Synthesis and Characterization of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ Nano-Particle by Aerosol Plasma Pyrolysis

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Abstract. Spherical $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ (LSGM) precursor powders were synthesized by aerosol plasma pyrolysis using an aqueous solution of metal nitrate. As-prepared powders obtained by this method were found to have a spherical morphology with a bimodal size distribution of nanosized (primary) and submicron-sized (secondary) particles. The average size of the primary particles was less than 100 nm. X-ray diffraction (XRD) patterns showed that as-prepared powders crystallized to LSGM and other phases. XRD revealed that LSGM pellets were crystallized to a perovskite structure after sintering at 1300 °C for 10 h.

Introduction

The solid oxide fuel cell (SOFC) has attracted a lot of attention as an energy conversion device because of its high conversion efficiency and eco-friendliness. A typical high-temperature SOFC used 8 mol% yttria-stabilized zirconia (YSZ) with a fluorite structure as an electrolyte [1-3]. Strontium- and magnesium-doped lanthanum gallate (LSGM) ceramics are known to have superior oxygen-ion conducting properties [4-6] compared with YSZ electrolytes. In recent years, several researchers have synthesized LSGM ceramics using the conventional solid-state reaction, sol-gel method [7, 8] or Pechini method [9,10]. Spray pyrolysis is known to be a useful tool for the rapid production of multi-component powders in a continuous process. A precursor solution is misted into aerosol droplets that are introduced into an electric furnace before undergoing drying, droplet shrinkage, solute precipitation, decomposition, and sintering to form final particles. The advantages of spray pyrolysis process are: (a) resulting spherical morphology, (b) narrow particle size distribution, (c) easy preparation of the powder with a complex composition, (d) relatively homogeneous composition. In this work, we tried to synthesize $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ nano-particles [11] with high crystallinity, spherical morphology, and non-aggregation by aerosol

Fig.1. Schematic diagram of apparatus

plasma pyrolysis. Characteristics of the as-prepared particles, such as crystallinity and morphology, were investigated.

Experimental

Stoichiometric amounts of metal nitrates were used as starting materials for the synthesis of LSGM powders, and were dissolved in distilled water with nitric acid. The concentration of the total metal nitrate was 0.05 to 0.5 mol/dm³. An aerosol plasma pyrolysis system (Figure 1), consisting of ultrasonic generator, plasma furnace, and cyclone for produced powder capture, was used in this study. The starting solution was misted at a frequency of 1.6 MHz by an ultrasonic nebulizer and introduced into the atmospheric plasma reactor by carrier air. The flow rate was 3.5 dm³/min. The mist of starting solution was pyrolyzed by high temperature plasma (5000 to 7000 °C) in the atmosphere. LSGM precursor nano-particles were collected continuously using a cyclone, collision-type filter. However, many particles passed through the filter because the mesh size of the filter was similar to the particle size. As-prepared powders were calcined at 800 to 1450 °C for 10 h. The green compact of as-prepared powders (10 mm ϕ) was prepared by uniaxial pressing at 198 MPa at room temperature. The pellet was sintered at 1200 to 1300 °C for 10 h in a closed alumina crucible at a rate of 4 °C per min. Crystal phases of as-prepared powders and calcined powders were identified by powder X-ray diffraction (XRD, Shimadzu, XRD-6100) using CuK α radiation. Particle size and morphology were determined using a scanning electron microscope (SEM, JEOL, JSM-6390YH). The average particle size was determined using a fiber-optics particle analyzer (Otsuka Electronics, FPAR-1000). The thermal behavior of as-prepared powders was observed by differential thermal analysis-thermogravimetry (DTA-TG, DTG-60, shimadzu). Specific surface area (SSA) of as-prepared powders was measured by BET method using N₂ adsorption (SSA, BEL, BELSORP-miniII).

Results and Discussion

Figure 2 shows typical SEM photographs of LSGM nano-particles. A spherical morphology was observed with bimodal size distribution of nano-sized (primary) and submicron-sized (secondary) particles. The average size of the primary particles, as determined by SEM photography, was less than 100 nm in all samples. Such morphology is sometimes observed when ultrasonic spray pyrolysis is employed. DTA of 0.3 mol/dm³ as-prepared powders showed a broad endothermic peak in the DTA

Fig. 2 SEM photographs of as-prepared powders (a) 0.05 mol/dm³ (b) 0.1 mol/dm³ (c) 0.3 mol/dm³ (d) 0.5 mol/dm³

Fig. 3 Average particle size of LSGM at various the starting solution concentrations

Fig. 4 Particle morphology calcined at various temperatures
(a) 800 °C (b) 1000 °C (c) 1300 °C

curve. Weight-loss corresponding to the dehydration and undecomposed starting materials was approximately 6 wt% in the TG curve. SSA of 0.3 mol/dm^3 as-prepared powders was estimated to be $21.7 \text{ m}^2/\text{g}$ using the BET method. The production capacity of as-prepared powders was about 0.3 g/h for a solution concentration of 0.3 mol/dm^3 . The total yield of LSGM powders obtained was approximately 15 %.

Figure 3 shows the average particle size of LSGM at various solution concentrations. The average particle size includes primary and secondary particles. The average particle size of LSGM increased gradually with increasing concentration of the starting solution, except at a concentration of 0.3 mol/dm^3 .

Figure 4 shows particle morphology of a 0.5 mol/dm^3 solution calcined at various temperatures. After calcinations at 1000 °C , spherical particles, with primary particle diameters of approximately 100 to 250 nm, were bonded to one another. After calcinations at 1300 °C , 500 to 3000 nm sized flake-like particles were formed. Experiments with the other starting solution concentrations revealed similar results.

Figure 5 shows XRD patterns of as-prepared powders at various concentrations. These reveal that the perovskite phase exists in the calcined powders, but impurity phases are clearly seen as well.

Figure 6 shows XRD patterns of as-prepared powders obtained from 0.3 mol/dm^3 solution, and samples calcined for 10 h at different temperatures. Again, it can be seen that the perovskite phase exists in the calcined powders, but that impurity phases also exist. Even after calcinations at 1450 °C , the powder was not in a single phase. In fact, the most intense diffraction peaks of SrLaGaO_4 and $\text{SrLaGa}_3\text{O}_7$ [12] were still detectable in the XRD patterns. The crystallinity

Fig. 5 XRD patterns of LSGM as-prepared powders at various the starting solution concentrations

Fig. 6 XRD patterns of LSGM powders calcined at various temperatures (0.3 mol/dm^3)

of the powders gradually increased with increases in the calcination temperature.

Figure 7 shows XRD patterns of pellets sintered for 10 h at different temperatures. The samples can be indexed based on a perovskite-type structure after sintering at 1300 °C. No impurity-related peaks are observed in the XRD patterns.

It is thought that this result was caused by the slightly heterogeneous composition of the as-prepared powders. Therefore, solid-phase reaction was completely processed during sintering at 1300 °C for 10 h because a heterogeneous composition part contacts it enough to make it a pellet.

Conclusions

$\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ precursor nano-sized powders were successfully synthesized by an aerosol plasma pyrolysis process. The particles had a spherical morphology with a bimodal size distribution. The average size of the primary particles determined by SEM photographs was less than 100 nm in all samples. Pure powders could not be obtained even after 10 h calcinations at 1450 °C. In fact SrLaGaO_4 and $\text{SrLaGa}_3\text{O}_7$ phases were detected by XRD patterns in all calcined powders. However, XRD revealed that LSGM pellets were crystallized to a perovskite structure after sintering at 1300 °C for 10 h.

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References

- [1] S. C. Singhal: Solid State Ionics Vol. 135 (2000), p. 305
- [2] M. C. Williams, S. C. Singhal and M. Dokiya: Electrochem. Soc. Vol. 3 (1999)
- [3] A. J. Appleby: Energy Vol. 21 (1996), p. 521
- [4] T. Ishihara, H. Matsuda, and Y. Takita: J. Am. Chem. Soc. Vol. 116 (1994), p. 3801
- [5] M. Feng and J. B. Goodenough: Eur. J. Solid. State Inorg. Chem. Vol. T31 (1994), p. 663
- [6] P. Huang and A. Petric: J. Electrochem. Soc. Vol. 143 (1996), p.1644
- [7] O. Schulz and M. Martin: Solid State Ionics Vol. 135 (2000), p. 549
- [8] K. Huang, R. S. Tichy and J. B. Goodenough: J. Am. Ceram. Soc. Vol. 81 (1998), p. 2565
- [9] S. R. Jain, K. C. Adiga, and V. R. Verneker: Combustion and Flame Vol. 40 (1981), p. 71
- [10] K. Huang, M. Feng, and J. B. Goodenough: J. Am. Chem. Soc. Vol. 79 (1996), p. 1100
- [11] T. Y. Chen and K. Z. Fung: J. Eur. Ceram. Soc. Vol. 28 (2008), p. 803
- [12] A. C. Tas, P. Majewski, and F. Aldinger: J. Am. Ceram. Soc. Vol. 83 (2000), p. 2954

Fig. 7 XRD patterns of LSGM pellets sintered at various temperatures (0.3 mol/dm³)