

SYNTHESIS AND SINTERING BEHAVIOR OF NANO CRYSTALLINE Gd-DOPED CERIA

Seung Hwan Jo^{1, a}, Jong Ho Kim^{1, b}, Do Kyung Kim^{1, c}

¹Department of Material Science and Engineering, Korea Advanced Institute of Science and Technology(KAIST), 373-1 Kusong-dong, Yusong-gu, Daejeon, 305-701, South Korea

^aultrasammy@kaist.ac.kr, ^btruffle@kaist.ac.kr, ^cdkkim@kaist.ac.kr

Keywords: ceria, nano particle, solid oxide fuel cell, neutral precipitation, glycine nitrate combustion, sintering behavior

Abstract

Two kinds of nano crystalline Gd-doped CeO₂ particles were successfully synthesized via glycine-nitrate combustion and neutral precipitation with subsequent hydrothermal crystallization. It was revealed that the surface modification of nano particles significantly affected sintering behaviors and resulting physical properties. Glycine/nitrate ratio was a key parameter to control the surface state of nano particles in the glycine-nitrate process, but, in the neutral precipitation process, the solvent was important. To obtain the GDC nano particles with chemically and physically favorable properties, the effect of the surface state of nano particles on the sintering behavior was discussed with consideration of aggregation property and surface-adsorbed substances on nano particles.

Introduction

Gd-doped ceria(GDC) is one of the most promising solid electrolytes proposed for the intermediate temperature application of solid oxide fuel cell.[1]. Consequently, the synthesis of GDC nano particles with advantages such as fast densification and a lower sintering temperature has been attracting worldwide attention. Generally, some effective synthetic techniques have been used to produce oxide nano particles, including precipitation,[2-3] hydrothermal synthesis,[4] combustion,[5] electrochemical synthesis,[6] and solid-state reaction.[7] However, nano particles synthesized by an aqueous-based method usually contain some organic contents on the surface of the particles and have a tendency to form hard aggregations easily due to the bridging of adjacent particles with water by hydrogen bond and the subsequent huge capillary force during drying [8]. These undesirable impurities and hard aggregation make it difficult to maximize the advantages of nano particles. In consideration of this, the effects of preparation conditions on surface states such as aggregation property and surface adsorbed organic molecules and subsequent sintering behavior are very crucial to the optimization of the properties of ceramic materials. However, little research has been done about the relationship between sintering behavior and the surface state of nano particles.

In this study, two kinds of 20 mole % Gd-doped CeO₂ nano particles were synthesized via glycine-nitrate combustion and neutral precipitation with subsequent hydrothermal crystallization. To control the property of the nano particles, the hydrothermal crystallization temperature and glycine nitrate mole ratio were changed respectively in each process. In both processes, the effect of the dispersion solvent on the sintering behavior of GDC nano particles was examined. Also, the effect of the fuel to nitrate ratio on powder properties and consequent sintering behavior was inspected in glycine nitrate combustion process. Finally, the clear co-relationship between characteristics of GDC nano particles and sintering behavior was discussed with consideration of aggregation and surface state.

Experimental procedures

First, a neutral precipitation method was introduced to produce nanocrystalline Gd-doped CeO_2 particles. Separate solutions of 0.1 M Ce(III)/Gd(III) nitrates in deionized water and of 30 vol% hydrogen peroxide were mixed together by stirring. After 10 min, ammonium hydroxide solution was added to increase the pH value to 9 ± 9.2 . The orange precipitate settled rapidly from the solution when the pH value went up. The solution was decanted and the precipitate was washed out. Subsequent hydrothermal treatment at 180 °C for 4 hrs under autogenous pressure resulted in a crystalline oxide. After cooling, the yellowish precipitate was washed with distilled water or three different alcohols and then dried at 80 °C overnight. The dried particles were calcined at 450 °C for 2hrs, ball milled with the same solution for for 24 hours, and dried again at 80 °C overnight. Secondly, the GDC nano particles were prepared via a glycine nitrate combustion process. Stock solutions of one molar concentration were prepared by dissolving Ce(III)/Gd(III) nitrates in deionized water. Glycine was added in 1, 1.75, 2.5, 3 mol/mol of metal nitrates to control the particle size and surface state. The starting solution was concentrated on a hot plate at about 400 °C until it became a gel of a foamy consistency. As-synthesized foamy particles from the reaction were ball milled for 24 hours with deionized water and three different alcohols, and then dried at 80 °C overnight. Phase, morphology and composition of GDC nano particles were analyzed using XRD(Rigaku, Japan), TEM(Tecnai F20, USA) and SEM/EDS(Philips XL30, Netherlands), respectively. The Scherrer equation was used to calculate the crystallite size of the GDC nano particles from the XRD data. Thermal decomposition behavior of the GDC nano particles with different solvent treatments was analyzed using a TG-DTA analyzer(Rigaku, Japan) in a flowing air atmosphere with a heating rate of 5 °C/min. Densification behavior of the GDC nano particles was investigated in air by means of thermal mechanical analyzer(TMA, Setaram, France) and isothermal sintering carried out in an air atmosphere.

Results and discussion

Characteristics of Gd-doped CeO_2 nano particles

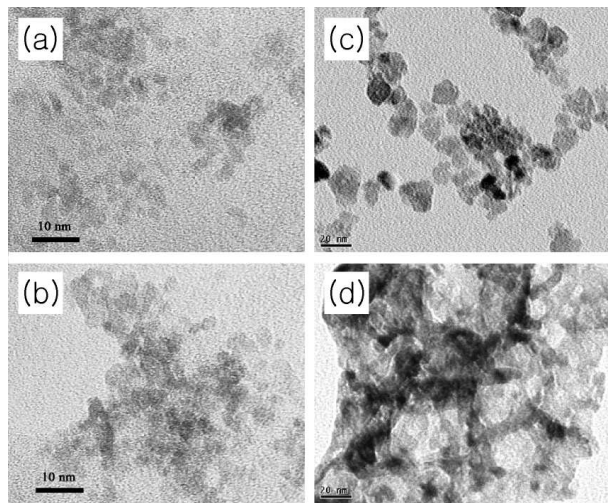


Fig 1. TEM micrographs of GDC nano particles synthesized via neutral precipitation and hydrothermal crystallization at (a) 140 °C, (b) 180 °C, and via glycine nitrate combustion process glycine/nitrate mole ratio (c) 1, (d) 1.75.

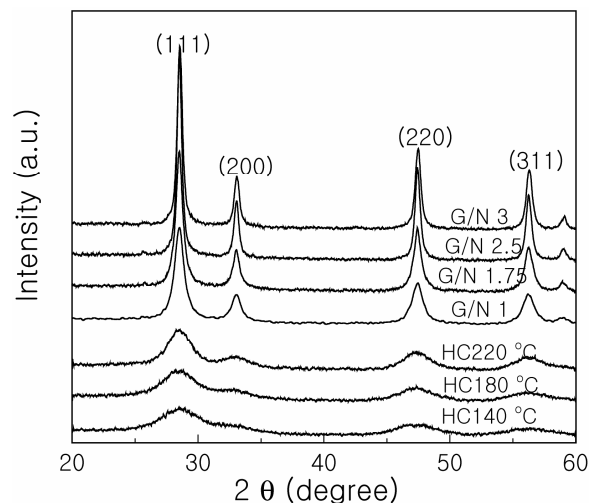


Fig 2. XRD pattern of GDC nano particles synthesized via (a) neutral precipitation, (b) glycine nitrate combustion process (GNP). G/N denotes glycine-to nitrate ratio in GNP process, and HC denotes hydrothermal crystallization.

Table 1. Synthesis conditions and characteristics of nano particles

Synthesis route		Temperature or G/N	Particle size (nm)*	Composition**
Routes				
Neutral precipitation	Hydrothermal Temperature	140 °C	2.8	Ce _{0.80} Gd _{0.20} O _{1.9}
		180 °C	3.3	Ce _{0.79} Gd _{0.21} O _{1.9}
		220 °C	4.0	Ce _{0.80} Gd _{0.20} O _{1.9}
Glycine nitrate combustion process	Glycine/Nitrate Mole ratio (G/N)	1	9.1	Ce _{0.79} Gd _{0.21} O _{1.9}
		1.75	12.5	Ce _{0.77} Gd _{0.23} O _{1.9}
		2.5	18.6	Ce _{0.76} Gd _{0.24} O _{1.9}
		3	17.8	Ce _{0.79} Gd _{0.21} O _{1.9}

* measured by Scherrer formula.

** characterized by energy-dispersive X-ray analysis.

Gd-doped CeO₂(GDC) nano particles were successfully synthesized by two processes, neutral precipitation with subsequent hydrothermal crystallization and glycine nitrate combustion process. TEM micrographs of Fig. 1 show the size and morphology of the synthesized particles. It can be seen that very fine GDC nano particles (~5 nm) are obtained from the neutral precipitation and subsequent hydrothermal crystallization process. Also, fine sized nano particles (~ 20 nm) can be obtain from glycine nitrate combustion process. Figure 2 shows XRD patterns of the GDC nano particles synthesized by each process. In both cases, major reflections of CeO₂ with the fluorite structure are displayed. Table 1 shows the particle size of the GDC nano particles calculated from the XRD result using the Scherrer equation and the composition from doping level results using EDS analysis. Particle size is controlled by the hydrothermal treating temperature in the neutral precipitation method and the glycine nitrate mole ratio in the glycine nitrate combustion process. Moreover, the composition is matches well with the expected value, that is, Ce_{0.80}Gd_{0.20}O_{1.9}.

Effect of dispersion solvent on sintering behavior of nano particles

Sintering behavior of GDC nano particles depending on dispersion solvent was investigated

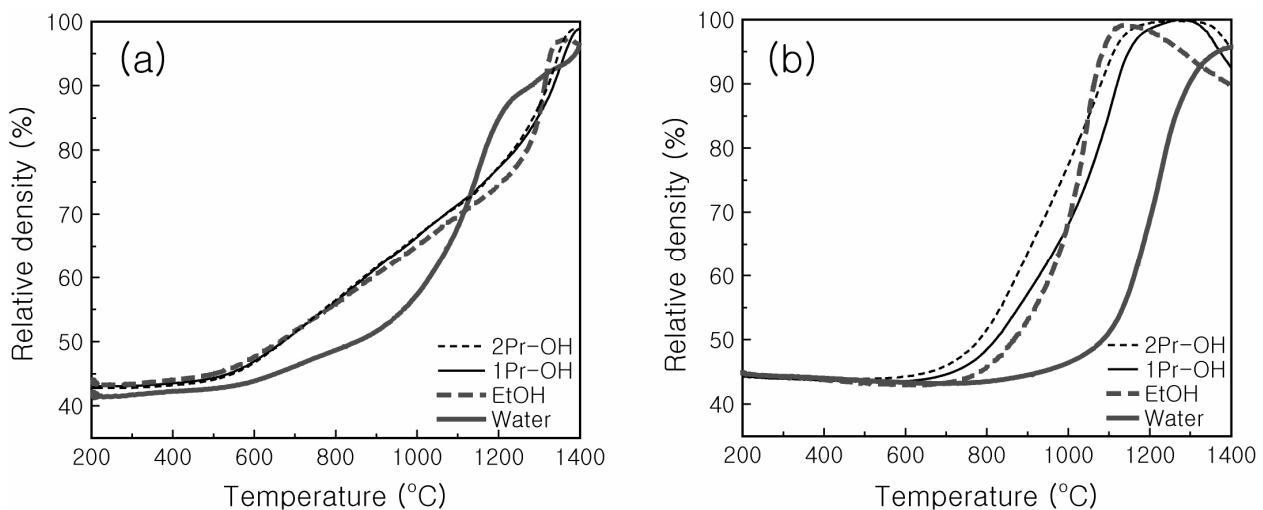


Fig. 3. Relative density versus temperature (according to solvent) in the case of (a) neutral precipitation, (b) glycine nitrate combustion process

by a thermal mechanical analyzer in air at the constant heating rate of 2 °C/min, and the results are presented in Fig. 3. Figure 3(a) shows the shrinkage curves of GDC nano particles synthesized by neutral precipitation with different dispersion solvents. Alcohol-dispersed nano particles begin to show shrinkage around 500 °C, and the shrinkage saturates near 1400 °C. However, the shrinking behavior of water-dispersed nano particles is quite complex. It shows a 2-stage shrinkage. The particles start to shrink when they reach a high temperature (over 500 °C). Shrinking is rapid at the range of 1000 ~ 1200 °C, and it continues to occur with a slower densification rate afterward. It can be concluded that dispersion solvent significantly affects the sintering behavior of GDC nano particles synthesized via neutral precipitation. Especially, alcohol dispersion enabled faster densification of GDC nano particles than water dispersion below 1100 °C. The shrinkage behavior of GDC nano particles synthesized by the glycine nitrate process according to dispersion solvent is shown in Fig. 3(b). Alcohol dispersed nano particles started to shrink earlier than water dispersed ones and reached full density relatively faster. Alcohol dispersed GDC nano particles showed drastic shrinkage from 700 °C and reached full density at 1200 °C before starting de-densification afterwards. This de-densification phenomenon results from the reduction of Ce^{4+} ions to Ce^{3+} ions at temperatures over 1200 °C.[9] On the other hand, water dispersed GDC nano particles started to shrink at 1000 °C and reached near full density at 1400 °C while showing no de-densification throughout the experimental temperature range. The slow densification of water dispersed GDC nano particles in both processing routes originates from the hard agglomeration formed between adjacent primary particles due to the high polarity and short organic chain length of water molecules, while alcohol induces weak agglomeration of nano particles due to its weak polarity and long organic chains. Thus, it can be concluded that alcohol dispersion is advantageous for forming weak agglomeration of primary particles and consequent faster densification than water dispersed ones in the case of nano-sized particles. However, no significant difference in the shrinkage rate depending on the property of alcohols was detected.

Effect of fuel-to-nitrate ratio on sintering behavior of nano particles

Figure 4 shows a thermal analysis of GDC nano particles synthesized at different glycine/nitrate mole ratios in the glycine nitrate combustion process. GDC nano particles synthesized from different glycine/nitrate mole ratios have different surface states as well as diverse particle size. Weight loss is due to water evaporation or thermal decomposition of organic molecules on the surface of GDC nano particles, and the exothermic peaks are from the crystallization of the residual amorphous phase during continuous heating up to 1000 °C.

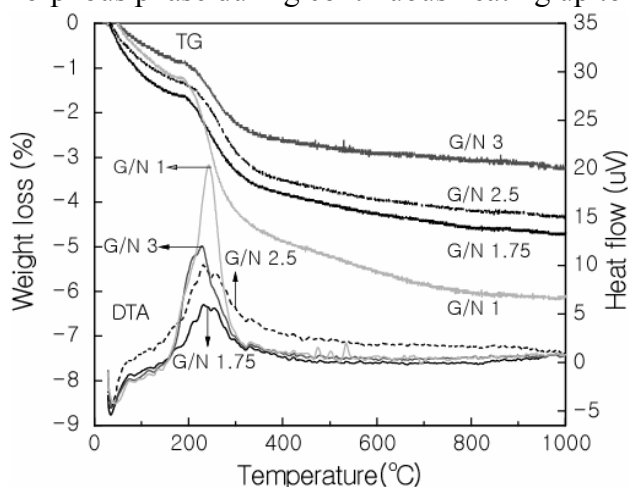


Fig. 4. Thermal decomposition property of GDC nano particles according to glycine/nitrate mole ratio

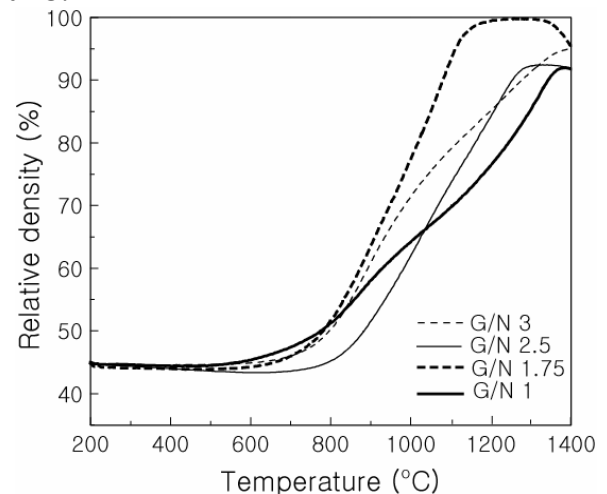


Fig. 5. Relative density versus temperature according to glycine/nitrate mole ratio

GDC nano particles synthesized at glycine/nitrate mole ratio 1.75 have the lowest weight loss and exothermic peak at near 250 °C, while ones synthesized at glycine/nitrate mole ratio 1 have the highest values. This means the cleanest surface state and best crystallization state can be obtained in the case of a glycine/nitrate mole ratio of 1.75. Thus, nano particles synthesized in an aqueous system contain some residual amorphous phases and organic molecules on the surface.[10] These undesirable impurities on the surface of nano particles are expected to slow down the densification rate while producing gas molecules during the sintering process. Consequently, the study of optimistic conditions of nano particles in consideration of the surface state is needed.[11].

The shrinkage of GDC nano particles according to glycine/nitrate mole ratio is displayed in Fig. 5. It can be concluded that the sintering behavior of GDC nano particles was affected significantly by organic contents on the surface. GDC nano particles synthesized at glycine/nitrate mole ratio 1.75 showed the fastest densification rate compared to those under other conditions. On the contrary, nano particles synthesized at glycine/nitrate mole ratio 1 showed the slowest densification behavior because of a high content of organic molecules on the surface and large amount of amorphous phase, even though they have the smallest particle size.

Figure 6 shows densification and grain growth behavior according to glycine/nitrate mole ratio. GDC nano particles from glycine/nitrate mole ratio 1 produced a fine grained microstructure (~ 500 nm) nearly without grain growth at an increased sintering temperature. On the other hand, the ones from glycine/nitrate mole ratio 1.75 already produced a fully dense microstructure with relatively coarse grains at 1200 °C and showed drastic grain growth (up to 4 μm) and de-densification behavior at 1400 °C.

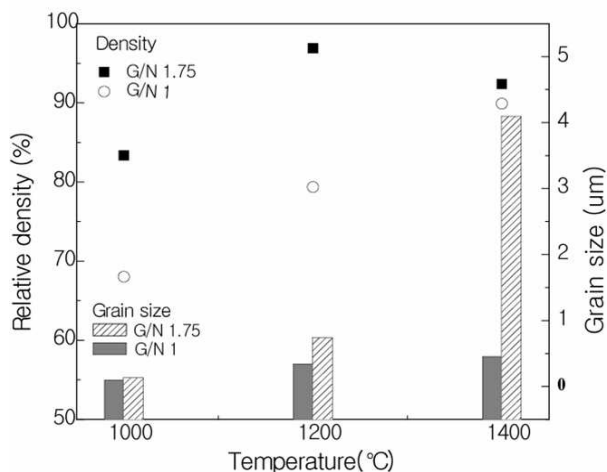


Fig. 6. Relative density & grain size vs. sintering temperature according to glycine / nitrate mole ratio

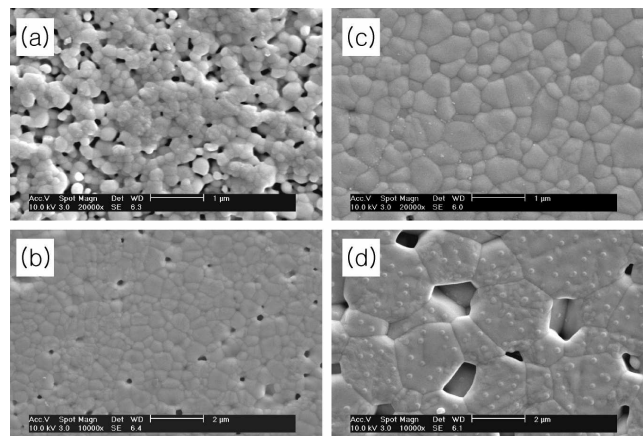


Fig. 7. SEM micrographs of sintered GDC nano particles at (a) 1200 °C, (b) 1400 °C from glycine/nitrate mole ratio 1 (c) 1200 °C, (d) 1400 °C from glycine/nitrate mole ratio 1.75

This means that the surface-adsorbed organic molecules or amorphous remainders prevent the densification of GDC nano particles and suppress grain growth, while fewer organic molecules and amorphous remainders are advantageous for shortening densification time and lowering sintering temperature.

Figure 7 shows SEM micrographs of polished and thermally etched GDC bulk prepared by pressureless sintering at 1200 °C and 1400 °C with nano particles that have come from different mole ratios of glycine/nitrate. These well confirm the densification and grain growth behavior of GDC nano particles as shown in Fig. 6.

Summary

GDC nano particles were synthesized successfully via neutral precipitation and subsequent hydrothermal crystallization and a glycine nitrate combustion process. The sintering behavior of GDC nano particles was significantly affected by the kind of dispersion solvent used. Especially, alcohol dispersion induced highly sinterable GDC nano particles with soft agglomeration between adjacent primary particles due to its weak polarity and steric force because of long chain molecules. Fuel to nitrate ratio was a key factor to control the surface state of GDC nano particles and subsequent sintering characteristics in the glycine nitrate combustion process. Surface adsorbed organic molecules and residual amorphous hydroxide slowed down the densification rate and suppressed grain growth, while ones with little organic content on the surface and high crystallinity showed fast densification and rapid grain growth. Finally, it can be concluded that the surface condition is a very important factor in affecting the sintering behavior of nano particles in comparison to micron-sized particles. Thus, the effective control of the surface state of nano particles is needed to maximize the sintering properties of GDC nano particles.

References

- [1] B. C. H. Steele, *Nature* 414 (2001) p. 345-352
- [2] P.-L. Chen and I-W. Chen, *J. Am. Ceram. Soc.*, 76 [6] (1993) p. 1577-83
- [3] J.-G. Li, T. Ikegami, J.-H. Lee, and T. Mori, *Acta Mater.*, 49 (2001) p. 419-26
- [4] C. H. Cho, D. H. Kim, and D. K. Kim, *J. Am. Ceram. Soc.*, 86 [7] (2003) p. 1138-45
- [5] Y. K. Kim, H. K. Kim, G. S. Cho, and D. K. Kim, *J. Mater. Res.*, 19 [2] (2004) p. 413-416
- [6] Y. C. Zhou, R. J. Philips, and J. A. Switzer, *J. Am. Ceram. Soc.*, 78[4] (1995) p. 981-85
- [7] X. Yu, F. Li, X. Ye, X. Xin, and Z. Xue, *J. Am. Ceram. Soc.*, 83[4] (2000) p. 964-66
- [8] Kaliszewski, M. S. and Heuer, A. H., *J. Am. Ceram. Soc.*, 73[6] (1990) p. 1504
- [9] W. Huang, P. Shuk, and M. Greenblat, *Solid State Ionics* 100 (1997) p. 23-27
- [10] B. Djuricic and S. Pickering, *J. Eur. Ceram. Soc.*, 19 (1999) p. 1925-1934
- [11] M. F. Bianchetti, R. E. Juarez, D. G. Lamas, N. E. Walsoe de Reca, L. Perez, and E. Cabanillas, *J. Mater. Res.*, 17[9] (2002) p. 2185-2188