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Short communication

A simple and effective process for fabrication of $Gd_{0.1}Ce_{0.9}O_{1.95}$ solid electrolyte ceramics

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Abstract

$Ce_{0.9}Gd_{0.1}O_{1.95}$ ceramics were prepared using a simple and effective process in this study. Without any prior calcination, the mixture of raw materials was pressed and sintered directly. The reaction of the raw materials occurred during the heating up period by passing the calcination stage in the conventional solid-state reaction method. More than 99.5% of theoretical density was obtained for $Ce_{0.9}Gd_{0.1}O_{1.95}$ sintering at 1500–1600 °C. Fine grains (<1 μm) formed in pellets sintered at 1450 °C. The homogeneity of grains increased with the sintering temperature. The grains grew to >4.5 μm in pellets sintered at 1600 °C. The reactive-sintering process is proved to be a simple and effective method in preparing $Ce_{0.9}Gd_{0.1}O_{1.95}$ ceramics for solid electrolyte application.

Keywords: $Ce_{0.9}Gd_{0.1}O_{1.95}$; Solid electrolyte; Reactive-sintering process

1. Introduction

Solid oxide fuel cells (SOFCs) transform chemical energy to electrical energy with high conversion efficiency and low pollution. Research and development of SOFCs have received much attention recently [1–4]. A single cell consists of three parts: the electrolyte, the anode, and the cathode. A dense electrolyte could prevent gas mixing, whereas the anode and cathode must be porous to allow gas transport to the reaction sites. Yttria-stabilized zirconia (YSZ) generally is used as the electrolyte in SOFCs due to its good ionic conductivity and chemical stability in both oxidizing and reducing atmospheres. However, a high operating temperature in the range 800–1000 °C is required for YSZ-based SOFCs. This will result in higher manufacturing costs and application limitation [5]. There are several advantages when the SOFCs are operated at an intermediate temperature range of 500–700 °C, such as lower degradation rate of cell performance, higher theoretical voltage, and lower fabrication cost through the use of metallic components. CeO_2-based oxides with a fluorite type structure showed much higher oxide-ion conductivities than ZrO_2-based oxides, and thus are expected to be candidates for the electrolyte of the SOFC operated at an intermediate temperature range of 500–700 °C. Kudo and Obayashi found that $\sigma = 4.5 \times 10^{-2}$ S cm^{-1} and the activation energy $E_a = 70$ kJ/mol (0.73 eV) at 700 °C for $Ce_{0.8}Gd_{0.2}O_{1.9}$ [6,7]. Dirstine et al. obtained $\sigma = 1.5 \times 10^{-2}$ S cm^{-1} and $E_a = 85$ kJ/mol (0.88 eV) at 700 °C for $Ce_{0.8}Gd_{0.2}O_{1.9}$ [8]. Riess et al. obtained $\sigma = \sim 2.6 \times 10^{-2}$ S cm^{-1} at 700 °C for $(CeO_2)_{0.82}(GdO_{1.5})_{0.18}$ sintered at 1700 °C for 3 h [9]. Xia and Liu obtained $\sigma = 4.5 \times 10^{-3}$ S cm^{-1} and $E_a = 65.5$ kJ/mol at 500 °C for $Ce_{0.9}Gd_{0.1}O_{1.95}$ using a glycine-nitrate combustion process [10]. Hari Prasad et al. prepared nano-crystalline $Ce_{0.9}Gd_{0.1}O_{1.95}$ powder via a novel sol–gel thermolysis method using a unique combination of urea and PVA. Ionic conductivity of 2.21×10^{-2} S cm^{-1} at 700 °C in air was found for $Ce_{0.9}Gd_{0.1}O_{1.95}$ calcined at 400 °C for 2 h and sintered at 1500 °C for 4 h [11].

In previous studies, our group had prepared Pb-based perovskite relaxor ferroelectric ceramics [12,13], microwave dielectric ceramics [14,15], thermoelectric ceramics [16,17], and ceramics for SOFCs [18–20] via a simple and effective reactive-sintering process. Without any calcination involved, the mixture of raw materials was pressed and sintered directly. The reaction of the raw materials occurred during the heating up period bypassing the calcination stage in the conventional

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solid-state reaction method. In this study, $Ce_{0.9}Gd_{0.1}O_{1.95}$ ceramic prepared using a simple and effective reaction-sintering process was investigated.

2. Experimental procedures

$Ce_{0.9}Gd_{0.1}O_{1.95}$ ceramics in this study were prepared from reagent-grade CeO_2 (99.9%, SHOWA, Japan) and Gd_2O_3 (99.9%, SHOWA, Japan) powders. Appropriate amounts of raw materials were milled in acetone with zirconia balls for 12 h. After the mixtures had been dried and pulverized, they were formed into pellets 12 mm in diameter and 1–2 mm thickness. The pellets were then heated at a rate 10 °C/min and sintered in a covered alumina crucible for 2–6 h in air at temperatures ranging from 1400 to 1600 °C.

We analyzed the sintered pellets using X-ray diffraction (XRD) to check the nature of the phases present in the samples. Microstructures were observed by scanning electron microscopy (SEM). The density of the sintered pellets was measured using the Archimedes method.

3. Results and discussion

XRD profiles of $Ce_{0.9}Gd_{0.1}O_{1.95}$ sintered at 1400 °C and 1450 °C for 2 h are shown in Fig. 1. Reflections matched with those in $Ce_{0.9}Gd_{0.1}O_{1.95}$ (JCPDS PDF # 75-0161) of fluorite type structure can easily be identified. Therefore, $Ce_{0.9}Gd_{0.1}O_{1.95}$ without second phases could be obtained via the reactive-sintering process. Mori et al. [21] prepared $Ce_{0.9}Gd_{0.1}O_{1.95}$ ceramics from $Ce(NO_3)_3$ and $Gd(NO_3)_3$ using a coprecipitation method. Calcination at 700 °C for 5 h was needed. Milliken et al. [22] prepared cation-doped CeO_2 ceramics via the conventional solid-state reaction method. A mixture of raw materials was calcined at 1050 °C for 8 h and then milled before the second calcination at 1050 °C for 8 h. Dudek [23] used citrate method to prepare CeO_2-based ceramics and calcination at 800 °C for 1 h was needed. In comparison with these studies, reaction-sintering process appears to be a simple and effective process to obtain single phase $Ce_{0.9}Gd_{0.1}O_{1.95}$ ceramics. The calcination stage is not necessary and can be bypassed.

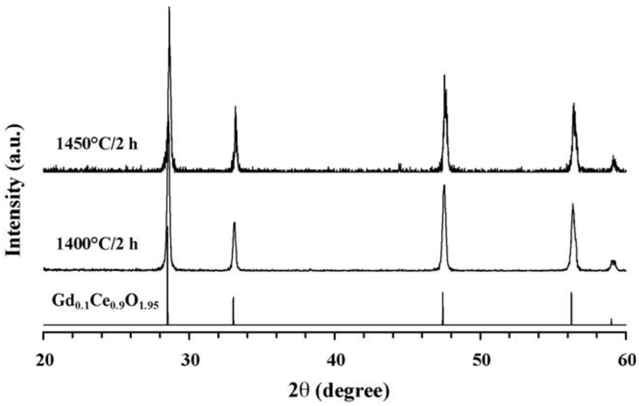

Fig. 1. XRD patterns of $Ce_{0.9}Gd_{0.1}O_{1.95}$ sintered at 1400 °C and 1450 °C for 2 h.

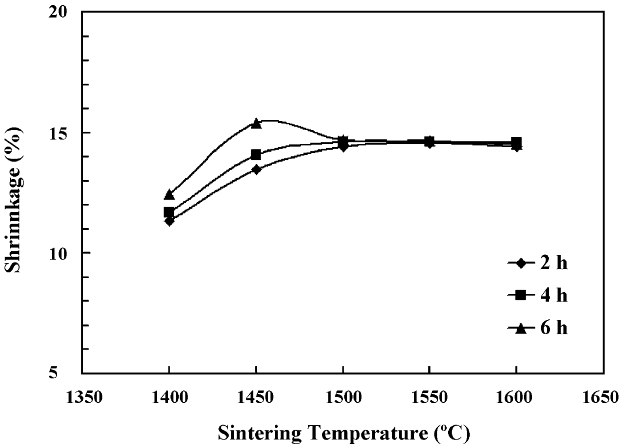

Fig. 2. Shrinkage percentages of $Ce_{0.9}Gd_{0.1}O_{1.95}$ ceramics sintered at various temperatures and soak time.

Relative shrinkage percentages for $Ce_{0.9}Gd_{0.1}O_{1.95}$ sintered at 1400 °C are found to be 11.3–12.5% as shown in Fig. 2. This implies that 1400 °C is not high enough for the densification. It increased with sintering temperature and saturated at ~14.6% when sintered at temperatures above 1500 °C. Hari Prasad et al. [11] found shrinkage of ~18% for $Ce_{0.9}Gd_{0.1}O_{1.95}$ after calcining at 400 °C for 2 h and sintering at 1100 °C via a sol–gel thermolysis method. Li et al. [24] observed shrinkage of ~20% for CeO_2 and ~23% for $Ce_{0.8}Gd_{0.2}O_{1.9}$ after sintering at 1200 °C for 4 h via a homogeneous precipitation method. Chen et al. [25] observed shrinkage of 25.3% for ZrO_2 doped with 8 mol% Y_2O_3 after sintering at 1400 °C for 2 h. Density of $Ce_{0.9}Gd_{0.1}O_{1.95}$ ceramics sintered at various temperatures and soaking times are illustrated in Fig. 3. The variation of density shows similar trends to the variation observed for the shrinkage. Density of 6.45–6.63 g/cm^3 is found for pellets sintered at 1400 °C. It increased with sintering temperature and saturate at ~7.21 g/cm^3 (>99.5% of theoretical density 7.226 g/cm^3) when sintered at temperatures above 1500 °C. A dense electrolyte is needed in SOFCs to prevent gas mixing. Tianshu and co-workers [26] obtained a relative density ~97.1% for

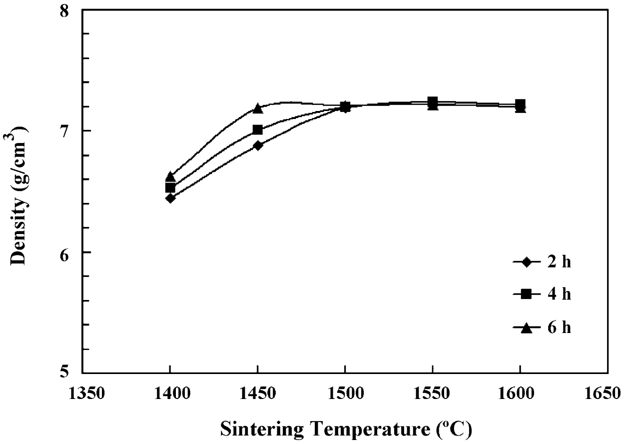

Fig. 3. Density of $Ce_{0.9}Gd_{0.1}O_{1.95}$ ceramics sintered at various temperatures and soak time.

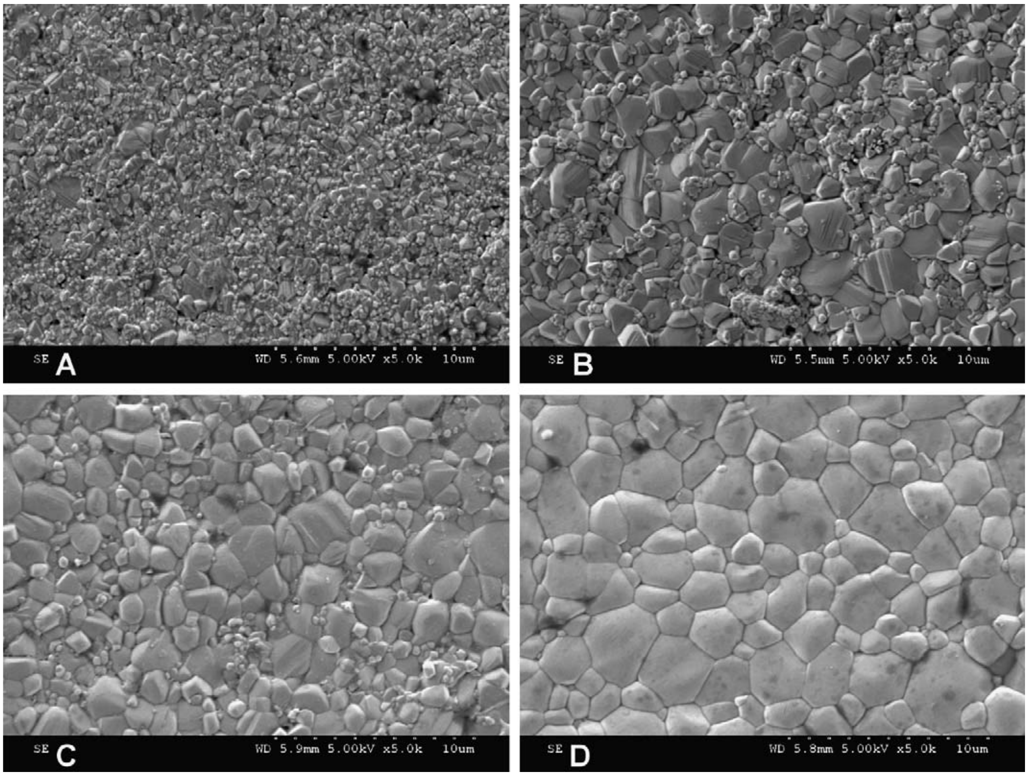

Fig. 4. SEM photographs of $Ce_{0.9}Gd_{0.1}O_{1.95}$ ceramics sintered at (A) 1450 °C, (B) 1500 °C, (C) 1550 °C, and (D) 1600 °C for 2 h.

$Ce_{0.9}Gd_{0.1}O_{1.95}$ after calcining at 800 °C and sintering at 1550 °C for 5 h via an oxalate coprecipitation method. Chourashiya et al. [27] observed a low relative density ~84% for $Ce_{0.9}Gd_{0.1}O_{1.95}$ after calcining at 750 °C for 2 h and sintering at 1500 °C for 2 h. Xia and Liu [28] reported a relative density ~97% for $Ce_{0.9}Gd_{0.1}O_{1.95}$ after calcining at 600 °C for 2 h and sintering at 1450 °C for 5 h via a glycine-nitrate process. In comparison with these studies, the reactive-sintering

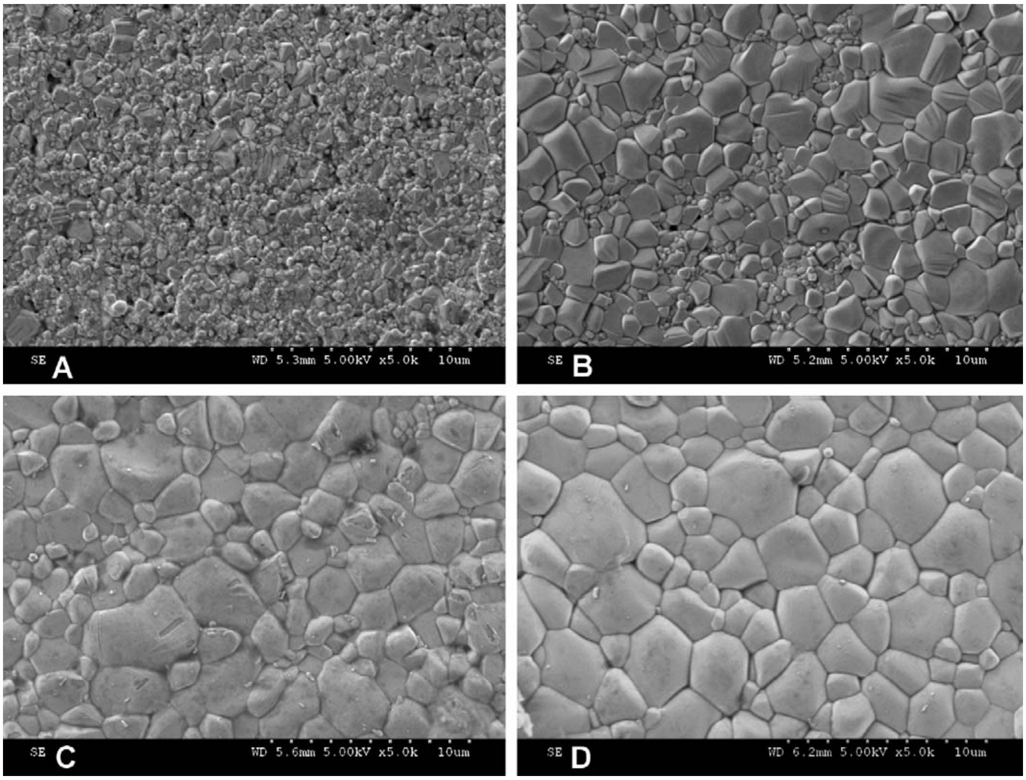

Fig. 5. SEM photographs of $Ce_{0.9}Gd_{0.1}O_{1.95}$ ceramics sintered at (A) 1450 °C, (B) 1500 °C, (C) 1550 °C, and (D) 1600 °C for 4 h.

process appears to be a very effective process to obtain highly dense $Ce_{0.9}Gd_{0.1}O_{1.95}$ ceramics.

SEM photos of $Ce_{0.9}Gd_{0.1}O_{1.95}$ sintered at 1450–1600 °C for 2 h are shown in Fig. 4. Fine grains <1 μm formed in the most parts of pellets sintered at 1450 °C. 1–3 μm grains accompanied with some submicron fine grains were observed for pellets sintered at 1500 °C. The homogeneity of grains increased with the sintering temperature. The fine grains disappeared and grains >4.5 μm existed in pellets sintered at 1600 °C. Grain sizes increased for $Ce_{0.9}Gd_{0.1}O_{1.95}$ sintered at 1450–1600 °C for 4 h. In Fig. 5, less submicron fine grains and more homogeneous microstructure were observed for $Ce_{0.9}Gd_{0.1}O_{1.95}$ sintered at 1500–1600 °C for 4 h. Tianshu and co-workers [26] observed $Ce_{0.9}Gd_{0.1}O_{1.95}$ of ~5.1 μm grains after calcining at 800 °C and sintering at 1550 °C for 5 h via an oxalate coprecipitation method. Chourashiya et al. [27] observed $Ce_{0.9}Gd_{0.1}O_{1.95}$ with average grain size 2.5 μm and 3 μm after 2 h sintering at 1400 °C and 1500 °C, respectively. Xia and Liu [28] found $Ce_{0.9}Gd_{0.1}O_{1.95}$ of ~2 μm grains after calcining at 600 °C for 2 h and sintering at 1450 °C for 5 h via a glycine-nitrate process. It is noted that submicron fine grains were not observed in the above mentioned studies. We believe that the formation of submicron fine grains as shown in Figs. 4 and 5 is mainly due to the bypassing of calcinations stage. The reaction of the reactants CeO_2 and Gd_2O_3 occurred during the heating up period. According to the study of Chourashiya et al. [27], the mixture of raw materials was calcined at 750 °C for 2 h. In this study, there was only 70 min for the temperature to raise from 750 °C to 1450 °C at a rate 10 °C/min. Therefore, the reaction of reactants CeO_2 and Gd_2O_3 may not be completed in the beginning of sintering stage. Consequently, the nucleation and grain growth could not be completed for pellets sintered at a lower temperature or a shorter soaking time. This could be seen in Figs. 4 and 5. Such phenomenon was not observed in our previous studies of Pb-based perovskite relaxor ferroelectric ceramics [12,13], microwave dielectric ceramics [14,15], thermoelectric ceramics [16,17], and ceramics for SOFCs [18,19] via a reactive-sintering process.

4. Conclusions

Single phase $Ce_{0.9}Gd_{0.1}O_{1.95}$ ceramics can be obtained via the reactive-sintering process with the calcination stage bypassed. More than 99.5% of theoretical density was obtained for $Ce_{0.9}Gd_{0.1}O_{1.95}$ sintering at 1500–1600 °C. Fine grains <1 μm formed in pellets sintered at 1450 °C. The homogeneity of grains increased with the sintering temperature. The grains grew to >4.5 μm existed in pellets sintered at 1600 °C. The reactive-sintering process is proved to be a simple and effective method in preparing $Ce_{0.9}Gd_{0.1}O_{1.95}$ ceramics for solid electrolyte application.

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