

## Chapter 3

### Experimental Procedure

#### 3.1 Raw materials and characterization

##### 3.1.1 Starting raw materials

Oxides and carbonate as listed in Table 3.1 were used as starting raw materials for conventional oxide mixing method. The result of purity for each material was received from suppliers.

**Table 3.1** Chemicals used in preparation of  $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{1-x}\text{B}_x\text{O}_3$  (B = Co or Fe)

Materials	Purity (%)	Manufacturers
Lanthanum Oxide ( $\text{La}_2\text{O}_3$ )	99.9	Aldrich
Strontium Carbonate ( $\text{SrCO}_3$ )	98+	Aldrich
Manganese Oxide ( $\text{Mn}_2\text{O}_3$ )	99	Aldrich
Cobalt (II,III) Oxide ( $\text{Co}_3\text{O}_4$ )	-	Aldrich
Iron Oxide ( $\text{Fe}_2\text{O}_3$ )	>98	Fluka

##### 3.1.2 Raw materials characterization

###### 3.1.2.1 Phase analysis

All starting raw materials were characterized by X-ray diffraction (XRD) to investigate the existing phase before using. The powder was mounted in a sample holder and subjected to the room temperature X-ray diffractometer (Jeol, JDX 3530), using  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) and operating at 30 kV and 30 mA. The XRD data were collected in the range of  $2\theta$  20-60°, using the step scan of 0.02° and the count time of 1 minute.

### 3.1.2.2 Thermal analysis

In order to remove the undesirable phases, if existing, calcination of as-received raw material was necessary before weighing. The suitable calcination temperature was determined by thermal analysis, both of differential thermal analysis (DTA) and thermogravimetric analysis (TGA). DTA7 of Perkin-Elmer was operated from 100 to 1000°C with a heating rate of 10°C min<sup>-1</sup> to investigate the reaction temperatures of materials having the mixed phases. Weight loss at high temperature was also conducted by using TGA7 of Perkin-Elmer operated between 100 and 1000°C as the same condition of DTA measurement.

### 3.2 Preparation of $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{1-x}\text{B}_x\text{O}_3$ (B = Co or Fe)

Five compositions were prepared by conventional oxide mixing process. The flow chart of preparation was illustrated in Fig.3.1. Before batch preparation, the undesirable phases were eliminated from the raw material with the calcining schedule obtained from the thermal analysis measurements. After heat treatment, the raw materials were weighed according to the stoichiometric ratio as shown in Table 3.2 and then wet mixed in polypropylene bottle for 6 hrs, using alumina balls as grinding media and ethanol as solvent. To remove the solvent, the mixture was filtrated and dried at 100°C overnight. Then, the dried powder was put in an alumina crucible and calcined. The appropriate calcining temperature was determined by DTA in order to obtain a single phase of  $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{1-x}\text{B}_x\text{O}_3$  (B = Co or Fe). The DTA7 was operated from 100 to 1200°C with a heating rate of 10°C min<sup>-1</sup>. Three compositions of uncalcined powder were selected to study: LSM, LSMC4, and LSMF4. LSMC2 and LSMF2 were expected to show the similar results as LSMC4 and LSMF4, respectively, since a larger amount of dopants should have a significant effect on the reaction temperatures. From the DTA results, the calcining schedule was applied to all compositions. After calcining, the phases and crystal structure were obtained from XRD. Silicon was used as an internal standard in order to identify the lattice parameter of undoped and doped compositions. The XRD data were collected in the range of  $2\theta$  20-70°. After a correction of peak shifts compared to those of Si standard, the calculations of lattice parameters and x-ray

density were carried out. In general, the crystal structure of Sr-doped LaMnO<sub>3</sub> can be either orthorhombic or monoclinic, depending upon the amount of Sr and preparation method.

After calcining, the powder was milled for 8 hrs to break agglomerates and then was sieved through a 100 mesh screen. Before forming, fine powder was well mixed with 1.5 wt% of polyvinyl alcohol (PVA with 9,000-10,000 MW) acted as a binder and then pressed into the rectangular bars (0.7x3.2 cm<sup>2</sup>) and pellets (1.3 cm in diameter) by a hydraulic press with a 79 MPa pressure. To avoid contamination that may take place from the direct contact between specimens and alumina plate during sintering, the calcined powder was placed under specimens. The sintering was performed in the box furnace. All specimens were heated to 520°C for 30 minutes with a heating rate of 2°C min<sup>-1</sup> for binder removal and further raised the temperature at a heating rate of 4°C min<sup>-1</sup> to 1450°C with a soaking period of 2 hours for densification. The sintered samples were cooled in the furnace with a cooling rate of 5°C min<sup>-1</sup>. The sintering schedule was shown in Fig.3.2.

Table 3.2 The stoichiometric ratio of La<sub>0.84</sub>Sr<sub>0.16</sub>Mn<sub>1-x</sub>B<sub>x</sub>O<sub>3</sub> (B = Co or Fe)

Composition	MW.	Molar ratio				
		La <sub>2</sub> O <sub>3</sub>	SrCO <sub>3</sub>	Mn <sub>2</sub> O <sub>3</sub>	Co <sub>3</sub> O <sub>4</sub>	Fe <sub>2</sub> O <sub>3</sub>
La <sub>0.84</sub> Sr <sub>0.16</sub> MnO <sub>3</sub> (LSM)	223.624	0.42	0.16	0.50	-	-
La <sub>0.84</sub> Sr <sub>0.16</sub> Mn <sub>0.8</sub> Co <sub>0.2</sub> O <sub>3</sub> (LSMC2)	234.423	0.42	0.16	0.40	2/30	-
La <sub>0.84</sub> Sr <sub>0.16</sub> Mn <sub>0.6</sub> Co <sub>0.4</sub> O <sub>3</sub> (LSMC4)	235.222	0.42	0.16	0.30	4/30	-
La <sub>0.84</sub> Sr <sub>0.16</sub> Mn <sub>0.8</sub> Fe <sub>0.2</sub> O <sub>3</sub> (LSMF2)	233.805	0.42	0.16	0.40	-	0.10
La <sub>0.84</sub> Sr <sub>0.16</sub> Mn <sub>0.6</sub> Fe <sub>0.4</sub> O <sub>3</sub> (LSMF4)	233.987	0.42	0.16	0.30	-	0.20

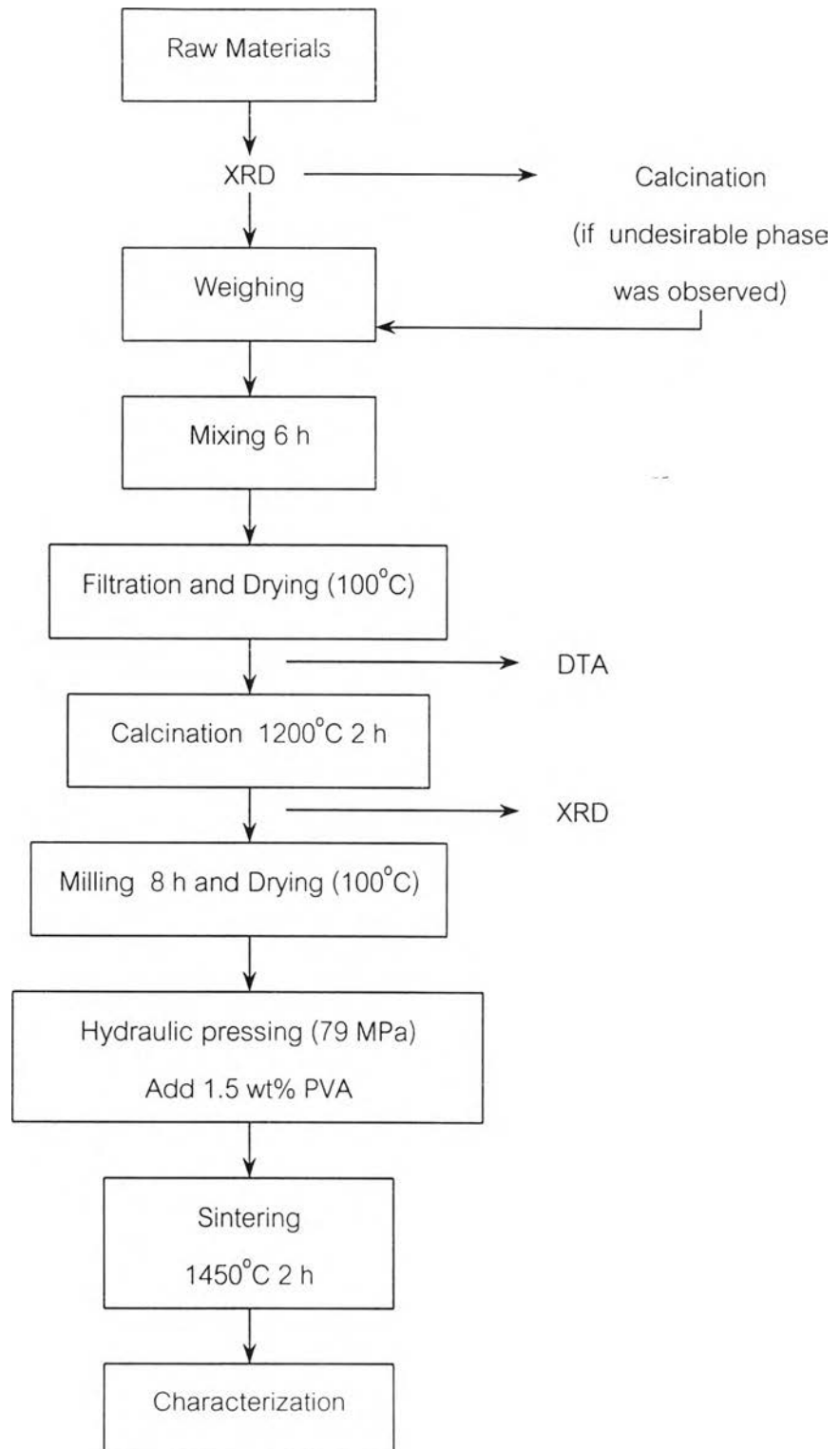


Fig.3.1 Flow chart of material preparation process

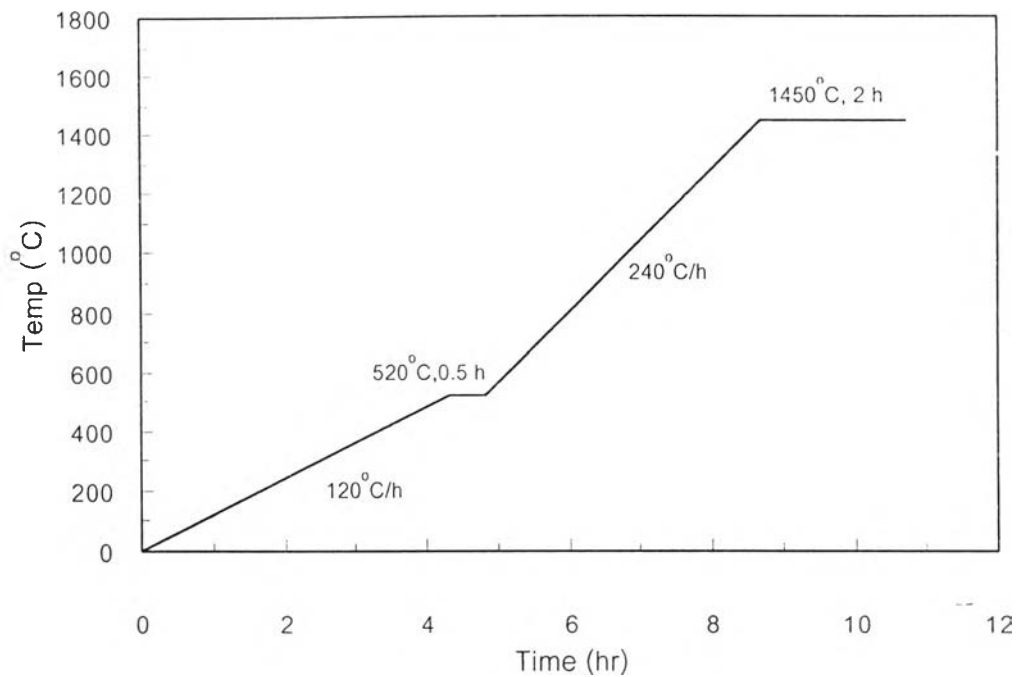


Fig.3.2 The sintering schedule for  $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{1-x}\text{B}_x\text{O}_3$  (B = Co or Fe)

### 3.3 Characterization of specimens sintered at 1450°C for 2 hours

#### 3.3.1 Phase analysis

The phases of all sintered compositions were determined by XRD to investigate the other phases which may take place after firing at higher temperature. The analysis was performed on the surface of pellets.

#### 3.3.2 Density measurement

The bulk density of specimens was measured according to Archimedes method. The vacuum pressure was used to remove the air from opened pore of specimens. The dry weight  $D$ , saturated weight  $W$  and suspended weight  $S$  were measured and used to calculate the bulk density by

$$\text{Bulk density} = \frac{D}{W - S} \rho \quad (3.1)$$

### 3.3.3 Electrical conductivity measurement

The electrical conductivity was measured as a function of temperature on the sintered rectangular bars using a DC four-point method. The gold electrodes were painted at the four points of the rectangular bars and then fired at 800°C for 20 mins with a heating rate of 2°C min<sup>-1</sup>. The electroded specimen was put in the sample holder as shown in Fig.3.3 and subjected into the tube furnace. Platinum wires were used to lead current and voltage. DC current was applied to the specimen over electrode point a and d, using a power supply (TPS-4000D series). The current (I) in series and the applied voltage (V) between b and c were collected at every 5°C with an increasing temperature of 4°C min<sup>-1</sup> from 60 to 900°C. The electrical conductivity ( $\sigma$ ) of specimens was calculated by equation (3.4) and (3.5).

$$R = \frac{V}{I} \quad (3.2)$$

$$\text{and} \quad \sigma = \frac{1}{\rho} = \frac{L}{RA} \quad (3.3)$$

where  $\rho$  is the resistivity and L is the length of measurement

The electrical conductivities were plotted by  $\log(\sigma T)$  VS  $\frac{1}{T}$  according to the Arrhenius equation.

In this study, the electrical measurement of specimens with and without electrode was also performed as the followings:

#### a) Electrode effect

Since cathode material was presumed to act as a conductor at high temperature; therefore, the electrical conductivity without applying electrode was worth considering. The LSM and LSMC4 compositions were selected to study. The electrical conductivities of those sintered specimens with and without gold electrode were examined.

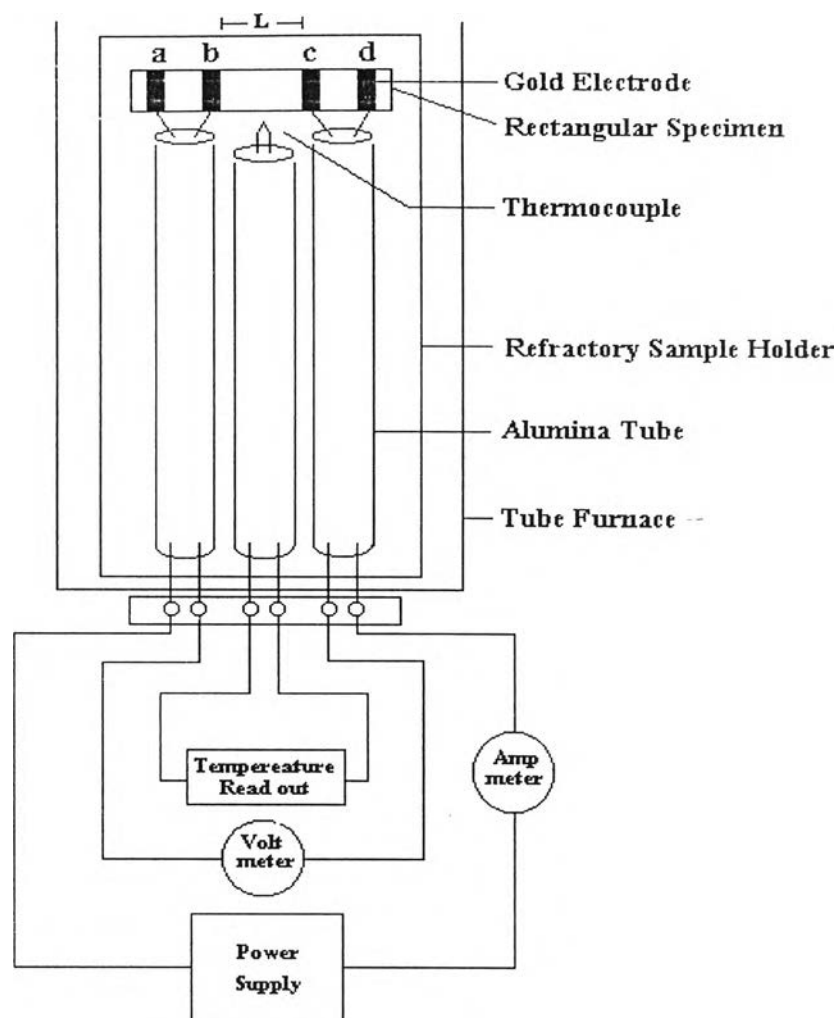


Fig.3.3 Schematic of apparatus used for the DC conductivity measurement

#### b) Atmospheric effect

Since the electrical conductivity of LSM ceramics varies with the oxygen atmosphere, a comparison of electrical property for LSM and LSMC4 sintered specimens, without gold electrode was determined in air and flowing oxygen measurements.

#### 3.3.4 Microstructural Evaluation

The microstructures of sintered pellets were examined using a scanning electron microscope (SEM) (Jeol, JSM-5410). The specimens were polished along the cross-section using SiC paper and diamond paste and then thermally etched at 1370°C for 2 hrs. The specimens were gold sputtered before subjected into the microscope.

#### 3.3.5 Thermal expansion coefficient measurement

The linear thermal expansion of sintered rectangular bar was measured using dilatometer (Netzsch, Dil402C). The measurements were carried out in the temperature range from 25 to 900°C with a heating rate of 5°C min<sup>-1</sup>. The standard calibration was done by Al<sub>2</sub>O<sub>3</sub> rod reference.

### 3.4 Effect of sintering temperature on the properties of sintered specimens

Since the second phases were found in specimens sintered at 1450°C for 2 hours, sintering at other temperatures was attempted to reduce the second phases.

Both of LSM and LSMC4 compositions were selected in this study. They were sintered at 1400°C for 2 hours and then their phases were analyzed by XRD in order to prove whether the sintering at 1450°C was so high that the second phase occurred. In addition, sintering at 1470°C with a shorter soaking time was performed to improve the properties of these specimens. The phase and density of these specimens were studied.