Chapter 3

Experimental procedure

3.1 Raw materials and characterization

3.1.1 Starting raw materials

Oxide and carbonate as listed in Table 3.1 were used as 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 $La_{1-x}Sr_xAl_{1-y}Mg_yO_{3.\delta}$

Materials	Purity (%)	Manufacturers
Lanthanum Oxide (La_2O_3)	99.9	Aldrich
Strontium Carbonate ($SrCO_3$)	98+	Aldrich
Alumina (Al_2O_3)	98.7	J.T.Baker
Magnesium Oxide (MgO)	98+	Fluka

3.1.2 Raw materials characterization

3.1.2.1. Phase analysis

To investigate the existing phase before using, all raw materials were characterized by X-ray diffraction (XRD). The powder was mounted in a sample holder and subjected to X-ray diffractometer (Jeol, JDX 3530), using CuK_α radiation (λ = 1.54056 Å) and operating at 30 kV. and 30 mA. The XRD data were collected in the range of 2θ 20-80°, using the step scan of 0.02° and the count time of 0.6 sec.

3.1.2.2 Thermal analysis

In order to remove the undesirable phases, if existing, calcination of as-received raw material was necessary before batching. 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 to investigate the reaction temperatures. Weight loss 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 $La_{1-x}Sr_xAl_{1-y}Mg_yO_{3-\delta}$

All compositions were prepared by conventional oxide mixing process as illustrated in Fig. 3.1. After the removal of undesirable phases, the raw material was weighed according to the stoichiometric ratio as shown in Table 3.2. Then it was wet-mixed in polypropylene bottle for 8 h, using alumina balls as grinding media and ethanol as solvent. After drying overnight at 100°C, the mixture was calcined in alumina crucible. The appropriate calcining temperature was determined from DTA result in order to obtain single phase of $La_{1-x}Sr_xAl_{1-y}Mg_yO_{3-\delta}$. The DTA7 was operated from 100°C to 1200°C with a heating rate of 10°C/min. The calcining schedule was applied to all compositions according to the DTA results. A slow heating rate with 2°C/min along with the soaking time for 4 hours during the calcination was necessary for a large amount of powder. In addition, the second calcining after grinding was provided to obtain homogeneous compositions. After calcining the phases and crystal structure were obtained from XRD. The data were collected in the range of 2θ 20-80° and Si was added as internal standard. The lattice parameters and X-ray density were calculated from the data after correction.

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                    ┌──────────────┐
                    │ Raw material │
                    └──────────────┘
                            │
                            ▼
                          XRD ───────────►   Calcination
                            │                (if undesirable phase
                            ▼                   was observed)
                    ┌──────────────┐  ◄──────────────┘
                    │   Weighing   │
                    └──────────────┘
                            │
                            ▼
                    ┌──────────────┐
                    │  Mixing 8 h  │
                    └──────────────┘
                            │
                            ▼
                    ┌──────────────────┐
                    │ Drying (100°C)   │
                    └──────────────────┘
                            │──────────────►  DTA
                            ▼
                    ┌────────────────────┐
                    │ Calcination (twice)│
                    └────────────────────┘
                            │──────────────►  XRD
                            ▼
                    ┌────────────────────┐
                    │ Milling 8 h and    │
                    │      Drying        │
                    └────────────────────┘
                            │
                            ▼
                    ┌────────────────────┐
                    │ Isostatic pressing │
                    └────────────────────┘
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                            ▼
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                    │  Sintering   │
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                    │  Characterization  │
                    └────────────────────┘
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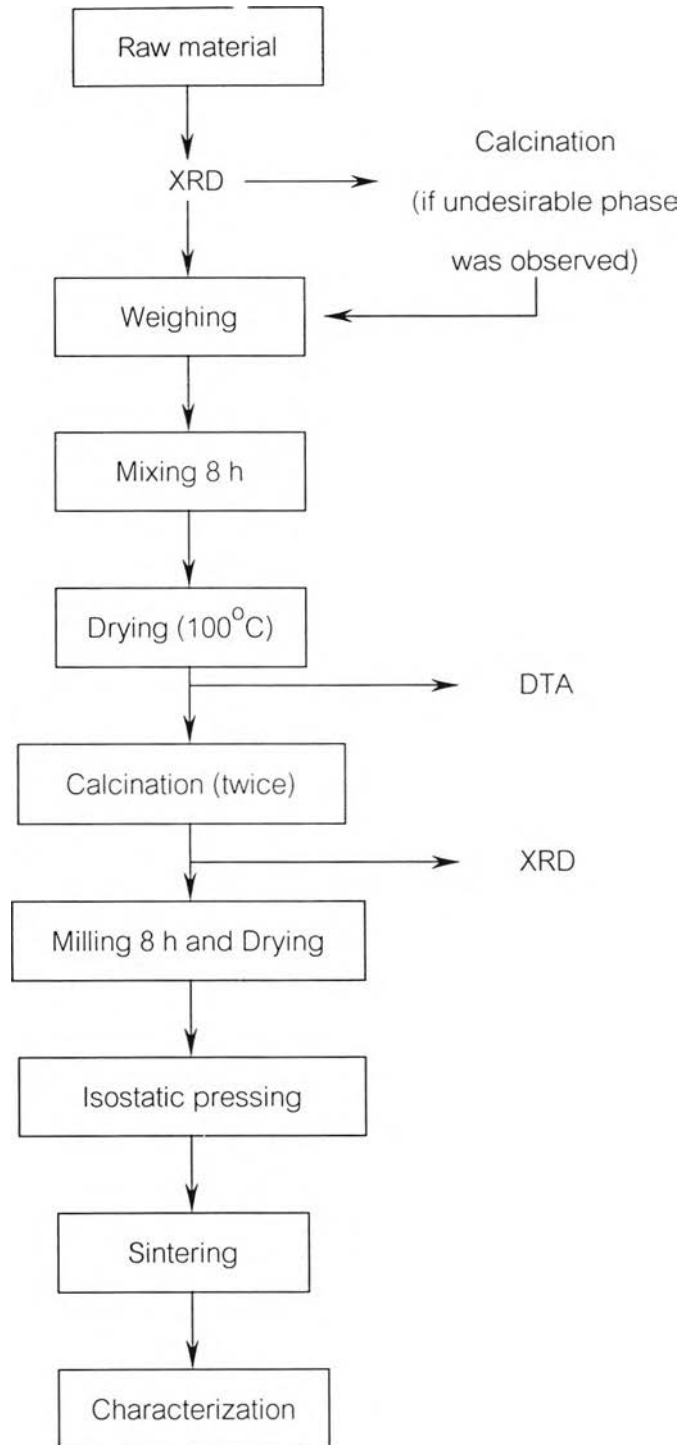
Fig 3.1 Flow chart of material preparation process

The calcined powder was milled for 8 hours and screened through a mesh no. 100. The powder was pressed uniaxially into pellets (1 cm. in diameter) and the rectangular bar (0.7×3.2 cm^2) on a single action dry-press and then followed by cold isostatic press with a pressure 196 MPa.

The pellets were sintered at 1500, 1550 and 1575 $^\circ$C for various compositions with a heating rate of 3°C/min and soaking period for 4 hours in order to obtain dense pellets. The sintered samples were cooled in the furnace with a cooling rate of 5°C /min.

Table 3.2 The stoichiometric ratio of $La_{1-x}Sr_xAl_{1-y}Mg_yO_{3-\delta}$

Composition			MW.	Molar ratio			
x	y	Notation		La_2O_3	$SrCO_3$	Al_2O_3	MgO
0	0	Std.	213.88	0.5	-	0.5	-
0.05	0	S5	210.916	0.475	0.05	0.5	-
0.1	0	S10	207.952	0.45	0.10	0.5	-
0.1	0.05	M5	207.421	0.45	0.10	0.475	0.05
0.1	0.1	M10	206.854	0.45	0.10	0.45	0.1
0.1	0.15	M15	206.359	0.45	0.10	0.425	0.15
0.15	0	S15	204.988	0.425	0.15	0.5	-

3.3 Characterization of sintered materials

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 pore of specimens during measurement. The dry weight D, saturated weight W, suspended weight S and density of water ρ were measured and used to calculate the bulk density by using the equation as below.

$$\text{Bulk density} = \frac{D}{W - S}\,\rho \tag{3.1}$$

3.3.3 Electrical conductivity measurement

A comparison of electrical conductivity determined by AC and DC was investigated. The electrical measurement was carried out by an AC impedance spectroscopy and a DC four-probe for compositions which were not doped with Mg. The electrical conductivity of y equal to 0.05, 0.1 and 0.15 was determined only from AC method.

3.3.3.1 AC impedance spectroscopy

The pellet was measured for thickness and radius and then was electroded with gold paste by painting both sides of the pellet before collecting the data. After firing at 820°C for 20 min with a heating rate of 2°C/min, the sample was put

in the sample holder as shown in Fig. 3.2 and subjected into the tube furnace. A Hewlett-Packard 4192A LF impedance analyzer was used for measuring complex impedance over a frequency range from 5 Hz. to 13 MHz. The measurements were conducted in air in a temperature range of 300 to 800°C. Resistance (R) of each sample was determined from the intercept on the real axis and the electrical conductivity (σ) was calculated by using equation 3.2

$$\sigma = \frac{L}{RA} \qquad (3.2)$$

Where L is thickness and A is an area of the electrode.

The activation energy and the electrical conductivity at 1000°C were calculated from the plot of log (σT) vs. $\frac{1}{T}$ according to the Arrhennius equation to compare with other electrolyte materials.
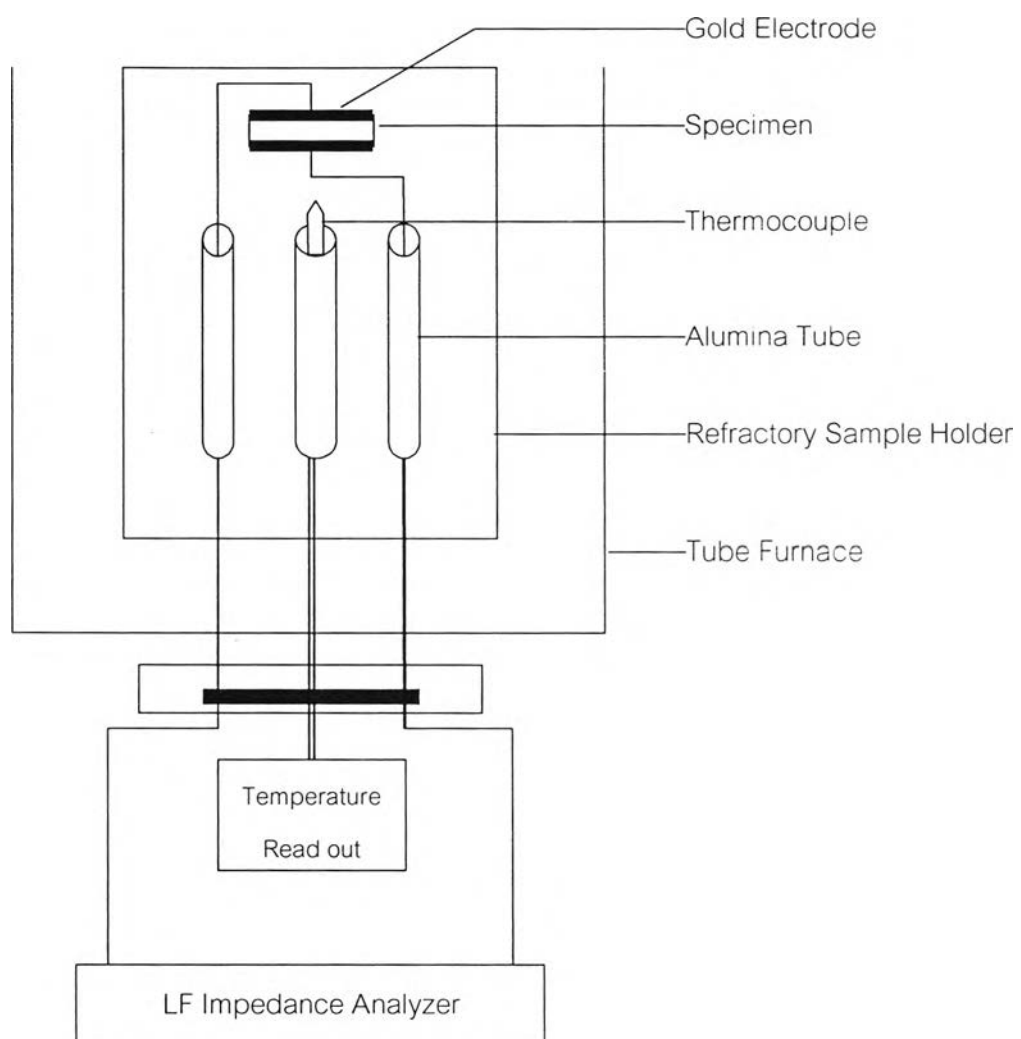
Fig 3.2 Schematic of apparatus used for the AC conductivity measurement

3.3.3.2 DC four-point method

The dc conductivity was measured as a function of temperature of the sintered rectangular bars. Before collecting the data, the sample was painted with gold paste in the area shown in Fig 3.3, and then fired at the same condition as previously described for AC impedance measurement. The electroded specimen in the sample holder was subjected into the tube furnace. Platinum wires were used to lead current and voltage. A dc power supply (TPS-4000D series) used to apply the voltage to the specimen over electrode point a and d. The current (I) in series and the voltage (V) between b and c were collected at every 5°C with an increasing temperature of 5°C/min range from 300 to 800°C. The resistance of the specimen was calculated from the ratio of V and I and the electrical conductivity was obtained by using equation 3.2.

3.3.4 Microstructure

The microstructure of the sintered pellets was observed with a scanning electron microscope (SEM) (Jeol, JSM-5410). The specimens were polished along the cross-section using SiC paper and diamond paste down to 1μm and then thermally etched for 2 hours at the temperature less than sintering temperature for 100°C. The specimens were gold sputtered on the polished surface before subjected into the microscope.

3.3.5 Thermal expansion coefficient

The linear thermal expansion of sintered rectangular bars was measured using dilatometer (Netzsch, Dil402C). The measurements were carried out in the temperature range from 30 to 900°C with a heating rate of 5°C/min. The standard calibration was done by Al_2O_3 as a reference with the same condition.
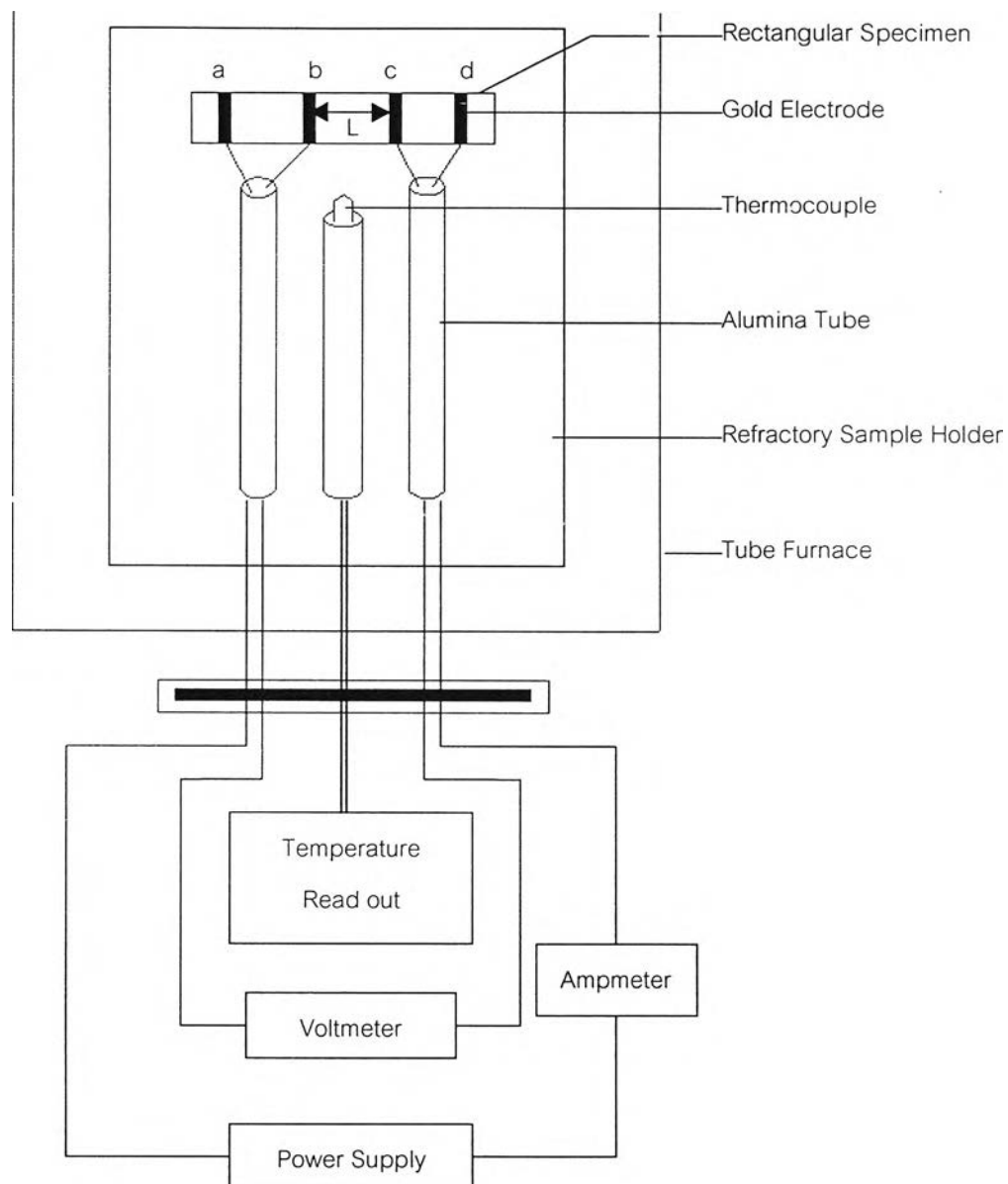
Fig 3.3 Schematic of apparatus used for the DC conductivity measurement