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Solid-state synthesis of Sr- and Co-doped $LaMnO_3$ perovskites①

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[Abstract] The synthesis process for $La_{1-x}Sr_xMn_{1-y}Co_yO_{3-\delta}$ ($x = 0.2, 0.3$; $y = 0.2, 0.8$, designated as LSMC below) perovskite oxides prepared by solid state reaction was investigated using DSC/TG, XRD, EPMA and particle size analysis methods. It was found that LSMCs were all of single phase and the synthesis process might be divided into three stages: the decomposition of reactants, the formation of $LaMn(Co)O_3$-based oxides, and the formation of LSMC solid solution. Typical average and the peak value of particle size, and the specific surface area are 14.65 μm, 16.4 μm and 1.38 m^2/mL, respectively, for mixed reactants and are 23.81 μm, 32.11 μm and 0.5 m^2/mL, respectively, for powder synthesized at 1200 ℃ for 8 h in air.

[Key words] solid-state reaction synthesis; $La_{1-x}Sr_xMn_{1-y}Co_yO_{3-\delta}$; perovskite; intermediate temperature SOFCs
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1 INTRODUCTION

An important goal in the development of solid oxide fuel cells (SOFCs) is to reduce the operating temperature of the fuel cell stack from 1000 ℃ to below 850 ℃. The primary drivers are: 1) to get an optimum trade-off between performance and life time of the stack and 2) to reduce the overall system cost[1]. To reduce the operating temperature of SOFCs, one of the problems to solve is development of high performance cathodes compatible with the electrolyte materials. For instance, a single-phase $La_{0.9}Sr_{0.1}MnO_3$ cathode exhibits a cathodic polarization resistance below 1 Ω·cm^2 at 1000 ℃, but it increases to above 2000 Ω·cm^2 at 500 ℃[2]. Therefore, significantly better cathode materials and microstructures with a high catalytic activity for the electrochemical reactions have been sought for.

$La_{1-x}Sr_xMn_{1-y}Co_yO_{3-\delta}$ (LSMC) has been found to be a promising cathode material for intermediate temperature solid oxide fuel cells, when $LaCoO_3$ was added to $LaMnO_3$ both the cathode thermal expansion and the cathode electrical conductivity were greatly improved as reported by Nguyen[3]. Erning et al[4] studied the electrochemical properties of the doubly doped composite LSMCs, and found that the over-potential of these composites (e. g. $La_{0.8}Sr_{0.2}Mn_{0.5}Co_{0.5}O_{3-\delta}$) decrease significantly due to the reduction of oxygen content, and the apparent activation energy of the oxygen reduction reaction for $La_{0.79}Sr_{0.16}Mn_{0.8}Co_{0.2}O_{3-\delta}$ is about 1.3 eV lower than that of the $La_{0.84}Sr_{0.16}MnO_3$ (2.2 eV without catalyst) under the same conditions. de Souza et al[5] investigated the kinetics of oxygen surface exchange for some selected LSMC perovskite oxides systems.

Many methods for synthesis of SOFCs cathode materials have been reported, such as sol-gel synthesis[6], coprecipitation process[7], spray pyrolysis[8] and emulsion processing[9]. The solid state reaction was found to be most accessible since the composition of products may be conveniently controlled and effective method suitable to synthesize a large amount of perovskite type powders[10, 11]. In this paper the solid state synthesis process for LSMCs is reported.

2 EXPERIMENTAL

Composites within the system $La_{1-x}Sr_xMn_{1-y}Co_yO_{3-\delta}$ ($x = 0.2, 0.3$; $y = 0.2, 0.8$) were prepared using solid reaction synthesis technique. Starting materials were La_2O_3 (the first factory of Shanghai reagents, 99.95% purity), $SrCO_3$ (the first factory of Shanghai reagents, 99.99% purity), MnO_2 (the first factory of Shanghai reagents, specpure), and Co_3O_4 (the first factory of Shanghai reagents, specpure). These oxides were first dried (La_2O_3 at 900 ℃ and the others at 300 ℃, respectively) for 3 h, weighted out in appropriately stoichiometric quantities, mixed thoroughly in absolute alcohol for 2 h, and then calcined at 1200 ℃ for 8 h in air. The calcined powders were cooled with the furnace, then reground.

The calcination process of the mixed reactants and thermal stability of the synthesized powders were monitored with thermal analyzer (STA1500) in air or N_2 atmosphere (flow rate 50 mL/min) and at a heating and cooling rate of 6 ℃/min between room tem-

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perature and 1200 ℃[12]. Phase change were determined by X-ray diffraction (XRD, 3015X). The particle size distribution and microphotograph for mixed reactants well-dried and selected LSMC powder sample were measured with particle size analyzer (LS 100Q) and EPMA (EPMA-1600).

3 RESULTS AND DISCUSSION

3.1 Thermal analysis

The DSC/TG curves of the mixed oxide in the synthesis process taken at 6 ℃/min in air or N_2 atmosphere flowing of 50 mL/min were shown in Fig. 1. The pronounced endothermic peak (e. g. for producing $La_{0.8}Sr_{0.2}Mn_{0.8}Co_{0.2}O_{3-\delta}$, see Fig. 1(a)) near 356 ℃ in the DSC curve can be attributed primarily to the decomposition of the lanthanum hydroxide and lanthanum carbonate formed during the mix process[13]. The first endothermic peak is followed by an endothermic peak having a minimum near 514 ℃, and the TG curve indicates additional mass loss occurring at the temperature. The second endothermic peak may be attributed to the decomposition of reactant MnO_2 according to the mass loss calculations from the TG curve (Fig. 1(b)) and the thermodynamic calculations. The third endothermic peak having a minimum near 610 ℃ may be corresponding to the formation of $LaMn(Co)O_3$-based oxides at different temperature for $La_{1-x-y}Sr_xCa_yMn_{1-z}Co_zO_{3-\delta}$ system. The endothermic peak at about 890 ℃ in the DSC curve must be discussed in detail. And then mass increase with the increase of temperature in air, which suggested that the mass change may be resulted from the absorption of oxygen. Therefore, the calcination process of LSMC may be divided into three steps: (Ⅰ) decomposition of reactants; (Ⅱ) formation of $LaMn(Co)O_3$-based oxides; (Ⅲ) creation of LSMC solid solution[14].

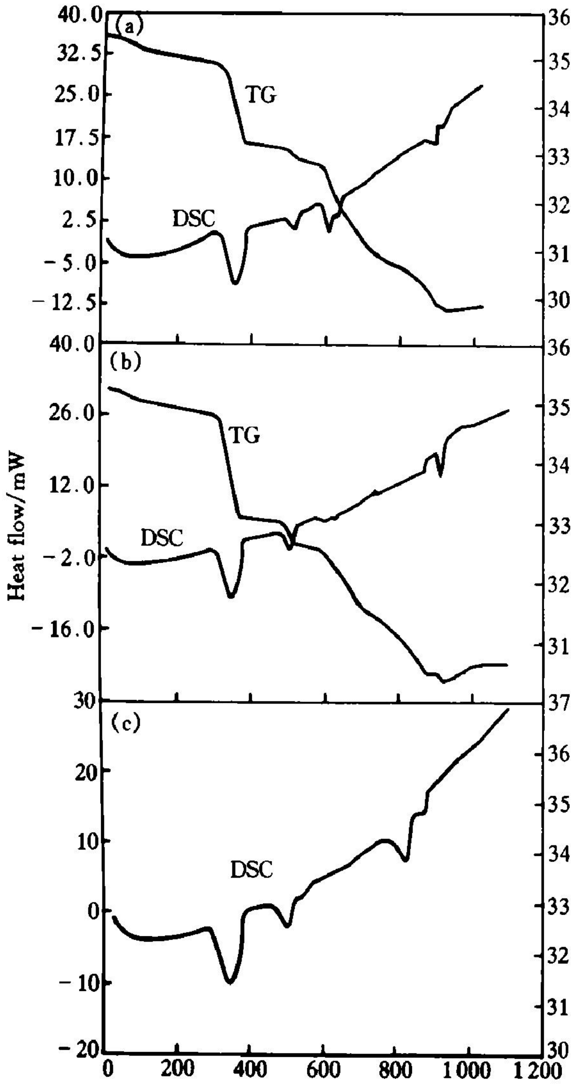

Fig. 1 DSC/TG curves of components in synthesis of LSMCs

(a) —$La_{0.8}Sr_{0.2}Mn_{0.8}Co_{0.2}O_3$ (in air);

(b) —$La_{0.8}Sr_{0.2}Mn_{0.2}Co_{0.8}O_3$ (in air);

(c) —$La_{0.8}Sr_{0.2}Mn_{0.2}Co_{0.8}O_{3-\delta}$ (in N_2 atmosphere)

The mass change for LSMC (e. g. $La_{0.8}Sr_{0.2}Mn_{0.8}Co_{0.2}O_{3-\delta}$) powder sample is almost completely reversible upon heating and cooling in air, as shown in Fig. 2. It is similar with the $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF) composites[15]. There is no detectable mass loss below 400 ℃. The decomposition reaction is not observed even heating to 1200 ℃, which indicates that the composite is stable in air at high temperature. It is suggested that the observed mass change be resulted from the loss of lattice oxygen on heating (reduction) and the uptake of oxygen during cooling (oxidation). Because the TG runs were performed under a constant heating rate, mass loss data could not be used precisely to determine the equilibrium oxygen contents.

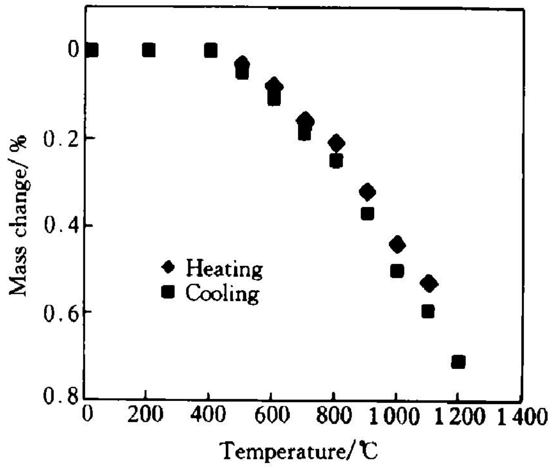

Fig. 2 TG mass change of $La_{0.8}Sr_{0.2}Mn_{0.8}Co_{0.2}O_{3-\delta}$ (sample synthesized, in air)

3.2 XRD analysis

Typical X-ray diffraction pattern shown in Fig. 3 shows the synthesized product is of single phase similar with $La_{1-x}Sr_xFe_{0.12}Mn_{0.88}O_3$ oxides[16]. The

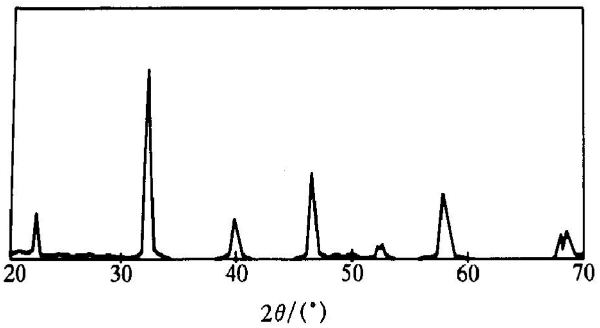

Fig. 3 XRD pattern of $La_{0.8}Sr_{0.2}Mn_{0.8}Co_{0.2}O_3$

structure of the undoped pervoskite $LaMnO_3$ is the rhombohedron having six formula units per unit cell at room temperature. Sr and Co doped for La and Mn sites, respectively, do not change the structure of the pervoskite phase. For example, LI et al[17] reported that the $La_{0.7}Sr_{0.3}Mn_{0.7}Co_{0.3}O_{3-\delta}$ is single phase with rhombohedral structure.

3.3 EPMA and particle size analysis

The microphotograph of powder (e.g. $La_{0.7}Sr_{0.3}Mn_{0.8}Co_{0.2}O_3$) was shown in Fig. 4 by use of EPMA analysis. The particle size distributions of powder for mixed reactants well-dried and synthesized product are shown in Fig. 5. The average particle size and peak value of particle size, and specific surface area are 14.65 μm, 16.4 μm and 1.38 m^2/mL, respectively, for mixed reactants powder and are 23.81 μm, 32.11 μm and 0.5 m^2/mL, respectively, for product. So the particle size grows with the synthesis process. Maric et al[9] found the cathodic polarization and particle size for $La_{1-x}Sr_xCoO_3$ depend strongly on the sintering temperature. Similarly, it is the subject of further investigation for LSMCs system.

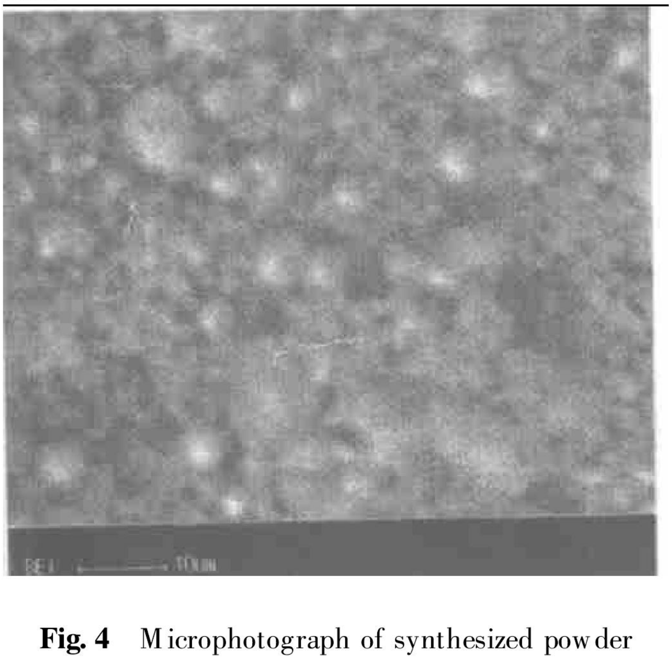

Fig. 4 Microphotograph of synthesized powder

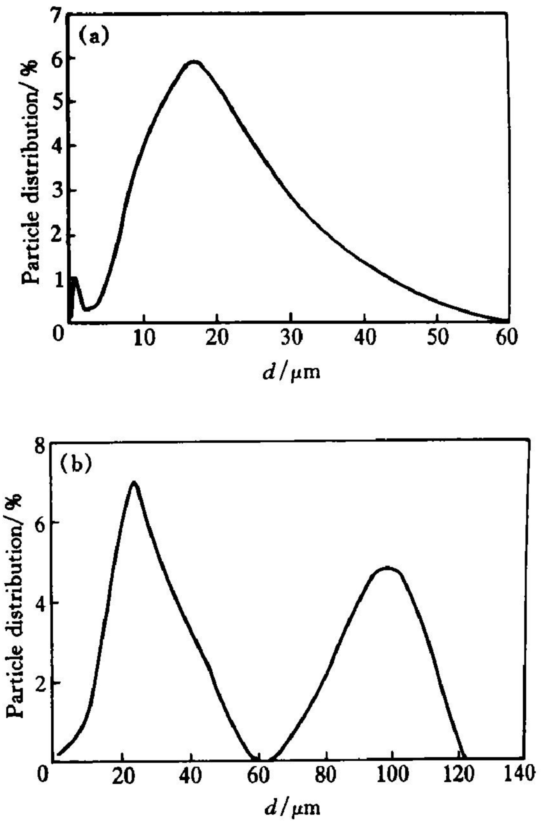

Fig. 5 Particle size distribution

(a) —Mixed reactants powder; (b) —Synthesized powder

4 CONCLUSIONS

1) LSMCs prepared by solid reaction synthesis is of single phase. Decomposition reaction of doped perovskite was not observed even when heated to 1200 ℃ and the mass change may be resulted from the loss of lattice oxygen on heating and the uptake of oxygen during cooling for the sintered specimen.

2) The synthesis process may be divided into three stages: (Ⅰ) decomposition of reactants; (Ⅱ) formation of $LaMn(Co)O_3$-based oxides; (Ⅲ) creation of LSMC solid solution.

3) Average and peak value of particle size, and specific surface area are 14.65 μm, 16.4 μm and 1.38 m^2/mL, respectively, for mixed reactants and are 23.81 μm, 32.11 μm and 0.5 m^2/mL, respectively, for product synthesized at 1200 ℃ for 8 h in air.

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