Preparation and Electric Characterization of Single Phase La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_3$ and La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.115}$Co$_{0.085}$O$_3$ Thin Films

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La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_3$ (LSGM) and La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.115}$Co$_{0.085}$O$_3$ (LSGMC) thin films were deposited on single crystalline (001) Al$_2$O$_3$ substrates using a pulsed laser deposition technique. The LSGM and LSGMC thin films exhibited only a single phase, which was verified through x-ray diffraction (XRD) experiments. Scanning electron microscopy (SEM) showed that the grain size of the LSGM film was smaller than that of the LSGMC films. Below 800 K, the ionic conductivity of both the thin films was higher than that of bulk sample. Furthermore, the LSGM thin film showed higher ionic conductivity than the LSGMC thin film at temperatures above 600 K.

**Keywords:** electrolyte thin film, single phase, LSGMC, ionic conductivity

1. INTRODUCTION

Fuel cells are devices which convert molecular atomic bonding (chemical) energy into electrical energy. Fuel cells have diverse applications, such as in motors, light bulbs, batteries, and portable electronic devices. In particular, solid oxide fuel cells (SOFCs) have attracted great interest due to their high energy conversion efficiency, flexibility in fuel selection, and clean operation free from the emission of toxic chemicals such as NO. SOFCs contain an electrolyte, cathode, and anode. An important issue is the high temperatures at which SOFCs operate. A recent study of solid electrolyte SOFCs focused on yttria-stabilized zirconia (YSZ) operating at a temperature of about 1,273 K. Lowering the operation temperature will increase the lifetime and make for a simpler fabrication process with lower costs.

There are two possible approaches to lowering the operation temperature will increase the lifetime and make for a simpler fabrication process with lower costs. The first option is to decrease the thickness of the electrolyte while maintaining a high power density. In particular, La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_3$ (LSGM) is especially attractive as an electrolyte in the operation temperature range of 873 - 973 K, since the power density of YSZ-based SOFCs is very low in this temperature range. However, one drawback to LSGM is its secondary phases, such as LaSrGaO$_6$, La$_3$Ga$_2$O$_7$, and SrLaGa$_2$O$_7$, which cause the decrease in ionic conductivity. Doping LSGM samples with transition metal ions such as Co and Fe on Ga sites resulted in an increase in ionic conductivity, and Co doping was the most effective at enhancing ionic conductivity. The Co-doped LSGM (LSGMC) showed the most potential for use as a SOFC that could operate at intermediate temperatures (IT), although the LSGMC did show secondary phases. In this study, we report the effect of Co doping of LSGM on ion conductivity. We fabricated LSGM and LSGMC thin films on single crystalline (001) Al$_2$O$_3$ substrates using pulsed laser deposition (PLD). We obtained single-phase LSGM and LSGMC thin films and further investigated their ionic conductivity.

2. EXPERIMENTAL PROCEDURE

LSGM and LSGMC thin films were deposited using a PLD technique. Ceramic single-phase La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_3$ (LSGM) and La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.115}$Co$_{0.085}$O$_3$ (LSGMC) pellets one inch in diameter were made using a solid-state reaction route (i.e., the conventional mixed-oxide route). To fabricate two ceramic pellets in the first process, we used the following materials: La$_2$O$_3$ (99.99%, Sigma-Aldrich, Steinheim, Germany), SrCO (99.9%, High Purity Chemicals, Japan), MgO (99.99%, High Purity Chemicals), Ga$_2$O$_3$ (99.99%,...
Sigma-Aldrich), and CoO (99.9%, High Purity Chemicals) in stoichiometric proportions. \( \text{La}_2\text{O}_3 \) and \( \text{MgO} \) were calcined at 1273 K for 4 hr before weighing due to their hygroscopic properties. We mixed them using a zirconia-ball milling method in high purity ethanol for 12 h. They were then dried in air at 353 K for a few hours and calcined at 1473 K in air for 6 h. The calcined powder was reground with a mortar and pestle and a disc was formed using a die-pressing technique and a cold isostatic pressing (CIP) technique at a pressure of 7500.6 Torr. The samples were sintered in static air for 6 h at 1500°C. After the sintering process, the PLD target was slowly cooled to room temperature (RT). The single phase of the two ceramic pellets was verified using x-ray diffraction (XRD: MAC Science M18XCE, Japan) with Cu-K\( \alpha \) radiation.

The PLD target was placed on a rotating target holder in a vacuum chamber. A KrF excimer laser (Lambda Physik, COMPex 102, maximum energy = 150 mJ, pulsed duration = 30 ns, wavelength = 248 nm) beam was injected into the chamber at an incident angle of 45° for 2 hr with a repetition rate of 10 Hz. The target was continuously rotated at a speed of 10 rpm during film deposition to minimize pitting. A single crystalline (001) \( \text{Al}_2\text{O}_3 \) substrate was placed in a holder with a heating coil at a target-substrate distance of 45 mm to provide sufficient interaction between the plasma plume and \( \text{O}_2 \) gas. During PLD, the substrate temperature was set to 750°C. The optimal oxygen pressures were 300 and 150 mTorr for LSGM and LSGMC thin films, respectively. After depositing the films, the thin films were cooled to RT in an \( \text{O}_2 \) atmosphere. We characterized the crystallinity of the films using XRD techniques and observed the microstructures of the films using field emission scanning electron microscopy (FESEM).

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the two thin films. From the XRD pattern, we concluded that the optimal oxygen pressures are 500 and 150 mTorr for the LSGM and LSGMC thin films, respectively, at 800°C. Under the optimal PLD conditions, the LSGM and LSGMC thin films exhibit a single perovskite phase with polycrystalline structures. The XRD pattern of the LSGM film shows (111), (110), and (200) satellite XRD peaks, which are evidence of polycrystalline structures. The XRD pattern of the LSGMC film also shows (110) and (200) satellites, which are slightly shifted from those of the LSGM film due to Co doping. From the (200) peak of the LSGMC (LSGM) film, the \( a, b, \) and \( c \) lattice constants were estimated to be about 3.903 (3.909), 3.904 (3.935), and 3.897 (3913) Å, respectively, which are slightly smaller than those of bulk LSGM. Co doping of LSGM results in shrunken crystalline structures. Since the cubic crystal structures of the two thin films are quite different from the hexagonal sapphire substrate, the two thin films have the possibility of having polycrystalline structures. The LSGM thin film exhibits outstanding satellite XRD peaks, more so than the LSGMC thin film, which implies that Co doping is crucial in the fabrication of films free from polycrystalline structures.

Figure 2 shows a cross-sectional SEM image of the LSGM (LSGMC) thin film in (a) and (c) and the surface morphology of the single-phase LSGM (LSGMC) thin films in (b) and (d). Island growth mode was observed in single-phase LSGM (LSGMC) thin films due to the high surface energy as well as the large lattice mismatch between the thin film and the single crystalline (001) \( \text{Al}_2\text{O}_3 \) substrate. The 500-nm-thick LSGM and LSGMC thin films show crack-free surfaces, as shown in Figs. 2(b) and (d). Note that the