

## Mechanical and electrical properties of rare earth oxide doped zirconia ceramics

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Zirconia ceramics stabilized by various metallic oxide such as yttria has tetragonal or cubic structure even at room temperature and shows significantly large oxide ionic conductivity by generating oxygen vacancies. It is thought that the strength of the stabilized zirconia greatly depends on the crystal structure and its ionic conductivity depends on the amount of the oxygen vacancy and the ionic radius of metal of added oxide. In this study, we have systematically changed the kind and the amount of the added rare earth oxide, evaluated the electrical and the mechanical properties of the zirconia ceramics and examined practical utility as ion conductive material.

Key words: zirconia, ionic conductor, rare earth oxide, bending strength

### 1. INTRODUCTION

It is difficult to obtain a crack free ceramics of pure zirconia because it shows tetragonal-to-monoclinic phase transformation at around 1100 °C on cooling associated with a large volume change ( ~9%). However, the addition of aliovalent oxide such as CaO and Y<sub>2</sub>O<sub>3</sub>, stabilizes the cubic fluorite structure from room temperature to melting point. The stabilization of zirconia is accompanied by direct substitution of divalent or trivalent cation for the host lattice cation (Zr<sup>4+</sup>).

This substitution not only stabilizes the cubic fluoride structure but also creates a large concentration of oxygen vacancies by charge compensation, enhancing the ionic conductivity [1]. In the case of yttria stabilized zirconia, its ionic conductivity increases with yttrium dopant concentration up to 8 mol%, which is the minimum quantity of dopant concentration required to fully stabilize the cubic phase. On further doping, the ionic conductivity then decreases due to defect ordering or vacancy clustering. On the other hand, YSZ containing less than 8 mol% yttria is known to be partially stabilized zirconia which possesses large mechanical strength and toughness as a consequence of the stress-induced tetragonal-to-monoclinic martensitic transformation [2].

Under these circumstances, fully stabilized zirconia (FSZ) showing the maximum ionic conductivity is used as an electrolyte in usual electrochemical devices. However, in the case of oxygen sensor for automobile, at which device reliability is much more respected, 3 mol% yttria stabilized zirconia is used while its conductivity is lower than that of 8YSZ [3]. On the other hand, in solid oxide fuel cell (SOFC), large mechanical strength as well as large ionic conductivity

is required because its solid electrolyte plays a role of separation wall.

We have already reported that alumina dispersed 8 mol% yttria stabilized zirconia ceramics exhibited large mechanical strength almost twice as that of monolithic 8YSZ while the ionic conductivity remained [4-6]. By using such material, the thickness of the separation wall can be thinned to be half maintaining the structural reliability. Then, the electrical resistance through the electrolyte can be lowered resulting in saving the ohmic loss at the electrolyte.

Considering the balance of mechanical strength and ionic conductivity, use of 5-6 mol% of yttria stabilized zirconia has been proposed recently [7]. Other rare earth oxides have also reported to stabilize the cubic phase of zirconia. But dependences of dopant concentration on mechanical strength have not been reported in rare earth oxide doped zirconia ceramics. In the present study, we fabricated rare earth oxide doped yttria stabilized zirconia changing the kind and concentration. And their mechanical and electrical properties were measured to evaluate the practical utility of rare earth oxide doped YSZ.

### 2. EXPERIMENTAL PROCEDURE

Zirconia base ceramics doped with several rare earth oxide with various concentration ((RE<sub>2</sub>O<sub>3</sub>)<sub>x</sub>(ZrO<sub>2</sub>)<sub>1-x</sub>, RE=Ho, Er, Tm, Yb, Y, x = 0.03 - 0.08) were fabricated through the conventional solid state reaction. Commercial zirconia powder (Tosoh, TZ-0) and rare earth oxide powder (RE<sub>2</sub>O<sub>3</sub>, High purity Chemical Co. Ltd, Purity 3N) were used as starting powders. They were weighed in a predetermined ratio and mixed in a planetary ball mill

(Fritch, pulverisette 6) using zirconia ball and ethanol for 2 h. After dried they were sieved using stainless mesh (75  $\mu\text{m}$ ). Following three kind of temperature programs were used to obtain rare earth doped zirconia ceramics.

(a) Powder compact was directly sintered at 1450  $^{\circ}\text{C}$  for 48 h.

(b) Powder compact was firstly calcined at 1000  $^{\circ}\text{C}$  for 48 h with subsequent sintering at 1450  $^{\circ}\text{C}$  for 4 h.

(c) Powder mixture was calcined at 1000  $^{\circ}\text{C}$  for 48 h, then crushed and sieved. Powder compact was fabricated and sintered at 1450  $^{\circ}\text{C}$  for 4 h.

Uniaxial pressing was conducted in a steel die (diameter, 20 mm) under 65 MPa, followed by hydrostatic pressing under 200 MPa. The pressed powder compacts were heated according to the above mentioned schedules. The heating and cooling rates were fixed to 120  $^{\circ}\text{C}/\text{h}$ . The crystal phase of the obtained sintered bodies were confirmed by XRD (Rint 2000, Rigaku-denki). The apparent densities of the sintered bodies were measured by the Archimedes method.

The ionic conductivity of the sintered body was measured by an a.c. two-probe method using an impedance analyzer (Solatron, SI1260) over the temperature range of 400 to 900  $^{\circ}\text{C}$  with frequency of  $10^7$  to 1 Hz. Platinum paste painted on both ends of the specimen followed by heat treatment was used as the electrodes.

Resultant sintered bodies were subjected to the three point bending test with span length of 10 mm and cross head speed of 0.5 mm/min

### 3. RESULTS AND DISCUSSION

The apparent densities of the sintered bodies are summarized in Table I. Figure 1 illustrates the XRD results for 6 mol% ytterbia doped zirconia heat-treated with different conditions (Fig.1-1), and sintered bodies with different ytterbia contents (Fig.1-2). No XRD peak assigned for rare earth oxide is identified

Table I Densities of the Samples.

	Y	Yb	Tm	Er	Ho
$(\text{RE}_2\text{O}_3)_{0.06}(\text{ZrO}_2)_{0.92}$ <sup>b)</sup>	5.64	6.14	-	-	-
$(\text{RE}_2\text{O}_3)_{0.06}(\text{ZrO}_2)_{0.94}$ <sup>a)</sup>	-	6.27	6.17	6.17	6.57
$(\text{RE}_2\text{O}_3)_{0.06}(\text{ZrO}_2)_{0.94}$ <sup>b)</sup>	5.72	5.98	6.05	5.92	6.13
$(\text{RE}_2\text{O}_3)_{0.06}(\text{ZrO}_2)_{0.94}$ <sup>c)</sup>	-	5.81	6.07	5.72	6.02
$(\text{RE}_2\text{O}_3)_{0.05}(\text{ZrO}_2)_{0.95}$ <sup>a)</sup>	-	6.43	-	-	-
$(\text{RE}_2\text{O}_3)_{0.05}(\text{ZrO}_2)_{0.95}$ <sup>b)</sup>	-	5.92	-	-	-
$(\text{RE}_2\text{O}_3)_{0.04}(\text{ZrO}_2)_{0.96}$ <sup>a)</sup>	-	5.87	6.10	6.09	5.86
$(\text{RE}_2\text{O}_3)_{0.04}(\text{ZrO}_2)_{0.96}$ <sup>b)</sup>	5.58	5.89	5.94	5.75	-
$(\text{RE}_2\text{O}_3)_{0.03}(\text{ZrO}_2)_{0.97}$ <sup>b)</sup>	5.54	5.73	5.82	5.68	-

a) Pellet was sintered at 1450  $^{\circ}\text{C}$  for 48 h.

( $\text{g}\cdot\text{cm}^{-3}$ )

b) Pellet was calcined at 1000  $^{\circ}\text{C}$  for 48 h and sintered at 1450  $^{\circ}\text{C}$  for 4 h.

c) Pellet was made from calcined powder and sintered at 1450  $^{\circ}\text{C}$  for 4 h.

after sintering while it remains after calcinations.

Theoretical densities for monoclinic zirconia and cubic zirconia without additive are reported to be 5.825  $\text{g}/\text{cm}^3$  and 6.206  $\text{g}/\text{cm}^3$ , respectively. Since the atomic weights of the present rare earths are much larger than that of zirconium while the ionic radii are comparable, rare earth substituted zirconia should have larger theoretical density than that of pure zirconia. Furthermore, when monoclinic phase coexists in a cubic zirconia matrix, theoretical density would be small compared with that expected for cubic single-phase zirconia.

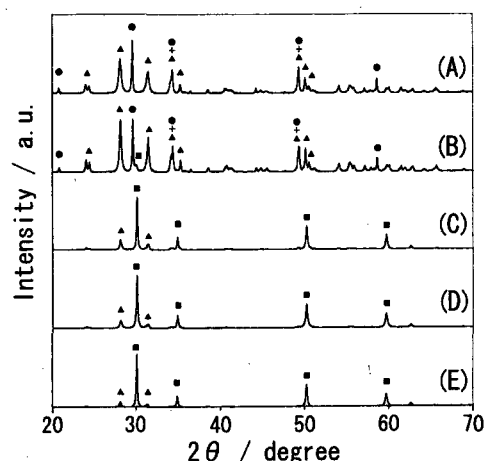


Fig.1-1 XRD patterns of the  $(\text{Yb}_2\text{O}_3)_{0.06}(\text{ZrO}_2)_{0.94}$ .

(A) raw powder mixture, (B) powder mixture calcined at 1000  $^{\circ}\text{C}$  for 48h, (C) sample made by method of heating program (c), (D) sample made by method of heating program (b), (E) sample made by method of heating program (a)  
 (●:Ytterbium oxide, ▲:Monoclinic zirconia, ■:Cubic zirconia)

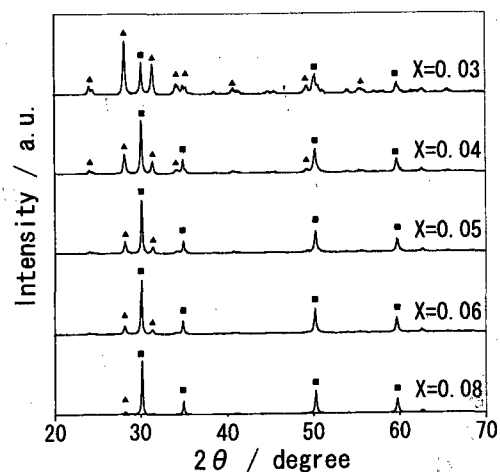


Fig.1-2 XRD patterns of  $(\text{Yb}_2\text{O}_3)_x(\text{ZrO}_2)_{1-x}$ .

(▲:Monoclinic zirconia, ■:Cubic zirconia)

In the present study, the apparent density increases with the rare earth oxide content when the heating

conditions are the same. In accordance with Fig.1-1, cubic phase becomes predominant with the rare earth oxide content. Furthermore, when powder mixtures with the same composition were heat-treated with different conditions, cubic phase is more predominant in sample sintered at 1450°C for 48h (heating program (a)) compared with that firstly calcined at 1000 °C for 48 h with subsequent sintering at 1450 °C for 4 h (heating program (b)).

Figure 2-1 shows the bending strength depending on the rare earth content in samples prepared by the heating program (b). Figure 2-2 demonstrates the heating schedule dependence of bending strength for 6 mol% rare earth oxide doped zirconia ceramics. In general, bending strengths in samples made by heating program (b) are larger than those by the other programs probably due to the homogeneous solid state reaction without grain growth.

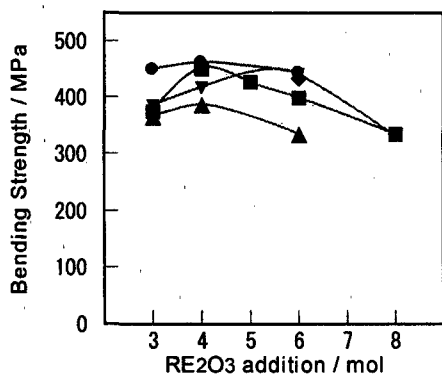


Fig.2-1 Bending Strength of the Samples.

■:Yb ●:Tm ▲:Er ◆:Ho ▼:Y  
Samples were made by method of heating program (b).

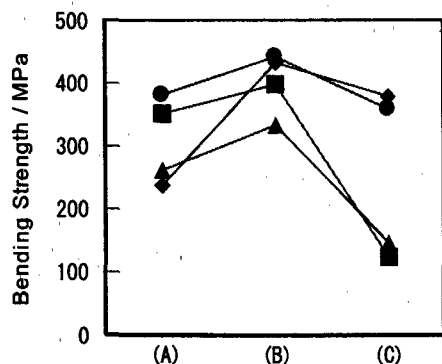


Fig.2-2 Bending Strength of the Samples.

(RE<sub>2</sub>O<sub>3</sub>)<sub>0.06</sub>(ZrO<sub>2</sub>)<sub>0.96</sub> ■:Yb ●:Tm ▲:Er ◆:Ho  
(A) Sample made by method of heating program (a)  
(B) Sample made by method of heating program (b)  
(C) Sample made by method of heating program (c)

In the case of heating program (b), bending strength of 6 mol% of each rare earth doped zirconia

ceramics is larger than that of 8 mol% doped one stemming from the phase transformation. However, 3 to 5 mol % rare earth oxide doped zirconia ceramics show smaller bending strength than those of 8 mol% ones even in the yttria doping. As mentioned in the introduction, 3 mol% doping is known to show the maximum mechanical strength in yttria stabilized zirconia ceramics. In the present study, however, some microstructural defects such as cracking probably affect the bending strength in 3 to 5 mol% doping samples while that for 6 mol% yttria stabilized zirconia is comparable to the reported value. Bending strength of 6 mol% ytterbia, thulium oxide, holmium oxide doped zirconia ceramics are almost the same as that for 6 mol% yttria doped one.

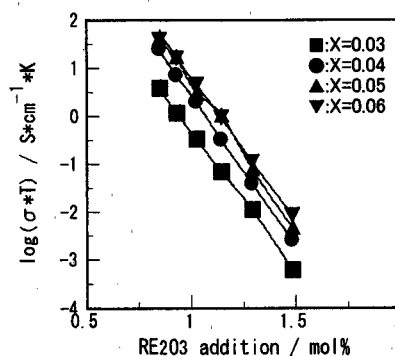


Fig.3 Arrhenius plots of the ionic conductivities on (Yb<sub>2</sub>O<sub>3</sub>)<sub>x</sub>(ZrO<sub>2</sub>)<sub>1-x</sub>.

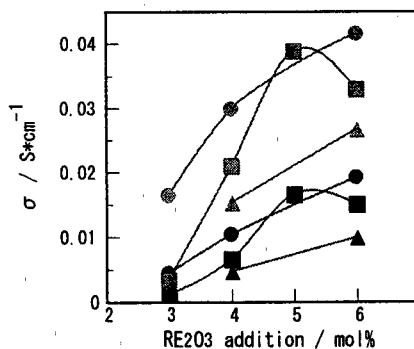


Fig.4 The dependence of ionic conductivities on doping amount of RE<sub>2</sub>O<sub>3</sub>.

800 °C/■:Yb, ●:Tm, ▲:Er 900 °C/■:Yb, ●:Tm, ▲:Er

The ionic conductivity was measured on variously rare earth oxide doped zirconia ceramics. The Arrhenius plots of the ionic conductivity on zirconia ceramics doped with various amount ytterbia are shown in Fig.3. The activation energies, calculated from the slopes, are roughly the same irrespective of the doping amount of ytterbia. Ionic conductivity increases with increasing the ytterbia content up to 6

mol%, then saturates. Figure 4 illustrates the dependence of ionic conductivities on doping amount of rare earth oxide at 800 and 900 °C, which is close to the practical operation temperature of SOFC. The ionic conductivities of ytterbia doped zirconia are larger than those of yttria doped one with the same doping level. It has already reported that maximum ionic conductivity of rare earth oxide doped zirconia is closely related to the ionic radius of dopant, i.e., maximum ionic conductivity increases with decreasing the ionic radius of dopant for stabilization of cubic phase[8].

Since 6 mol% yttria stabilized zirconia is a promising candidate for solid electrolyte of SOFC considering its balance of ionic conductivity and mechanical properties, other 5-6 mol% rare earth oxide stabilized zirconia ceramics exhibiting comparable bending strength and large ionic conductivity are thought to be more promising.

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