

Characterization of nanostructured $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ prepared by pulsed current activated sintering

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Dense nanophase $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ was sintered by a pulsed current activated sintering method within 6 minutes from $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ nanopowder synthesized by a co-precipitation method. Sintering was accomplished under the combined effect of a pulsed current and mechanical pressure. Highly dense $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ with a relative density of up to 97% was obtained by pulsed current activated sintering with a heating rate of $200 \text{ K} \cdot \text{minute}^{-1}$ under a pressure of 80 MPa at 1300°C . The hardness and fracture toughness of the sample sintered at 1300°C were about 740 kg/mm^2 and $1.5 \text{ MPa} \cdot \text{m}^{1/2}$, respectively. The grain boundary conductivity was relatively smaller than the grain interior conductivity.

Key words: Pulsed current activated sintering, $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$, Nanophase, Mechanical properties, Ionic conductivity.

Introduction

Yttria-stabilized zirconia (YSZ) is a traditional electrolyte material for solid oxide fuel cells (SOFC). 8YSZ electrolyte is generally operated at about 1000°C , where the ionic conductivity reaches the required high level. However, such a high temperature leads to a reaction between the components or thermal expansion mismatch. Recently, ceria-based solid solutions have been acknowledged to be the most promising electrolytes for use in intermediate temperature (600°C) fuel cells since they exhibit much higher ionic conductivity than YSZ. However, ceria-based ceramics are difficult to densify below 1600°C and it is also hard to obtain nanostructured materials by a conventional sintering method due to fast grain growth during the sintering process.

Nano-crystalline materials have received much attention as advanced engineering materials with improved physical and mechanical properties [1, 2]. Nano-materials exhibit high strength, high hardness, excellent ductility and toughness. Accordingly, much attention has been paid to the application of nanomaterials [3, 4]. In recent days, nanocrystalline powders have been developed by co-precipitation, the thermochemical and thermomechanical process named as the spray conversion process (SCP) and high energy milling [5, 6]. However, the grain size of sintered materials becomes much larger than that of

pre-sintered powders due to rapid grain growth during the conventional sintering process. Therefore, even though the initial particle size is less than 100 nm, the grain size increases rapidly up to 500 nm or larger during the conventional sintering [7]. So, controlling grain growth during sintering is one of the keys to the commercial success of nanostructured materials. In this regard, the pulsed current activated sintering process which can make dense materials within 2 minutes has been considered as an effective method to fabricate nanostructured materials [8, 9].

We present here the fabrication of nano-sized $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ powders and sintering of nanostructured $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ material by pulsed current activated sintering (PCAS) with a combined effect of pulsed current and high pressure. We also investigated the mechanical properties and ionic conductivity of the $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ electrolyte.

Experimental Procedure

Nanopowder of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ was synthesized by co-precipitation method using dilute ammonia as the precipitant. High purity ($> 99.99\%$) reagents $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were used as the starting materials.

The powder was placed in a graphite die (outside diameter, 45 mm; inside diameter, 20 mm; height, 40 mm) and then introduced into the pulsed current activated sintering system made by Eltek in South Korea, shown schematically in Fig. 1. The PCAS system mainly consists of a DC power supply, which provides a pulsed current with 20 μs on time and 10 μs off time through the sample and die, and

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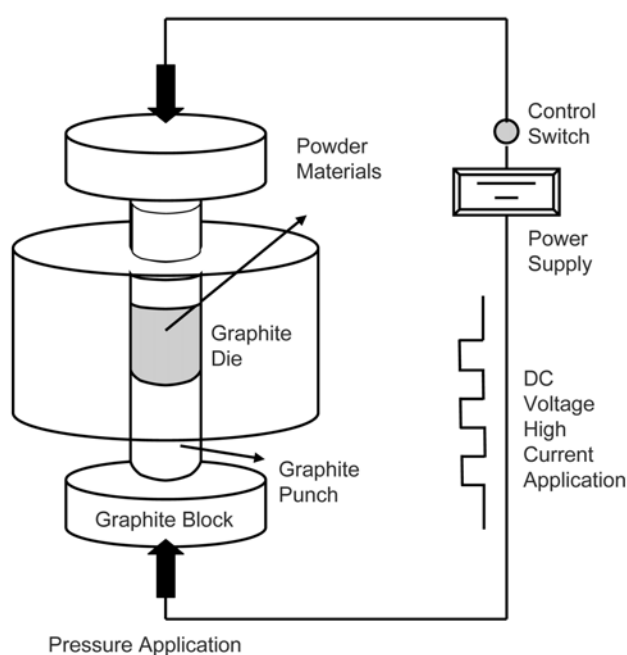


Fig. 1. Schematic diagram of apparatus for pulsed current activated sintering.

a uniaxial press with a maximum range of 50 kN. The system was first evacuated and a uniaxial pressure of 80 MPa was applied. A DC current was then activated. Sample shrinkage was measured in real time by a linear gauge measuring the vertical displacement and temperatures were measured by a pyrometer focused on the surface of the graphite die. A temperature gradient from the surface to the center of the sample is dependent on the heating rate, the electrical and thermal conductivities of the compact, and its relative density. The sample was sintered at various temperatures (900 °C, 1000 °C, 1100 °C, 1200 °C, 1300 °C) with heating rate of 200 K · minute⁻¹. At the end of the process, the current was turn off and the sample was allowed to cool to room temperature. The process was carried out under a vacuum of 40 mtorr (5.33 kPa).

The relative densities of the sintered sample were measured by the Archimedes method. Microstructural information was obtained from fracture surfaces of product

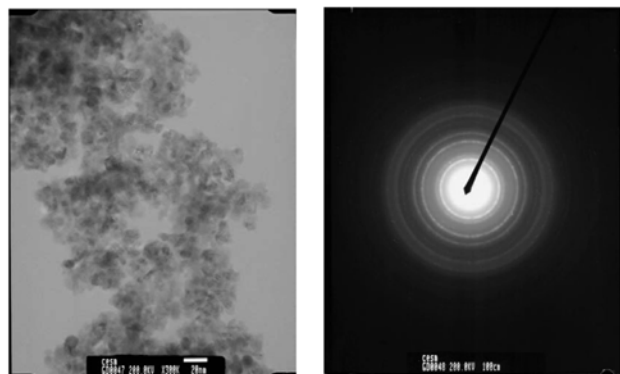


Fig. 2. TEM image and diffraction pattern of Ce_{0.8}Sm_{0.2}O_{2-δ} powder synthesized by a co-precipitation method.

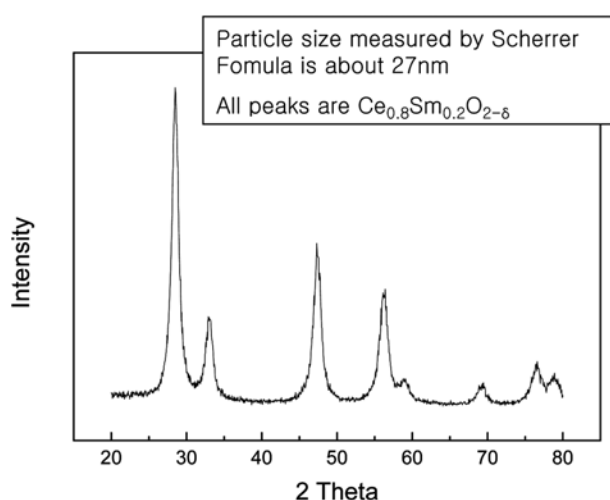


Fig. 3. XRD result of Ce_{0.8}Sm_{0.2}O_{2-δ} powder synthesized by a co-precipitation method.

samples. Compositional and microstructural analyses of the products were carried out through X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDAX) and field-emission scanning electron microscopy (FE-SEM). Vickers hardness was measured by performing indentations at a load of 1 kg_f and a dwell time of 15s on the samples. The ionic conductivity was measured in the temperature range of 300-550 °C in air using two-probe impedance spectroscopy (Zahner IM6, Germany) in the frequency range of 100 mHz to 3 MHz with a voltage amplitude of 50 mV. Pt was coated as electrodes on the both sides of the sintered pellets polished with SiC paper.

Results and Discussion

Powder characterization

Figure 2 shows TEM image of the precipitated powder calcined at 600 °C for 1 h in air. XRD results (Fig. 3) show that all the peaks of the powder calcined at 600 °C corresponded to the fluorite structure of CeO₂ (PDF card number: 34-0394). The lattice parameter determined by the least square refinement method was 0.5417 nm. This value agrees well with the theoretical lattice parameter of the fluorite structure of CeO₂ (theoretical lattice parameter, $a = 0.5411$ nm). The very slight difference between the calculated and theoretical lattice parameters is due to the replacement of Ce⁴⁺ ions by Sm³⁺ ions in the fluorite structure of CeO₂.

The grain size and the internal strain can be calculated by Stoke and Wilson's formula [10]:

$$b = b_d b_e = k\lambda / (d \cos \theta) + 4\epsilon \tan \theta \quad (1)$$

where b is the full width at half-maximum (FWHM) of the diffraction peak after instrument correction; b_d and b_e are FWHM caused by the small grain size and internal stress, respectively; K is a constant = 0.9; λ is

the wavelength of the X-ray radiation; d and ε are the grain size and internal stress, respectively; and θ is the Bragg angle. b and b_s follow a Cauchy form with the relationship: $B_0 = b + b_s$, where B_0 and b_s are FWHM of broadened Bragg peaks and the standard sample's Bragg peaks, respectively. The average grain size $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ estimated by the Stoke-Wilson equation were about 27 nm.

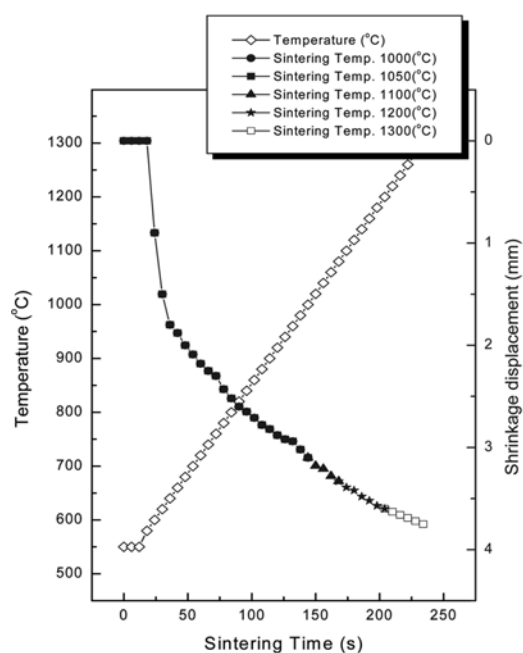


Fig. 4. Variation of shrinkage displacement and temperature with heating time during PCAS of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ at various sintering temperatures (a) 1000 °C, (b) 1050 °C, (c) 1100 °C, (d) 1200 °C and (e) 1300 °C.

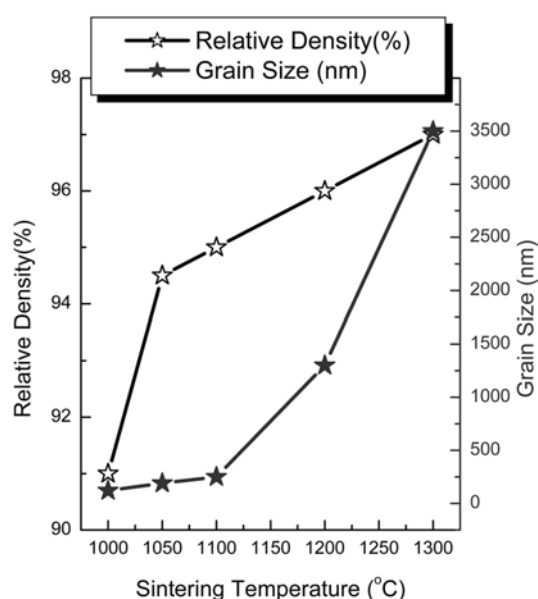


Fig. 5. Relative densities and grain sizes of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ fabricated by PCAS with heating rate of $200 \text{ K} \cdot \text{minute}^{-1}$ under pressure of 80 MPa.

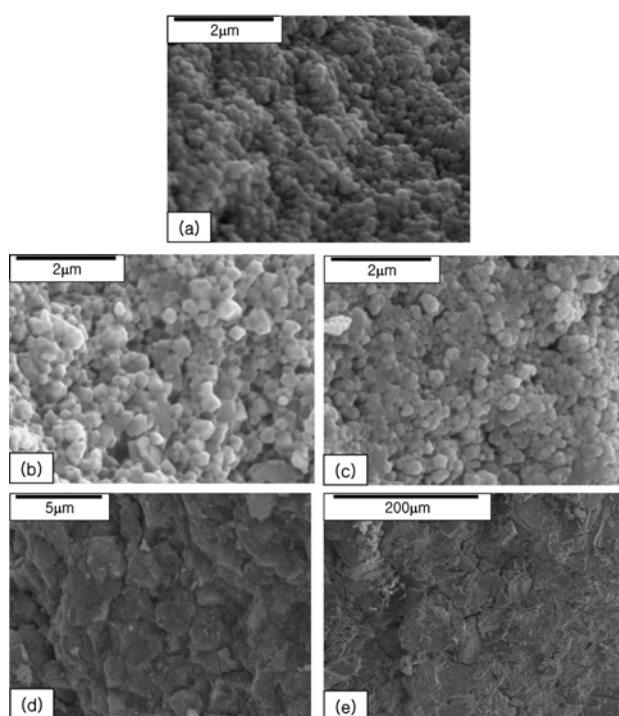


Fig. 6. SEM images of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ sintered at various temperatures (a) 1000 °C, (b) 1050 °C, (c) 1100 °C, (d) 1200 °C and (e) 1300 °C.

Densification behavior of the $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$

The variations in shrinkage displacement and temperature of the surface of the graphite die with heating time during the processing of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ under 80 MPa pressure are shown Fig. 4. As the pulsed current was applied, the shrinkage displacement increased with temperature up to 1300 °C. Figure 5 shows the sintering temperature dependence of the density and grain size of samples prepared by PCAS with a heating rate of $200 \text{ K} \cdot \text{minute}^{-1}$ under a pressure of 80 MPa. The average grain sizes determined by the linear intercept method were about 120, 190, 250, 1300 and 3500 nm for samples produced by PCAS at 1000, 1050, 1100, 1200 and 1300 °C, respectively. Significant densification was obtained only when the temperature was above 1300 °C. The grain size increased with an increase in sintering temperature from 1000 to 1300 °C. Significant grain growth occurred above 1100 °C. The microstructures of samples sintered at various temperatures are shown in Fig. 6. The grain size was noticeably different depending on the sintering temperature and the samples sintered at 1200 and 1300 °C showed significant grain growth.

Mechanical properties of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$

In order to investigate the mechanical properties, Vickers hardness and fracture toughness measurements were carried out on polished sections of the $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ ceramics with a 1 kg_f load and 15s dwell time. Indentation with large enough loads produced radial cracks emanating from the corners of the indent. The length of these cracks permits

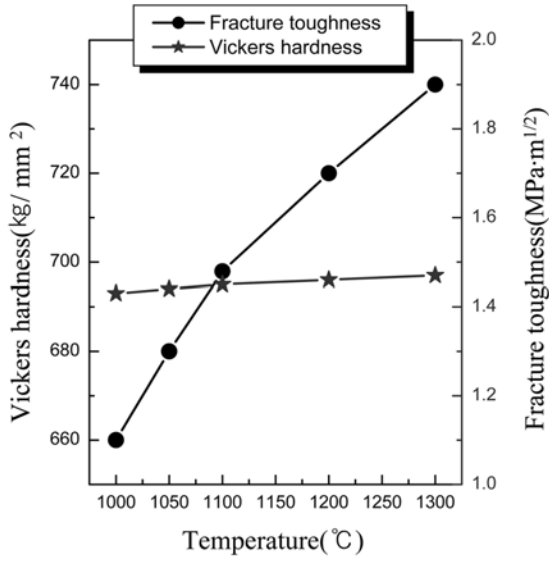


Fig. 7. Variation of Vickers hardness and fracture toughness of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ with sintering temperature.

an estimation of the fracture toughness of the material by means of the expression as [11, 12]:

$$K_{IC} = 0.204(c/a)^{-3/2} \cdot H_v \cdot a^{1/2} \quad (2)$$

where c is the trace length of the crack measured from the center of the indentation, a is half of the average length of two indent diagonals, and H_v is the hardness.

As shown in Fig. 7, the hardness increased with increasing sintering temperature and the fracture toughness is nearly constant regardless of sintering temperature. The hardness and fracture toughness of the sample sintered at 1300 °C is about 740 kg/mm² and 1.5 MPa·m^{1/2}, respectively. It is considered that the improvement in hardness with sintering temperature up to 1300 °C is due to the higher density of the sample.

Ionic conductivity of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$

Figure 8 shows the temperature dependence of the grain interior conductivity and the grain boundary conductivity of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ sintered at 1300 °C. The grain boundary conductivity is smaller than the grain interior conductivity. It has been reported that the grain boundary resistance seems to be due to the presence of siliceous phases [13]. By contrast it has also been reported that the grain boundary conductivity of samples with impurity-free grain boundaries is still about two orders of magnitude lower than the grain interior conductivity [14]. In a more recent investigation, it was suggested that oxygen vacancy depletion is effected by dopant ion segregation [15]. The ionic conductivity has been fitted as a function of temperature (T) following an Arrhenius law:

$$\sigma = (\sigma_o/T) \exp(-E_a/k_B T) \quad (3)$$

where E_a is the activation energy for ionic migration,

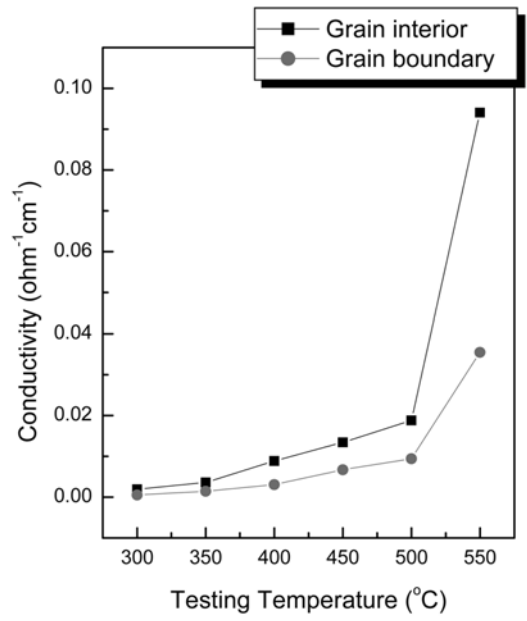


Fig. 8. Variation of the grain interior and grain boundary conductivity of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ sintered at 1300 °C.

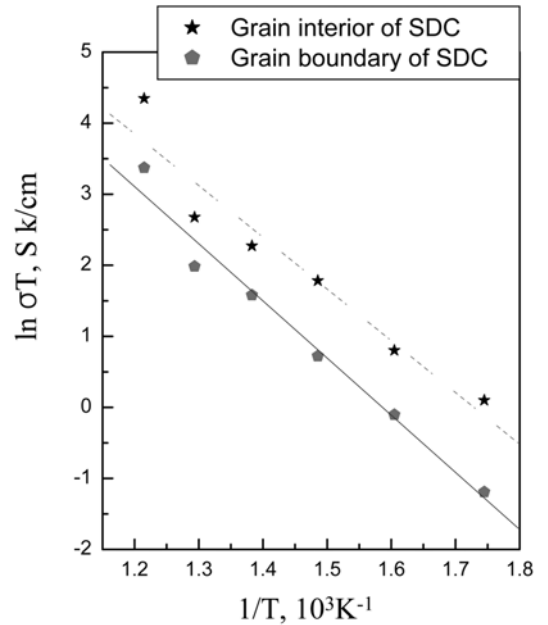


Fig. 9. Arrhenius plots of grain interior and grain boundary conductivity of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ sintered at 1300 °C.

k_B is the Boltzman constant, and σ_o the pre-exponential factor, is a constant related to the density of carriers (in this case, oxide vacancies). Figure 9 shows Arrhenius plots of the grain interior conductivity and the grain boundary conductivity of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ ceramic. The activation energies of grain interior and grain boundary conductivities calculated from equation (3) are 1.09 eV and 1.10 eV, respectively.

Summary

Using the pulsed current activated sintering method,

the densification of nanostructured $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ was accomplished from nanopowder of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$. The relative density of the $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ sample sintered with an applied pressure of 80 MPa and a pulsed current at 1300 °C was 97%. The hardness and fracture toughness of a sample sintered at 1300 °C is about 740 kg/mm² and 1.5 MPa·m^{1/2}, respectively. The grain boundary conductivity is smaller than the grain interior conductivity and the activation energies of grain interior and grain boundary conductivities are 1.09 eV and 1.10 eV, respectively.

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