SYNTHESIS OF $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ NANOPARTICLES VIA COPRECIPITATION

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Abstract

$Ce_{0.8}Sm_{0.2}O_{2-\delta}$ nanoparticles have been synthesized via carbonate coprecipitation method using ammonium carbonate (AC) as a precipitant. The AC:RE (RE = Ce + Sm) molar ratio (R) and the reaction temperature (T) affect particle size and morphology. The spherical nanoparticles can be obtained in a range of $R \leq 10$. The optimum processing condition to achieve the powder particle size of 20 - 25 nm is R = 10 and T = 70°C. However, the single phase of calcined powder can be detected from XRD regardless of synthesis conditions. SEM micrographs of samples sintered at 1,300°C with a soaking time of 2 h show uniform and small grains.

Keywords: Fuel cells, CeO_2, coprecipitation

Introduction

Rare earth doped CeO_2 solid solutions generally show better electrical conductivity than stabilized ZrO_2 and have a great potential for applications in solid oxide fuel cells (SOFCs) operating at intermediate temperatures (400 - 700°C) (Zhang *et al.*, 2004; Li *et al.*, 2005). One important property of electrolyte in SOFCs is high density to prevent gas leakage from one electrode to another. The powders produced via solid-state reaction from the component oxides have to be fired at ≈ 1,700 - 1,800°C to achieve the desired density (Li *et al.*, 2004). Another disadvantage for this conventional method is the contamination from repeated mechanical milling during the preparation process. It has been reported that a highly resistive glassy phase from impurities existed along grain boundaries, resulting in blocking electrical conduction (Li *et al.*, 2001).

The other synthesized method, namely coprecipitation, has been developed and successfully used for preparing doped-ceria materials, and the resultant powders show nanometer-sized particles. The morphology of precipitated powders significantly depends on the precipitant and conditions. Wang *et al.* (2003) have synthesized $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ via coprecipitaion using urea precipitant: total cations of 0.5:0.015 M at the reaction temperature of 90°C. The synthesized powder is composed of platelet-like and micrometer-sized

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particles. In addition, Wang *et al.* (2005) have prepared the nanospherical particles of $Ce_{0.8}Dy_{0.2}O_{2-\delta}$ from 1.5 M of ammonium carbonate and 0.15 M of cations at the reaction temperature of 70°C. Kamruddin *et al.* (2004) have shown that the homogeneous precipitation using hexamethylenetetramine: total cations molar ratio = 0.5:0.1 M at the reaction temperature of 80°C can produce largely agglomerated nanoparticles of ceria and form plate-like morphology after calcination. The main advantage of carbonate coprecipitation over other synthetic methods is less agglomeration after drying of the precipitated powder and the resultant oxides exhibit excellent sinterability (Li *et al.*, 2001). In this work, $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ has been synthesized by carbonate coprecipitation method using ammonium carbonate as the precipitant with different mole ratios and reaction temperatures.

Materials and Methods

$Ce_{0.8}Sm_{0.2}O_{2-\delta}$ was synthesized via a coprecipitation method using ammonium carbonate (AC) (Riedel-de Haën, Germany) as a precipitant. The starting salts were rare-earth nitrate hexahydrate (99.9% pure, Aldrich, USA) which were dissolved in deionized water. Table 1 shows the mole ratio of RE (Ce + Sm) and the precipitant used in this experiment. The precipitation was performed on a hot plate equipped with a thermocouple and a magnetic stirrer. The mixed salt solution was dripped at a speed of 4 mL/min from a buret into the precipitant solution at a controlled temperature under mild stirring. After aging at the reaction temperature for 1 h, the precipitates were filtered using a suction filter and were washed several times with deionized water and finally with anhydrous alcohol before drying overnight. The dried precursors were then lightly crushed in an agate mortar and calcined at 800°C for 1 h.

The particle size and morphology of the synthesized precursors were observed via transmission electron microscope (TEM, JEOL JEM-1020). Phase identification was performed via X-ray diffractometer (XRD, Bruker D5005) using Cu Ka radiation. The calcined powder was pressed into pellets with a uniaxial hydraulic press, followed by a cold-isostatic press at 190 MPa. All $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ samples were sintered at 1,300°C with a soaking time of 2 h. The cross-sectional sintered samples were polished with SiC papers from the number of 100 down to 1,200 and followed by diamond paste down to 1 mm. The polished samples were thermally etched at 1,200°C for 2 h to reveal grain boundaries and then coated with gold by sputtering. The microstructure of the sintered samples was observed using scanning electron microscope (SEM, JEOL JSM-6400). An average grain size was calculated from SEM micrographs using the linear intercept method.

Results

Figure 1(a-e) shows TEM micrographs of the $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ powder synthesized by using different mole ratios and reaction temperatures. The particle sizes of prepared nanopowder obtained from R = 6.67 and 10 with the reaction temperature of 70°C are 25 - 40 nm and 20 - 25 nm, respectively. In contrast, the particle size of nanorods precipitated from R = 13.33 is 20 - 30 nm in diameter. In addition, the bigger particle sizes of 25 - 30 nm and 50 - 60 nm can be obtained from R = 10 at the lower reaction temperatures of 29°C and 50°C, respectively.

The complete coprecipitation is investigated by dripping ammonium carbonate solution into the liquid remaining after filtration. The complete coprecipitation can be achieved for all synthesis conditions due to no precipitation after dripping ammonium carbonate solution.

Figure 2 shows XRD patterns of $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ synthesized via different synthesis conditions and calcined at 800°C for 1 h. The results show that a single phase similar to the fluorite-structure of CeO_2 (JCPDS: pattern 34-0394) appears regardless of the synthesis conditions.

The different nanopowder size and morphology are selected to investigate the effect on the grain size after sintering. Scanning electron micrographs of sintered samples synthesized using different synthesis conditions

are illustrated in Figure 3(a-c). The average grain sizes of the sintered samples determined from the linear intercept method are 0.27 mm and 0.38 mm as shown in Figures 3(a) and 3(b). These grain sizes are obtained from the synthesized spherical precipitated powder of 20 - 25 nm and 50 - 60 nm shown in Figures 1(b) and 1(e). The result implies that the smaller nanopowder tends to perform the smaller grain size. In addition, the synthesized nanorod of 20 - 30 nm in diameter illustrated in Figure 1(c) can sinter to the larger grain size of 0.49 mm as represented in Figure 3(c). The particle shape and size for all synthesis conditions and the average grain size of sintered samples calculated from the linear intercept method are given in Table 2.

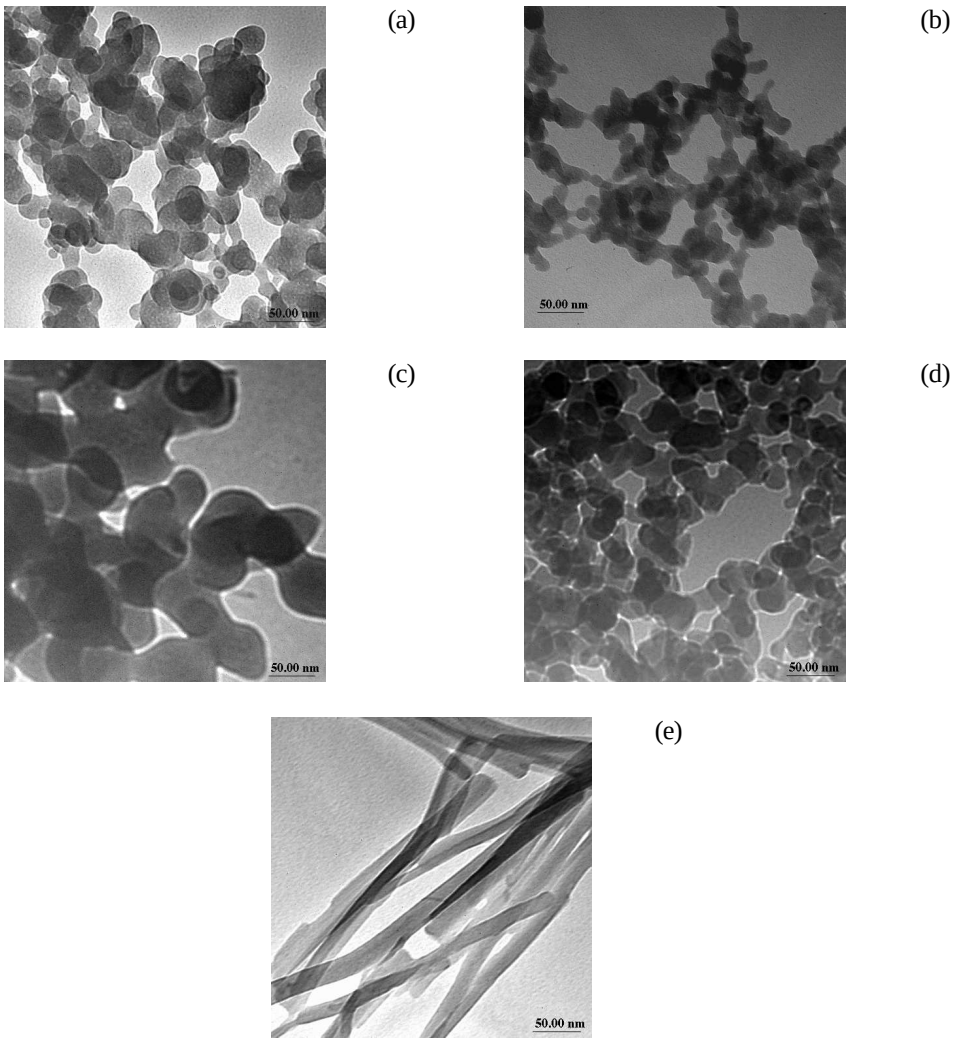

Figure 1. TEM micrographs of the $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ synthesized by using different mole ratios (R) and reaction temperatures (T) (50,000X): (a) R = 6.67, T = 70°C, (b) R = 10, T = 70°C, (c) R = 10, T = 50°C, (d) R = 10, T = 29°C, (e) R = 13.33, T = 70°C

Discussion

The molar ratio significantly affects the particle size and morphology. The rounded shape nanoparticles are obtained from R = 6.67 and 10 regardless of the reaction temperature while elongated particles from R = 13.33. The lower molar ratio at R = 6.67 yields the larger spherical particles compared to that of 10 with the same reaction temperature of 70°C. In addition, the reaction temperature also affects the particle size. The lower reaction temperatures at room temperature and 50°C can produce the larger particle sizes compared to that of 70°C with the same molar ratio of 10. The optimum condition to achieve the ultrafine particle size and spherical particle shape from this study is R = 10 and T = 70°C.

The synthesis conditions do not affect the phase present after calcination. In addition, there is no evidence that the second phase appeared on the patterns. This result is in agreement with Kamruddin *et al*'s work (2004), although they used hexamethylenetetramine as a precipitant.

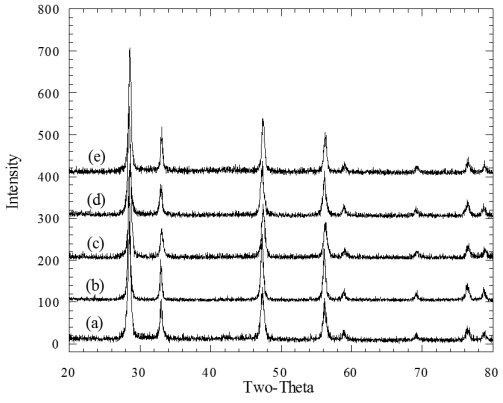

Figure 2. XRD patterns of $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ synthesized via different synthesis conditions after calcination at 800°C: (a) R = 6.67, T = 70°C, (b) R = 10, T = 70°C, (c) R = 10, T = 50°C, (d) R = 10, T = 29°C, (e) R = 13.33, T = 70°C

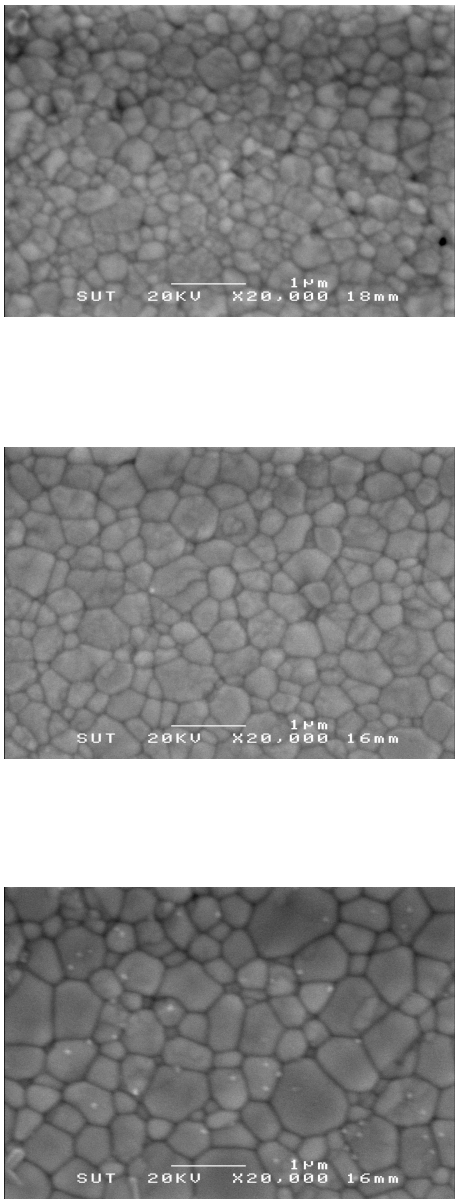

Figure 3. SEM micrographs of the $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ samples from the powders synthesized using different synthesis conditions after sintering at 1300°C for 2h: (a) R = 10, T = 70°C, (b) R = 10, T = 50°C, (c) R = 13.33, T = 70°C

Table 1. Mole ratio and reaction temperature used in this experiment

RE:AC (M)	Mole ratio (AC:RE)	Reaction temperature (°C)
0.15:1.0	6.67	70
0.15:1.5	10.00	70
0.15:1.5	10.00	50
0.15:1.5	10.00	29
0.15:2.0	13.33	70

Table 2. Particle shape and size for all synthesis conditions and the average grain size of the samples sintered at 1,300°C for 2 h

Mole ratio (AC:RE)	Reaction temperature (°C)	Particle shape / size (μm)	Average grain size (mm)
6.67	70	Round / 25 - 40	-
10.00	70	Round / 20 - 25	0.27
10.00	50	Round / 50 - 60	0.38
10.00	29	Round / 25 - 30	-
13.33	70	Elongated	0.49

SEM micrographs of sintered samples show small and uniform grains after sintering at 1,300°C with a soaking time of 2 h. This result indicates that the sintered grain size is dependent on the size and morphology of the starting powder. The average grain sizes of 0.27 mm, 0.38 mm and 0.49 mm obtained from the synthesized spherical particles of 20 - 25 nm, 50 - 60 nm and the elongated particle of 20 - 30 nm in diameter, respectively.

Conclusions

Nanocrystalline $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ particles have been successfully synthesized via coprecipitation using ammonium carbonate as the precipitant. The AC:RE molar ratio and reaction temperature affect particle size and morphology. The rounded shape nanoparticles can be obtained from $R \leq 10$ while elongated particles can be obtained from $R > 10$. The lower reaction temperature and lower molar ratio produce larger particle sizes. The single phase of the fluorite structure is formed during the calcination regardless of the synthesis conditions. The microstructure of all sintered samples shows uniform and small grains with different sizes corresponding to the morphology of the synthesized powder.

Acknowledgement

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References

Kamruddin, M., Ajikumar, P.K., Nithya, R., Tyagi, A.K., and Raj, B. (2004). Synthesis of nanocrystalline ceria by thermal decomposition and soft-chemistry methods. Scripta Materialia, 50:417-422.

Li, J.G., Ikegami, T., and Mori, T. (2004). Low temperature processing of dense samarium-doped CeO_2 ceramics: sintering and grain growth behaviors. Acta Materialia, 52:2,221-2,228.

Li, J.G., Ikegami, T., Mori, T., and Wada, T. (2001). Reactive $Ce_{0.8}RE_{0.2}O_{1.9}$ (RE = La, Nd, Sm, Gd, Dy, Y, Ho, Er and Yb) powders via carbonate coprecipitation: 1. Synthesis and characterization. Chemistry of Materials, 13:2,913-2,920.

Li, J.G., Wang, Y., Ikegami, T., Mori, T., and Ishigaki, T. (2005). Reactive 10 mol% RE_2O_3 (RE = Gd and Sm) doped CeO_2 nanopowders: Synthesis, characterization, and low-temperature sintering into dense ceramics. Material Science and Engineering B, 121:54-59.

Wang, Y., Mori, T., Li, J.G., and Drennan, J. (2005). Synthesis, characterization and electrical conduction of 10 mol% Dy_2O_3-doped CeO_2 ceramics. J. Eur. Ceram. Soc., 25:949-956.

Wang, Y., Mori, T., Li, J.G., and Yajima, Y. (2003). Low-temperature fabrication and electrical property of 10 mol% Sm_2O_3-doped CeO_2 ceramics. Science and Technology of Advanced Materials, 4:229-238.

Zhang, T.S., Ma, J., Chan, S.H., Hing, P., and Kilner, J.A. (2004). Intermediate-temperature ionic conductivity of ceria-based solid solutions as a function of gadolinia and silica contents. Solid State Sciences, 6:565-572.