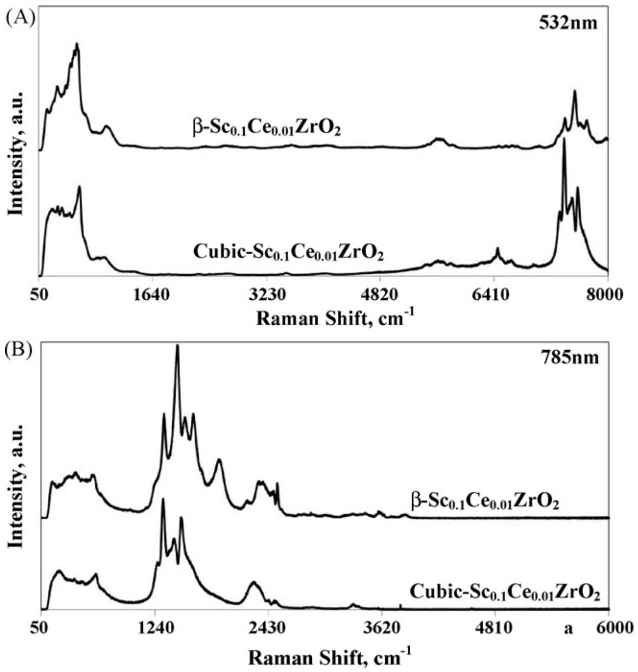

Fig. 1. The spectral range of cubic and rhombohedral $Sc_{0.1}Ce_{0.01}ZrO_2$ electrolyte ceramics collected by 532 nm solid Si and 785 nm NIR lasers.

3. Results and discussion

The whole spectral range of cubic and rhombohedral $Sc_{0.1}Ce_{0.01}ZrO_2$ phases collected using both 532 and 785 nm lasers are presented in Fig. 1. The assignment of the cubic and rhomboherdal phases were made based on the XRD analysis presented elsewhere [13]. While the spectra collected using 532 nm Si laser shows the most prominent features at ranges 100–1000 cm^{-1} and 7200–8000 cm^{-1} both for cubic and rhombohedral structures, the spectra collected using NIR 785 nm laser shows the strongest bands in the 1000–2000 cm^{-1} range. Thus, it is useful to study the vibrational response of the $Sc_{0.1}Ce_{0.01}ZrO_2$ using at least two lasers, as the structural information from the analysis of Raman spectra measured with only one laser could be incorrectly interpreted. A number of peaks showing up both in cubic and rhombohedral $Sc_{0.1}Ce_{0.01}ZrO_2$ in 1000–2000 cm^{-1} range using 785 nm excitation, are completely missing when 532 nm laser is used, Fig. 1. The bands with a Stokes shift higher than 800 cm^{-1} from the laser excitation line have been previously observed in zirconia based oxides [17–19], and bands have been assigned to electronic transitions in impurity ions [20] or to phonon-mediated de-excitation of excited states of the impurity-doped ZrO_2 lattice [21]. While the exact nature of the bands is not obvious, they could be tentatively assigned to the appearance of the luminescence bands related to Ln^{3+} (Ln: Pr^{3+}, Nd^{3+}, Mo^{3+}, Er^{3+}) or other impurities ions [22], and photoluminescence measurements need to be performed to establish the origin of each 1000 cm^{-1} and higher bands.

The spectra of cubic and rhombohedral $Sc_{0.1}Ce_{0.01}ZrO_2$ phases in 100–1000 cm^{-1} range taken by 532 and 785 nm lasers are presented in Fig. 2. The similar spectrum of cubic $Sc_{0.1}Ce_{0.01}ZrO_2$ electrolyte was published in [23]. The spectrum of pure cubic fluorite phase should consist of a single F_{2g} mode between 400 and 500 cm^{-1}, and it was reported that Raman spectrum of pure submicron cubic zirconia consists of a weak broad line assigned to a single allowed Raman mode F_{2g} symmetry [24]. The out-of-phase motion of the 2 oxygen atoms is assigned to this mode, therefore the frequency should be independent of the cation mass, and should vary inversely proportional to the square root of the cell volumes. It