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Sintering behavior of Ln-doped ceria compounds containing gallia

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Abstract

The sintering behavior of Ln-doped ceria (Ln = Y, Gd, Sm, Nd, La) containing gallia (Ga_2O_3) was investigated. Ln-doped ceria samples containing gallia were well sintered at 1500 °C by a common solid-state reaction method. On the other hand, Ln-doped ceria samples without gallia did not become well sintered until the sintering temperature was raised to 1600 °C. We investigated the crystal structures, microstructures, density, and electrical conductivity of Ln-doped ceria sintered with gallia. The grain sizes of Ln-doped ceria sintered with gallia were much larger than those of Ln-doped ceria sintered without gallia. All samples except Y-doped ceria showed improvement in conductivity by the addition of gallia. The variation in acceleration of grain growth with Ln^{3+} radius was consistent with the tendency of the melting points of solid solutions of Ln_2O_3 and gallia, indicating that the acceleration of sintering was due to the effect of the liquid phase partly formed from Ln_2O_3 and gallia during sintering.

Keywords: Doped ceria; Sintering behavior; Conductivity; Grain size; Gallia

1. Introduction

The solid oxide fuel cell (SOFC) has been well received due to its environmental compatibility and high efficiency in the generation of electricity. Accordingly, many companies and laboratories are investigating the SOFC. Operation of SOFC, in general, is carried out at 1000 °C to obtain high efficiency, and yttria-stabilized zirconia (YSZ) is usually used as the electrolyte material. Operation of the SOFC at 1000 °C, however, has certain drawbacks, for example, mechanical and thermal durability, interfacial diffusion between electrode and electrolyte, and the high cost of materials. Recently SOFCs operating at lower temperatures (<800 °C) have been investigated as a solution for commercialization.

Ceria (CeO_2)-based electrolytes are considered valuable as candidates for electrolyte materials in reduced temperature SOFCs [1,2]. However, ceria-based electrolyte materials do exhibit some problems [1], one of which is lower sinterability at lower temperatures. In the case of doped-ceria compounds, a sintering temperature above 1600 °C is required to prepare dense ceramics from oxide powder [3,4]. Though it has been reported that doped-ceria compounds were well sintered at a lower temperature than 1500 °C by a coprecipitation method [5,6], the control of many parameters (e.g. metal ion concentration, organic acid concentration, and pH of the solution) has to be taken into consideration. If dense ceria-based oxides could be prepared at lower temperatures from individual oxide powders, then ceria-based electrolytes with electrode materials could be sintered in one step (co-sintering), which reduces the number of preparation steps and also costs. In addition, this preparation method could be applied to a tape-casting technique.

We reported previously that the sintering of samaria-doped ceria (SDC) was extensively improved by the addition of a small quantity of gallia (Ga_2O_3) [7]. In the present paper, we investigate the variations of crystal structures, microstructures, density, and electrical conductivity of ceria-based compounds containing gallia as a function of the ionic radius of the dopant (Y, Gd, Sm, Nd, La), and the effects of the addition of gallia on the sintering behavior of Ln-doped ceria compounds (Ln = Y, Gd, Sm, Nd, La) are discussed.

2. Experimental

Doped ceria compounds both with and without gallia were prepared by common solid-state reaction method. CeO_2 (Shin-etsu Chemicals Co.), Ln_2O_3 (Y_2O_3 and Nd_2O_3; Nippon Yttrium Co., Gd_2O_3, Sm_2O_3, and La_2O_3; Shin-etsu Chemicals. Co.), and Ga_2O_3 (Kojyundo Chemicals. Co.) were weighted at the atomic ratio of Ce:Ln:Ga = 80:20:0 (without gallia) or 80:19.5:0.5 (with gallia), and

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mixed by ball-milling with ethanol for 24 h. The atomic ratio of gallium was selected to be 0.5% since this composition showed the greatest effect [7]. Mixed powders were dried and pulverized, followed by calcination at 1000 °C for 18 h. The powders were then pulverized and uniaxially pressed at 49 MPa, then at 294 MPa followed by sintering at 1600 °C (without gallia) or 1500 °C (with gallia) for 24 h.

A few pellets were sintered for each sample, and the measurement for density was carried out for all pellets using the Archimedes method. They were cut to the proper shapes

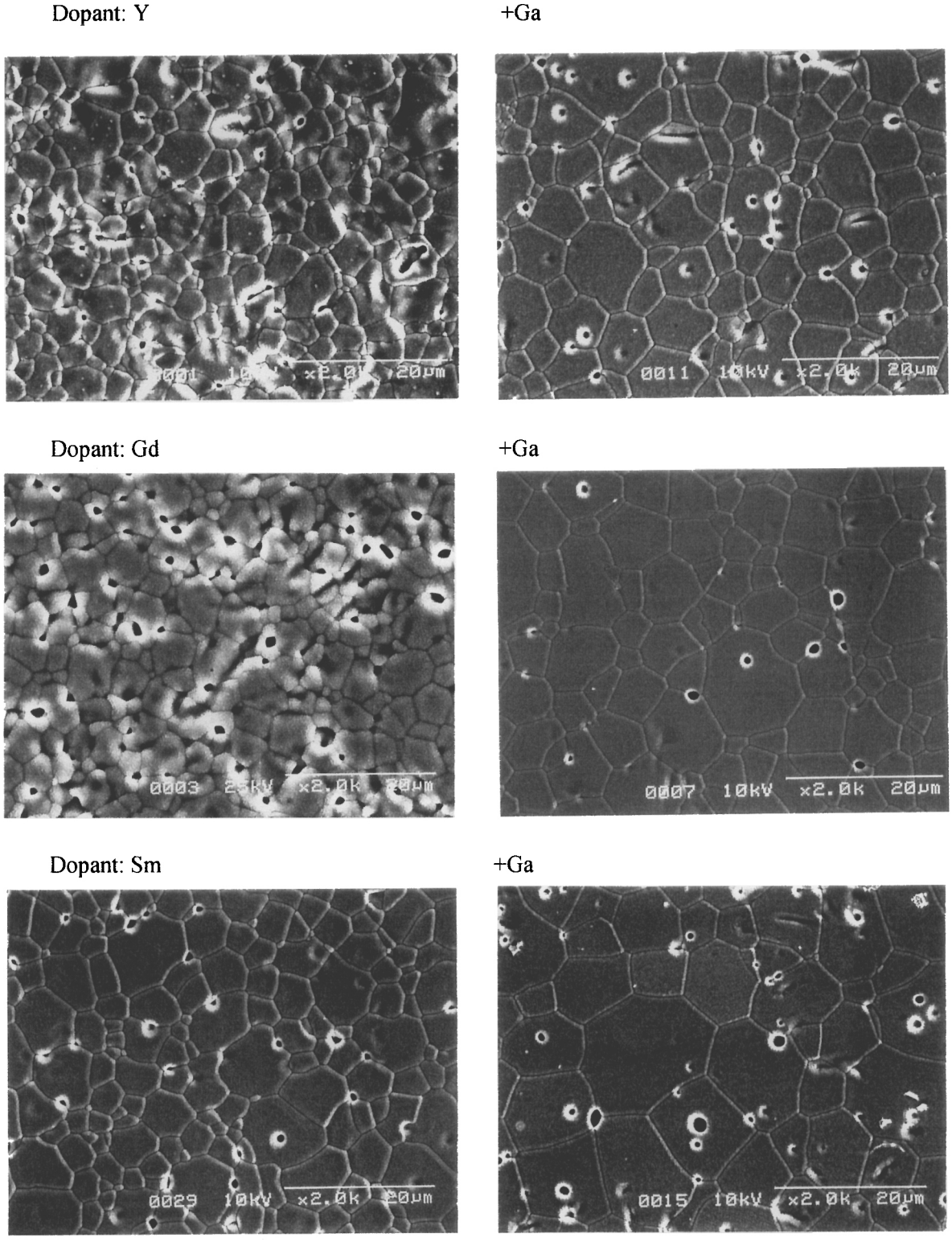

Fig. 1. SEM images of Ln-doped ceria (Ln = Y, Gd, Sm, Nd, La) with gallia sintered at 1500 °C and without gallia sintered at 1600 °C.

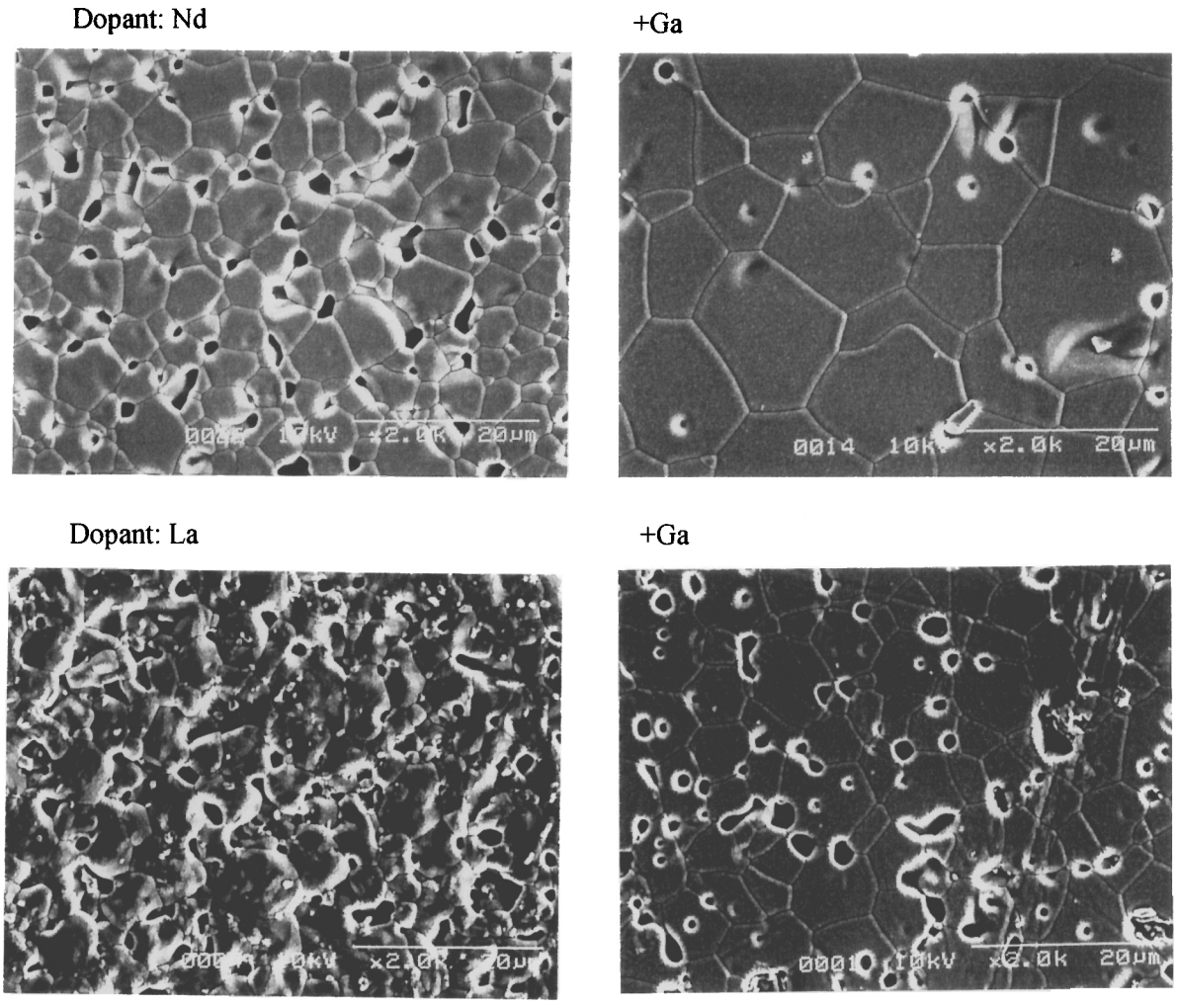

Fig. 1. (*Continued*).

for each measurement. One sintered pellet was ground by a mortar and pestle, and used for X-ray diffraction (XRD, Shimadzu XRD-6000) measurements.

The microstructures of all samples were observed using a scanning electron microscope (SEM, Hitachi S-2380N). The surfaces of the samples were polished and thermally etched at 100 °C lower than the sintering temperature prior to SEM observation. Average grain sizes were derived from SEM images using the intercept method. The electrical conductivity of the samples of 3 mm × 3 mm × 20 mm was measured at 800 °C in air using the conventional dc four-probe method.

3. Results

3.1. Crystal structures of Ln-doped ceria both with and without gallia

The XRD patterns of each sample prepared in this study showed that all samples were comprised of a single phase of a fluorite-type structure. A pattern of a garnet phase ($Ga_5Ln_3O_{12}$; Ln = Y, Gd, Sm, Nd, La) was not observed in this study since the amount of gallia was small. Even though a part of Ga cannot be substituted for Ce, the amount of gallia should be less than the detection limit.

3.2. Microstructures of Ln-doped ceria both with and without gallia

Fig. 1 shows SEM images of doped ceria compounds both with and without gallia. The surface of doped ceria without gallia was rougher and more porous than that with gallia. In all the rare-earth elements examined in this study, the grain sizes of doped ceria with gallia were larger than those without gallia even though doped ceria with gallia were sintered at 100 °C lower than the sintering temperature of doped ceria without gallia. These results show that doped ceria compounds are well sintered by the addition of gallia even though sintering temperature was decreased. Many pores were left in the grain in doped ceria with gallia, while most pores in doped ceria without gallia were at the grain

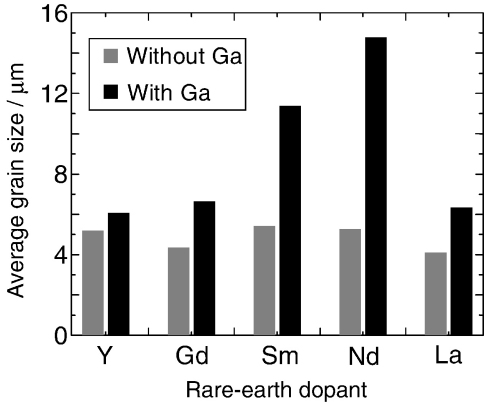

Fig. 2. Average grain sizes of Ln-doped ceria (Ln = Y, Gd, Sm, Nd, La) with gallia sintered at 1500 °C and without gallia sintered at 1600 °C.

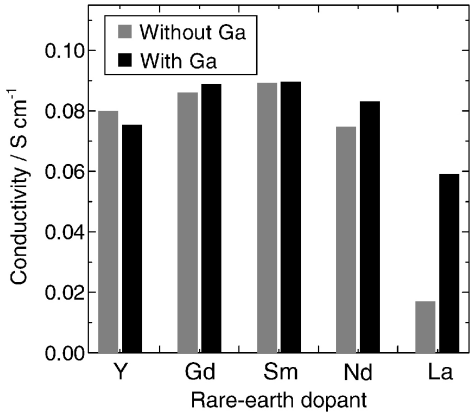

Fig. 4. Electrical conductivity of Ln-doped ceria (Ln = Y, Gd, Sm, Nd, La) with and without gallia at 800 °C in air.

boundaries. In general, pores are left in the grain when the mobility of grain boundaries is faster than that of pores during sintering [8]. As doped ceria with gallia is sintered faster than doped ceria without gallia, it suggests that the mobility of grain boundaries was increased during sintering by the addition of gallia.

From the SEM images shown in Fig. 1, average grain sizes were measured and are shown in Fig. 2. As expected from the SEM images, all doped ceria samples with gallia gave larger grain sizes than the samples without gallia. The accelerating effect of grain growth by the addition of gallia varied depending on the kind of rare-earth doping elements. Grain growth was markedly accelerated in the case of Nd-doped ceria. On the other hand, Y-doped ceria exhibited a small effect. This difference is discussed later.

3.3. Densities and electrical conductivities of Ln-doped ceria both with and without gallia

Densities of doped ceria compounds both with and without gallia are shown in Fig. 3. Densities of doped ceria with gallia were almost the same as those without gallia, while microstructures were different. This is due to the sufficiently high densities of doped ceria without gallia sintered at 1600 °C. Nd-doped ceria, again, showed the highest effectiveness regarding densification.

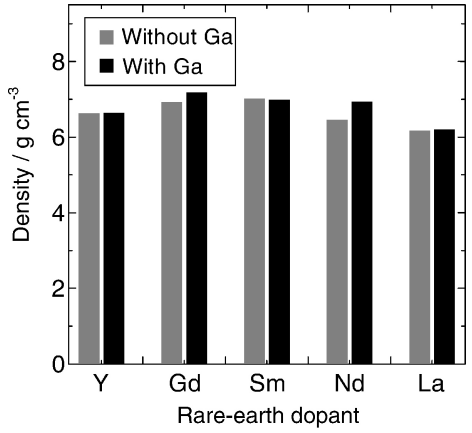

Fig. 3. Densities of Ln-doped ceria (Ln = Y, Gd, Sm, Nd, La) with and without gallia.

Fig. 4 shows the comparisons of electrical conductivity at 800 °C in air between doped ceria samples both with and without gallia. All samples except for Y-doped ceria showed an improvement in conductivity by the addition of gallia. Especially, La-doped ceria showed the largest increase. La-doped ceria without gallia was porous and the pores seemed to be connected to each other. Although La-doped ceria with gallia was also porous, the pores appeared to be closed. This difference in microstructure is thought to be related to the conductivity improvement by the addition of gallia. In the temperature range of 700–1000 °C, this tendency was almost the same as that at 800 °C.

4. Discussion

We re-present these results again briefly. From the microstructure observation, the addition of gallia was found to be effective for the grain growth of Ln-doped ceria compounds. Ln-doped ceria containing gallia gave almost the same or better densities than Ln-doped ceria without gallia. Conductivity was improved by the addition of gallia even though sintering temperature was lowered by 100 °C.

Since the change in grain size was the most remarkable among the properties measured in this study, increasing ratios of grain sizes of doped ceria compounds with gallia to that without gallia were plotted with the radius of the dopant cation and are shown in Fig. 5. Increasing ratios of grain growth became larger as the radius of dopant cation increased, and Nd-doped ceria gave the largest ratio. On the other hand, grain growth decreased in the case of La-doped ceria in spite of a larger dopant radius than in Nd-doped ceria. These results are thought to stem from the particular dopant cations, suggesting that gallia and rare-earth oxide instead of ceria interact during sintering process.

Assuming that Ga-containing second phase promotes sintering of doped ceria compounds, the following mechanisms

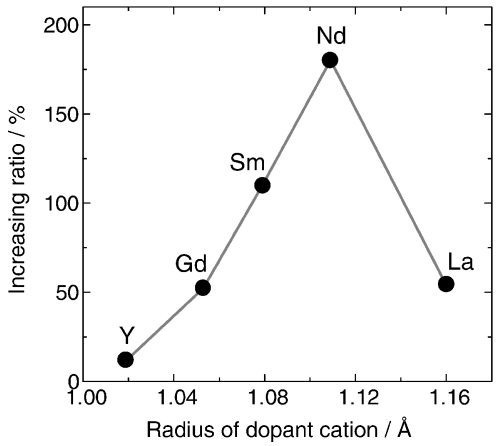

Fig. 5. Increasing ratios of grain sizes of Ln-doped ceria (Ln = Y, Gd, Sm, Nd, La) with gallia to those without gallia.

are considered. At the initial stage of sintering, gallia and rare-earth oxide react to form another phase different from the ceria phase, followed by the part-liquid phase, which smoothes the rearrangement of particles [9]. Then, densification occurs by solution and re-precipitation of the solid through the liquid phase. To confirm that this assumed mechanism was reasonable, the melting points of oxides composed of gallium and rare-earth elements picked out of references [10–12] were plotted against the radii of the dopant cations.

Fig. 6 shows the melting points of perovskite, garnet, and the monoclinic phases, reported for oxides composed of gallium and rare-earth element. The garnet phase containing La did not form due to the large ionic radius difference with Ga [11]. On the other hand, the perovskite phase formed only in the case of La and Nd. The melting point of the garnet phase became lower as the radius of the rare-earth cation increased, while that of the perovskite phase became higher as the radius of the rare-earth cation increased. The compounds having a monoclinic phase were observed except for Y, whose melting points of each monoclinic compound were almost the same among the samples shown

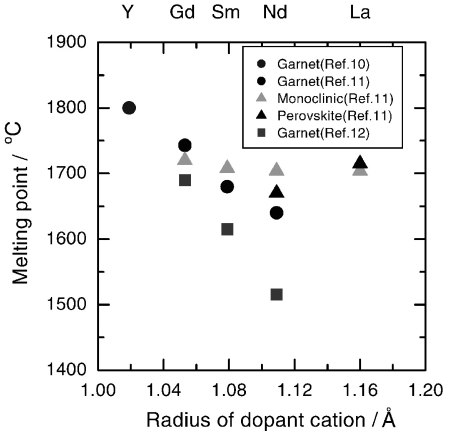

Fig. 6. Melting points of oxides produced from Ln_2O_3 (Ln = Y, Gd, Sm, Nd, La) and Ga_2O_3 [10–12].

in Fig. 6 and were the same or higher than those of the garnet phase. From these results, the melting point was the lowest in the case of Nd containing oxides. It was found that the acceleration of grain growth of doped ceria by the addition of gallia was related to the melting points of the compounds prepared from rare-earth oxide and gallia. This behavior is consistent with our assumption on sintering.

The melting points of oxides containing gallium and rare-earth element seem too high to promote grain growth during sintering at 1500 °C. However, they do not show the lowest temperature in the solid-solution system of gallia and rare-earth oxide. For example, in the case of the Ga_2O_3–Gd_2O_3 system, the liquid phase appeared at 1530 °C when the element ratio of Ga was about 70% [13], and the eutectic peak appeared at 1420 °C on DTA (differential thermal analysis) trace in the $GdGaO_3$–Ga_2O_3 system [14]. Thus, the liquid phase can partly exist during sintering at 1500 °C. Fig. 6 reflects the tendency of melting in the Ga_2O_3–Ln_2O_3 system.

In general, the corners of grains are rounded when the liquid phase exists during sintering [9]. Grains of doped ceria with gallia have corners in spite of our assumption that the liquid phase promotes grain growth during sintering. In our case, the amount of the liquid phase was not enough to change the grains to a round shape. The corners of the grains were rounded off when a large amount of gallia was added ($Ce_{0.8}Sm_{0.15}Ga_{0.05}O_{2-x}$:Ga = 5%) [7], which does not conflict with the existence of the liquid phase during sintering by the addition of gallia. While our assumption was consistent with the results, no trace of the liquid phase was observed in SEM images, because of the small amount of gallium added.

The effectiveness of the addition of gallia to Y-doped ceria was not obvious, probably due to the high melting point in the Y_2O_3–Ga_2O_3 system. Although La-doped ceria showed accelerated grain growth and a dramatic increase in electrical conductivity by the addition of gallia, the density was not enough to be used as the electrolyte of SOFC.

The addition of gallia was effective for the electrolyte of SOFC in the case of the Gd-, Sm-, and Nd-doped ceria compounds. $Ce_{0.8}Sm_{0.19}Ga_{0.01}O_{2-x}$ (Ga = 1%) sintered at 1450 °C showed almost the same properties as $Ce_{0.8}Sm_{0.2}O_{1.9}$ sintered at 1600 °C [7]. 0.5% Ga-containing Sm-doped ceria sintered at 1450 °C is expected to show good performance as the electrolyte. Nd-doped ceria with gallia is expected to become a dense pellet by sintering at 1400 °C. These compounds can be used as the materials for tape-casting and co-sintering.

5. Conclusions

A series of Ln-doped ceria materials (Ln = Y, Gd, Sm, Nd, La) were prepared both with and without gallia. Investigation into the microstructure showed that the addition of gallia was effective in improving the grain growth of all the

ceria compounds used in this study. Ln-doped ceria samples, except that of Y-doped ceria, showed improvement in conductivity through the addition of gallia even though the sintering temperature was lowered by 100 °C. This result could be ascribed to the microstructure change. Promotion of grain growth could be due to the formation of a liquid phase by Ln-oxide and gallia during sintering.

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