Effect of Laser Rapid Sintering on the Electrical Properties of Sr- and Mg-doped $LaGaO_3$

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Abstract. Materials $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ and $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17-x}Co_xO_{3-\delta}$ with x=0, 0.05, 0.085, 0.10 and 0.15 are synthesized by laser rapid sintering (LRS). It is found that the total conductivities of $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17-x}Co_xO_{3-\delta}$ by LRS are obviously improved by Co doping, showing a general increase with the content Co except that for x=0.15. The conductivities of the $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ and $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.085}Co_{0.085}O_{3-\delta}$ samples synthesized by LRS are superior to those of both samples for the same compositions by solid state reaction (SSR) at any temperatures. The conductivities of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ and $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.085}Co_{0.085}O_{3-\delta}$ samples synthesized by LRS are about twice and thrice as much as those of the samples for the same compositions synthesized by SSR, respectively. The improved conductivities of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ and $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.085}Co_{0.085}O_{3-\delta}$ prepared by laser rapid sintering with respect to that by solid state reactions for the same composition is attributed to the unique microstructures of the samples generated during laser rapid sintering.

Introduction

The perovskite oxide, strontium- and magnesium-doped $LaGaO_3$ (LSGM), exhibits a higher ionic conductivity (~ 0.10 S cm^{-1} at 800°C) [1, 2] than conventional YSZ over a wide range of oxygen partial pressure. These superior electrical and stable properties make Sr- and Mg-doped $LaGaO_3$ (LSGM) the most promising candidates as electrolytes for intermediate temperature SOFCs. LSGM powders were generally synthesized by solid state reactions (SSR)[3-5] or wet chemical routes [6-9]. However, the synthesis of a pure single phase material of LSGM is a rather difficult task. Therefore, it is necessary to explore new and rapid synthetic methods. In a previous study, we developed a new laser rapid solidification (LRS) to synthesize $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ electrolyte [10]. It has been proved that Sr- and Mg-doped $LaGaO_3$ with other compositions can also been synthesized by this technology. Furthermore the samples prepared by LRS exhibit much higher electrical conductivity with respect to the LSGMs by SSR. In this paper, the effect of laser rapid sintering on the electrical properties of Sr- and Mg-doped $LaGaO_3$ has been analyzed.

Experiment

$La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ and $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17-x}Co_xO_{3-\delta}$ (x=0, 0.05, 0.085, 0.10, 0.15) samples were prepared with starting materials of La_2O_3 (99.99%), Ga_2O_3 (99.99%), $SrCO_3$ (99%), MgO (98%) and and Co_2O_3 (99.9%). Two series of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ samples were prepared by high-temperature solid state reactions and laser rapid sintering, respectively. Five series of $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17-x}Co_xO_{3-\delta}$ (x=0, 0.05, 0.085, 0.10, 0.15) samples were prepared by laser rapid sintering, for comparison the $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.085}Co_{0.085}O_{3-\delta}$ sample was synthesized by high-temperature solid state reactions. The high-temperature solid state reactions were carried out with pressed pellets by calcinating at 1250˚C for 10 h and then sintering at 1500˚C for 6 h and at 1600˚C for 2h with intermediate grindings (denoted as SSR), respectively. The laser rapid sintering (LRS) was performed by using a 5 kW continuous-wave CO_2 laser and the method was described in detail previously [10]. The optimized synthesis conditions are 1100 W laser power and 1 mms^{-1} scan speed. The samples were analyzed by XRD with an X'Pert PRO X-Ray Diffractometer. The electrical conductivities were measured in air as a function of temperature (250-950˚C) by AC impedance spectra with Pastat 2273 (Princeton Applied Research). The range of ac frequency is 0.1 Hz–10^6 Hz. Platinum paste was fired on opposite sides of the pellets as the electrodes.

Results and Discussions

Phase Composition. Figure 1a and 1b show the XRD patterns of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ powders synthesized by solid state reaction at respectively 1250˚C for 10 h, 1500˚C for 6 h and 1600˚C for 2h (Fig.1a, denoted as 9182-SSR) and laser rapid sintering with 1100W laser powers at 1mms^{-1} scan speed (Fig.1b, denoted as 9182-LRS). It can been seen that the pure $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ phase can be obtained by SSR and LRS. Figure 1c~1g show the XRD patterns of $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17-x}Co_xO_{3-\delta}$ with different compositions prepared by laser rapid sintering with 1100W laser powers at 1mms^{-1} scan speed for (c) x=0; (d) x= 0.05; (e) x= 0.085; (f) x= 0.10; (g) x=0.15. For comparison the XRD pattern of $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.085}Co_{0.085}O_{3-\delta}$ sample by SSR (1250°C for 10 h, 1500°C for 6 h and 1600°C for 2 h) is also shown in 1h. It shows that with optimized synthesis conditions the series of $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17-x}Co_xO_{3-\delta}$ materials can be successfully synthesized by LRS except the one with x=0.15 which contains a little amount of a secondary phase of $LaSrGa_3O_7$.

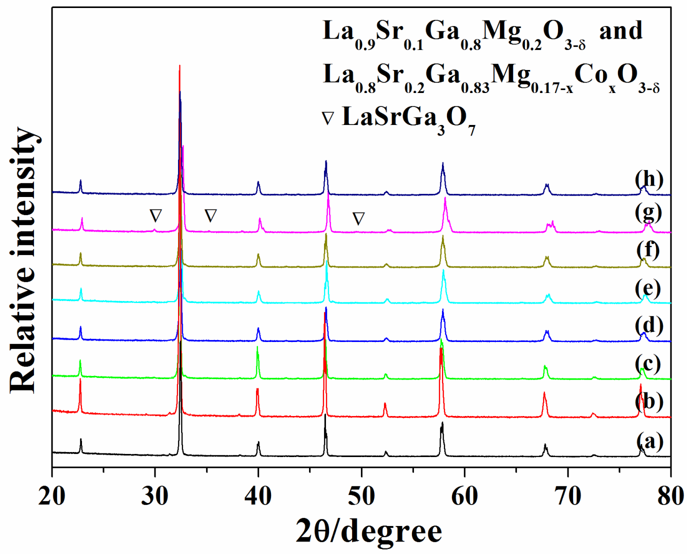

Figure 1. XRD patterns of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ powders synthesized by (a) solid state reaction at respectively 1250˚C for 10 h, 1500˚C for 6 h and 1600˚C for 2h (SSR); (b) laser rapid sintering (LRS) with 1100W laser powers at 1mms^{-1} scan speed, and $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17-x}Co_xO_{3-\delta}$ samples by LRS; (c) x=0; (d) x= 0.05; (e) x= 0.085; (f) x= 0.10; (g) x=0.15 and (h) $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.085}Co_{0.085}O_{3-\delta}$ sample by SSR.

Electrical Properties. The total conductivities plots of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ synthesized by SSR (2a) and LRS (2b) are shown in Figure 2. It can be seen that the conductivities of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ synthesized by LRS (2b) are much higher than those of the samples synthesized by solid state reactions (2a) with the same composition at any temperatures. The conductivities of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ synthesized by LRS (2b) are 0.027, 0.079 and 0.134 Scm^{-1} measured at 600, 700 and 800℃, respectively, while the conductivities of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ synthesized by SSR (2a) are 0.019, 0.034 and 0.041 Scm^{-1}. Figure

2c~2h show the total conductivities of the $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17-x}Co_xO_{3-\delta}$ samples with different compositions prepared by laser rapid sintering with 1100W laser powers at $1mms^{-1}$ scan speed for (c) x=0; (d) x= 0.05; (e) x= 0.085; (f) x= 0.10; (g) x=0.15 and (h) $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.085}Co_{0.085}O_{3-\delta}$ sample by SSR. It is obvious that the total conductivities of $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17-x}Co_xO_{3-\delta}$ by LRS are obviously improved by Co doping, showing a general increase with the content Co except that for x=0.15. The total conductivity of $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.085}Co_{0.085}O_{3-\delta}$ prepared by LRS reaches 0.067, 0.124 and 0.202 Scm^{-1} at 600, 700 and 800°C, respectively, being much higher than the corresponding values (0.026, 0.065 and 0.105 Scm^{-1}) of the same composition prepared by SSR.

From figure 2 it is found that the conductivities of the $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ and $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.085}Co_{0.085}O_{3-\delta}$ samples synthesized by LRS are superior to those of both samples for the same compositions by SSR at any temperatures. The conductivities of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ and $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.085}Co_{0.085}O_{3-\delta}$ samples synthesized by LRS are about twice and thrice as much as those of the samples for the same compositions synthesized by SSR (see Fig. 2b, 2e), respectively. From the XRD patterns (Fig.1a, 1b, 1e and 1h) and the results of relative density it can be seen that the $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ and $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.085}Co_{0.085}O_{3-\delta}$ samples synthesized by LRS show the similar purity and density to those of both samples for the same compositions by SSR. Therefore, the $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ and $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.085}Co_{0.085}O_{3-\delta}$ samples synthesized by LRS exhibit superior electrical properties to those samples by SSR possibly due to their unique microstructure formed in laser rapid sintering. In the laser synthetic route, the raw materials were heated to melt immediately upon illumination of the laser beam and formed a molten pool where the chemical reaction took place. The products solidified rapidly as the laser beam moved ahead. The sufficiently high temperature ensured sufficient melting of the raw materials and consequently rapid and uniform reactions. As the laser energy was absorbed by the top layer of the raw materials, heat transfer in a sample was mainly directed from the top surface to the bottom and also governed by the moving direction of the laser beam. The unique microstructures of the samples produced in the laser synthetic route can be attributed to the relatively oriented crystalline growth governed by heat transfer directions in the liquid droplet-like molten pool.

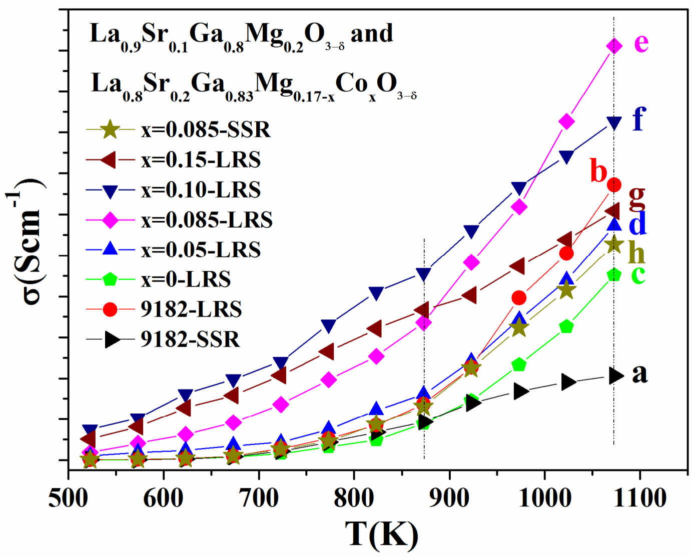

Figure 2. The total conductivities plots of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ powders synthesized by (a) solid state reaction at respectively 1250°C for 10 h, 1500°C for 6 h and 1600°C for 2h (SSR); (b) laser rapid sintering (LRS) with 1100W laser powers at $1mms^{-1}$ scan speed, and $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17-x}Co_xO_{3-\delta}$ samples by LRS; (c) x=0; (d) x= 0.05; (e) x= 0.085; (f) x= 0.10; (g) x=0.15 and (h) $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.085}Co_{0.085}O_{3-\delta}$ sample by SSR.

Conclusion

Laser rapid sintering (LRS) has been used for the synthesis of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ and $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17-x}Co_xO_{3-\delta}$ (x=0, 0.05, 0.085, 0.10, 0.15) materials. It is shown that the laser rapid sintering method is suitable for rapid synthesis of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ and $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17-x}Co_xO_{3-\delta}$ with controlled compositions. It is found that the total conductivities of $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17-x}Co_xO_{3-\delta}$ by LRS are obviously improved by Co doping, showing a general increase with the content Co except that for x=0.15. The $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ and $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.085}Co_{0.085}O_{3-\delta}$ samples prepared by LRS give rise to better electrical properties with respect to that prepared by solid state reactions for the same compositions at any temperatures. The conductivities of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ and $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.085}Co_{0.085}O_{3-\delta}$ samples synthesized by LRS are about twice and thrice as much as those of the samples for the same compositions synthesized by SSR, respectively. The improved conductivities of the samples by LRS is attributed to the unique microstructures of the samples generated during laser rapid solidification. Therefore, the laser rapid sintering technology can greatly improve the electrical properties of the sintered sample by generating the unique microstructures.

Acknowledgements

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