Available online at www.sciencedirect.com
SCIENCE DIRECT®
Solid State Ionics 176 (2005) 2535 – 2543
SOLID STATE IONICS
www.elsevier.com/locate/ssi

Co-doping effects on crystal structure and electric conduction in $((Y_{0.75}La_{0.25})_{1-x}Gd_x)_{0.18}Zr_{0.82}O_{2-\delta}$

S. Komine [a,b,*], T. Iimure [a], E. Iguchi [a]

[a] *Division of Materials Science and Engineering, Graduate School of Engineering, Yokohama National University, Tokiwadai, Hodogaya-Ku, Yokohama, 240-8501 Japan*
[b] *Seimi Chemical Co., Ltd. Chigasaki 3-2-10, Chigasaki, 253-8585 Japan*

Received 9 March 2005; received in revised form 13 July 2005; accepted 30 July 2005

Abstract

In order to clarify co-doping effects of trivalent rare earth ions to the ionic conduction and the crystal structure in ZrO_2, dc- and ac-measurements along with XRD observations have been carried out to $((Y_{0.75}La_{0.25})_{1-x}Gd_x)_{0.18}Zr_{0.82}O_{2-\delta}$ by changing x from 0 to 1, where the average ionic radius of $(Y_{0.75}La_{0.25})_{1-x}Gd_x$ is constant, i.e., 1.053 Å, being independent of x. These specimens contain dual phases, i.e., cubic and monoclinic phases. Dc conductivity in the heating process differs from that in the cooling process. This hysteresis has been discussed in terms of the monoclinic–cubic phase transition on the basis of XRD results at high temperatures. The x-dependencies of the energy values required for the bulk and grain boundary conductions are strongly related to the ionic radii of the trivalent rare earth ions because the states of oxygen vacancies, which are substantially responsible for ionic conductions, depend upon the rare earth ions that capture the vacancies at lower temperatures. Many combinations of oxygen vacancies and rare earth ions lead to the long-ranged hysteresis.

PACS: 61.72.Ji (Point defects); 66.30.Hs (Self-diffusion and ionic conduction in nonmetals); 77.22.Gm (Dielectric loss and relaxation); 81.05.Je (Ceramics and refractories); 84.60.Dn (Electrochemical conversion and storage: electrochemical cells and batteries, fuel cells)
Keywords: Ionic conduction; Co-doping of trivalent rare earth ions; O^{2-} migration; Oxide electrolyte; Solid oxide fuel cell (SOFC); Stabilized zirconia

1. Introduction

As is well known, yttria-stabilized zirconia (YSZ), which has the fluorite lattice, is widely used as the electrolyte in solid oxide fuel cells (SOFC) because it fulfills most of the following requirements; (1) high ionic conductivity, (2) exclusion of electronic conduction, (3) thermodynamic stability in both oxidizing and reducing atmospheres at high temperatures, (4) less reactivity with materials in other parts of the SOFC, and (5) good agreement of thermomechanical properties with other constituent components [1–3].

Non-doped ZrO_2 undergoes two phase-transitions: the monoclinic-to-tetragonal around 1400 K and the tetragonal-to-cubic around 2000 K [4–6]. However, these transitions are effectively suppressed by a partial substitution of trivalent rare earth (RE) ions like Y^{3+} for Zr^{4+}, and, as a result, the stabilized zirconia with the cubic fluorite structure is stable even at room temperature. The typical illustration is 8 mol% YSZ [7,8]. Though it is still unknown why such phase transitions occur in non-doped ZrO_2, the small ionic radius of Zr^{4+} as compared to the RE ions must play an important role [9,10].

In the cubic fluorite structure of ZrO_2, the cation normally forms an eight-fold coordination with the O^{2-} ions and the fully ionic packing requires that the ratio of the ionic radius of the cation to that of O^{2-} is 0.73 at room temperature [10]. However, the real ratio in the cubic ZrO_2 is 0.59. Such a large misfit ratio destabilizes the cubic phase

---

* Corresponding author. Seimi Chemical Co., Ltd. Chigasaki 3-2-10, Chigasaki, 253-8585, Japan. Tel.: +81 467 82 4131; fax: +81 467 88 1778.
E-mail address: sgkkomine@seimichemical.co.jp (S. Komine).

0167-2738/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.ssi.2005.07.017

in ZrO_2. At low temperatures, therefore, non-doped ZrO_2 favors potentially to the tetragonal or monoclinic structure which has a lower coordination number of the cation. Consequently, ZrO_2 can dissolve preferentially RE ions with ionic radii larger than Zr^{4+} such that they stabilize.

Furthermore, the substitution of trivalent RE ions for Zr^{4+} creates oxygen vacancies which are significant for the oxygen ionic conduction because the O^{2-} ions migrate with the assistance of the oxygen vacancies, i.e., the oxygen ionic conductivity is proportional to the density of the oxygen vacancies [11–13]. The amount of the oxygen vacancies created in thermal equilibrium is very small because of high formation energy of an oxygen vacancy in an oxide [14], and then their contribution to the ionic conduction may be ignored. This is one of the main reasons for the high ionic conductivity of doped ZrO_2 [15]. When the amount of trivalent RE ions which are substituted for the Zr^{4+} ions is fixed and then the density of the oxygen vacancies is maintained at a constant, the electric conductivity in doped ZrO_2 is likely to depend very sensitively on the ionic radii of the RE ions because the electric conductivity increases as the ionic radius decreases [16]. For such a correlation between the electric conductivity and the ionic radius of the RE ion, the previous literature has tried various interpretations [17].

Since the oxygen vacancies are first captured by trapping centers at low temperatures and the free mobile oxygen vacancies dissociated thermally from the trapping centers assist the O^{2-} migrations [11–13,18], the dissociation energy is a very important parameter for the oxygen ionic conduction. In order to investigate the trapping states of oxygen vacancies, an EXAFS study was carried out for YSZ, and the results indicate that an oxygen vacancy is sited adjacent to Zr^{4+} [19]. There is also the calculation using molecular dynamics analysis, which shows that oxygen vacancies are trapped at the second-neighbor positions of Y^{3+} [20]. These situations imply that further investigations are required in order to clarify the relation of the oxygen ionic conductivity and the trivalent RE ions.

Along this line, a trial has been carried out in the present study. Three RE ions, Y^{3+}, La^{3+} and Gd^{3+}, have been co-doped into ZrO_2 by changing their relative ratios but the average ionic radius of these three ions is maintained at a constant. Then the variations of the ionic conduction and the phase structure due to the co-doping have been investigated. The illustrative example treated here is $((Y_{0.75}La_{0.25})_{1-x}Gd_x)_{0.18}Zr_{0.82}O_{2-\delta}$, where the average ionic radius of $Y_{0.75}La_{0.25}$ is equal to the ionic radius of Gd^{3+}, i.e., 1.053 Å [10]. Five specimens ($x=0$, 0.25, 0.5, 0.75 and 1) have been prepared, and the degree of oxygen deficiency is nominally the same for every specimen, i.e., $\delta=0.2$. If the conductive behaviors, including the activation energy for the ionic conduction, differ with each specimen, each ionic radius of these RE ions rather than the average ionic radius is mainly responsible for the variation in the electric transport properties. From this point of view, the electric conduction in this oxide-system has been investigated as a parametric function of x, using mainly 4-probe dc-measurements in both heating and cooling runs. The ac-measurements have been also carried out. Furthermore, X-ray diffraction patterns (XRD) at high temperatures have been obtained for the $x=0.5$ specimen in order to elucidate the variations of the lattice structure.

2. Experimental details

$((Y_{0.75}La_{0.25})_{1-x}Gd_x)_{0.18}Zr_{0.82}O_{2-\delta}$ specimens ($x=0$, 0.25, 0.5, 0.75 and 1) have been synthesized by a conventional solid-state reaction technique using ZrO_2, Y_2O_3, La_2O_3, and Gd_2O_3 powders (3 N). The mixtures were calcined in air at 1400 °C for 10 h. After grounding, the calcined powders were pressed into pellets, and finally sintered in air at 1600 °C for 5 h. The main powder diffraction in these specimens using $K\alpha$ Cu X-ray (XRD) at room temperature indicate the cubic fluorite structure phase. The XRD includes the satellite lines due to the monoclinic fluorite structure. For the $x=0.5$ specimen, XRD patterns at 673, 873 and 1273 K in both heating and cooling runs have been obtained.

The dc conductivity-values have been measured by the 4-probe method, using Advantest R6161 power supply, Keithley 619 Electrometer/Multimeter and Advantest TR6871 Digital Multimeter as a function of temperature over the range 673–1073 K. All measurements have been carried under the constant electric current, during heating and cooling runs in air. The heating rate is 100 K/h but the furnace cooling is employed in the cooling run. Pt paste has been used for the electrodes. The ac-measurements (capacitances and impedances) have been also carried out in the same way as the previous studies [11–13,21–23], using an Agilent 4294 A precision impedance analyzer with a frequency range of 20 Hz–10 MHz. Only the cooling process has been employed in the ac-measurements because the noises caused by the electric current for heating disturb seriously the ac-measurements. Pt paste has been used also for the electrode of ac measurements.

3. Results and discussion

3.1. Dual phases in $((Y_{0.75}La_{0.25})_{1-x}Gd_x)_{0.18}Zr_{0.82}O_{2-\delta}$ at room temperature

Fig. 1 displays the XRD pattern of the $x=0$ specimen at room temperature. As well as $Gd_{0.18}Zr_{0.82}O_{2-\delta}$ [24], $((Y_{0.75}La_{0.25})_{1-x}Gd_x)_{0.18}Zr_{0.82}O_{2-\delta}$ has the fluorite structure, but this XRD includes two phases, i.e., the cubic and monoclinic phases. The $(11\bar{1})$ and (111) peaks of the monoclinic phase are unequivocally recognized at $2\theta \cong 28.5°$ and 31° in XRD. Though other specimens show the very similar XRD patterns, the integrated intensity ratio