

## CHAPTER II

### EXPERIMENTAL

The chemicals, apparatus and experimental procedures such as processing of perovskite powders synthesis, perovskite membranes preparation and characterization of materials, are described as below:

#### 2.1 Chemicals

The chemicals listed in Table 2.1, were used without further purification.

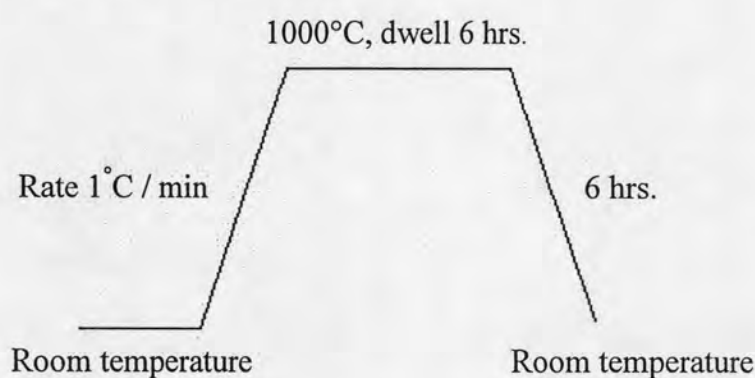
**Table 2.1** Reagents for synthesis of perovskites

Reagents	Formula Weight	Purity%	Company
$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	433.02	$\geq 99.0$	Fluka
$\text{Sr}(\text{NO}_3)_2$	211.63	$\geq 99.0$	Fluka
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	404.00	98.0	Fluka
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	290.79	98.0	Wako
$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	241.60	99.0	Fluka
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	375.13	$\geq 98.0$	Fluka
$\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$	178.95	99.99	Aldrich
$\text{C}_6\text{H}_8\text{O}_7$	192.43	99.5	Fluka
$\text{HNO}_3$	63.01	65	Merck

## 2.2 Synthesis of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{1-x}\text{M}_x\text{O}_3$ by modified citrate method

The perovskite powders  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{1-x}\text{M}_x\text{O}_3$  ( $M = \text{Ni}$ ,  $x = 0.1, 0.2$  and  $0.3$  /  $M = \text{Cu}$ ,  $x = 0.1$  and  $0.2$  /  $M = \text{Al}$ ,  $x = 0.1, 0.2, 0.3$  and  $0.4$  /  $M = \text{Mn}$ ,  $x = 0.1$  and  $0.2$ ) were synthesized in basic solution. Stoichiometric amounts of corresponding high purity metal nitrates (based on 4 g. of perovskite powder) were partially dissolved in 15 ml distilled water. Then citric acid was added at a ratio of citric acid to metal ions (2:1). The mixture solution was then titrated with  $\text{NH}_3 \cdot \text{H}_2\text{O}$  at the controlled rate of 2-3 ml/min. The pH value of the solution was adjusted to ~9.

The combustion of the homogeneous solution was carried out on a hot plate at around 200-300°C by slowly heating temperature in a three-liter beaker covered with a fine sieve to prevent the loss of fine powder. The water was evaporated until a sticky gel was obtained. Then it became a large swelling viscous mass and finally self ignited by  $\text{NH}_4\text{NO}_3$ . The combustion lasted for about 10-20 seconds. The resulting powder was ground by mortar and pestle, subsequently the synthesized perovskite oxide was calcined in a Carbolite RHF 1600 muffle furnace in air to achieve phase purity and remove the residual carbon. The conditions used for the calcination of the perovskite powders were set as follows:



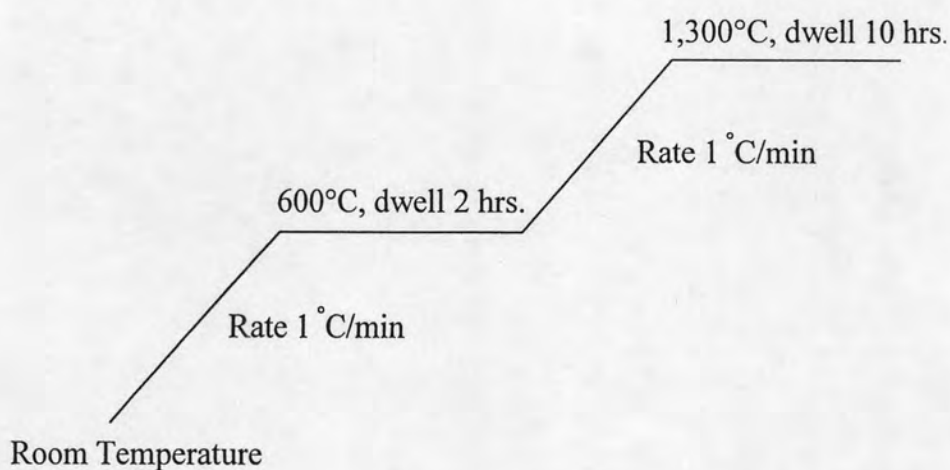
**Figure 2.1** The calcination condition of perovskite powder. The particle was ground completely well by mortar before characterization.

### 2.3 Perovskite disc preparation

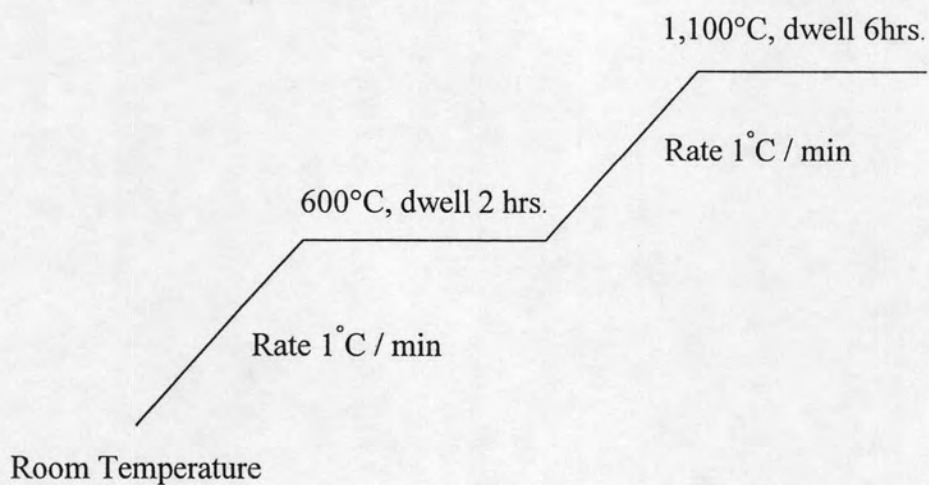
The very fine perovskite powder was loaded into the cavity, the plunger was brought to the surface of the powder gently for final leveling and then rotates for smooth surface. About 2 tons was applied on the plunger by the uniaxial pressing machine. At the beginning of pressing, the pressure was slowly applied to 2 tons for 20 minutes. The pressure was released and then the die was removed from the press. Then the assembly was held while the press until the pellet ejected. The disc is around 1 mm thick, 13 mm diameter from 1,700–1,800 mg of powder. Then the discs were generally sintered in air at 1,100–1,300°C for 10-15 hours, depending on the composition. Finally the sample was cooled to room temperature.

### 2.4 The Sintering of the Perovskite Oxides

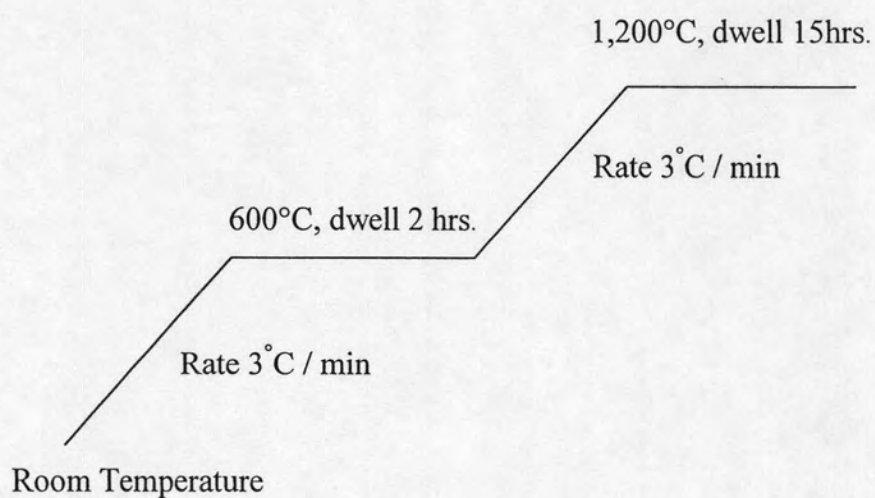
The ceramic specimen were generally sintered in air under different conditions, depending on the composition. The conditions used for sintering were set as follows:



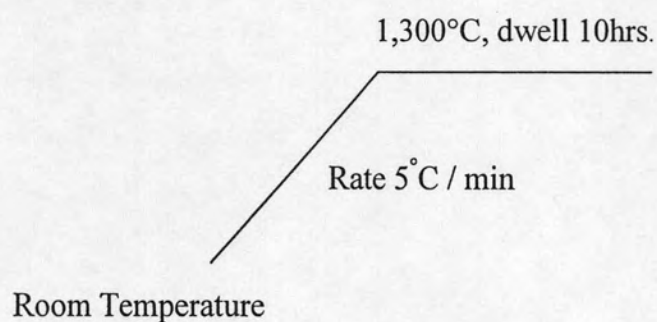
(a)



(b)



(c)



(d)

**Figure 2.2** The sintering conditions of perovskite (a)  $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$  (b)  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_x\text{Cu}_{1-x}\text{O}_3$  (c)  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_x\text{Ni}_{1-x}\text{O}_3$  (d)  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$  and  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_x\text{Al}_{1-x}\text{O}_3$

## **2.5 Characterization Techniques**

### **2.5.1 X-Ray Diffractometry (XRD)**

The phase formations of perovskite oxide were characterized after calcination and sintering by X-ray powder diffraction (XRD). The XRD patterns, for both powder and disc, were taken by using Rigaku, DMAX 2002 Ultima Plus X-Ray powder diffractometer equipped with a monochromator and a Cu-target X-ray tube (40 kV, 30 mA) and angles of  $2\theta$  ranged from 20–70 degree (step time 0.5 sec., scan step 0.020 degree) at Department of Chemistry, Faculty of Science, Chulalongkorn University.

### **2.5.2 Scanning Electron Microscopy (SEM)**

The morphology of the sintered discs was carried out using a JEOL JSM-5800LV scanning electron microscopy, Oxford Instrument (Link ISIS series 300) at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University. This instrument uses X-rays or electrons scattered back from the surface “illuminated” by a restored electron beam to generate an image with remarkable three-dimensional qualities.

### **2.5.3 Density**

Density of perovskite disc was determined by the Archimedes immersion method using water as a medium, Precisa Gravimetrics AG (model R 2055M-DR), at Department of Chemistry, Faculty of Science, Chulalongkorn University.

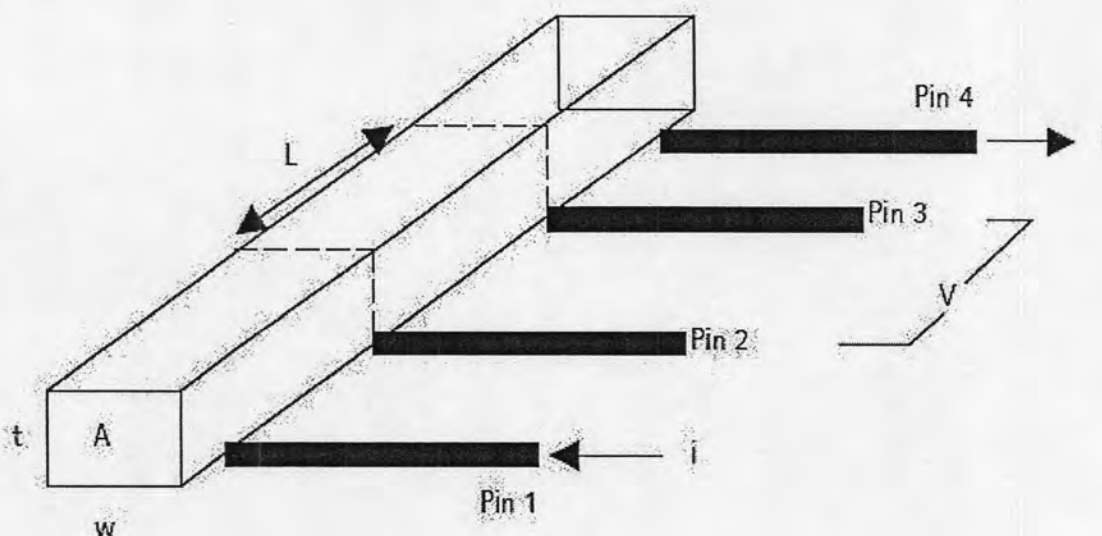
### **2.5.4 Temperature-Programmed reduction (TPR)**

Temperature programmed reduction (TPR) experiments were measured using H<sub>2</sub>/Ar temperature-programmed reduction, BEL JAP INC, at Department of Chemistry, Faculty of Science, Chulalongkorn University. The sintered perovskite

powder was first pretreated in  $O_2$  atmosphere (30 ml/min) at  $500^\circ C$  for 1 hours, then cooling in flowing  $O_2$  down to  $100^\circ C$ , and thereafter reduced with 5%  $H_2/Ar$  mixture heating  $10^\circ C/min$  up to  $900^\circ C$ . Water produced by the sample reduction was condensed in a cold trap before reaching the detectors. Only  $H_2$  was detected in the outlet gas confirming the effectiveness of the cold trap. TCD was used on line with a computer data acquisition system.

### 2.5.5 Electrical Conductivity Measurement

The electrical conductivity in air of the specimens was measured by a conventional DC 4-probes method using Pt as an electrode. The sintered disc was cut into a rectangular shape and four electrodes were fabricated with Pt paste. After firing at  $950^\circ C$ , measurements were performed in the temperature range of room temperature to  $800^\circ C$  at a rate of  $5^\circ C/min$ . In this method a wire is contacted at four locations (pin 1, 2, 3, 4) as shown in Figure 2.3



**Figure 2.3** DC four-probe methods

The measurement method then includes a forced current  $I$  through the outer pins 1 and 4 and a measurement of the voltage drop over pin 2 and 3, using a very high Ohmic measurement device, so that the current flowing through pin 2 and 3 is

nearly zero. In that case the individual, additional contact resistance does not play a role as it cancels out of the equation. To study the behavior of the structure an I/V curve is generated, typically in the mA to the mA range. If the graph shows a straight line, the structure behaves as an Ohmic resistor [25]. If assume that the resistance of a structure to be R then the following applies:

$$S = (I/V) * (L/(W*T)) \dots \dots \dots (2.2)$$

S = electrical conductivity

I = applied current (A)

V = resulting potential (V)

L = length between Pt (cm)

T = thickness of membrane (cm)

W = wide of membrane (cm)

### 2.5.6 Dilatometer

The disc samples (after sintered) were cut to bar (about 12 mm in length, 5 mm in width and 1.5 mm in thickness). The thermal expansion coefficients were measured from room temperature to 800°C in air with a heating rate of 10 K/min by dilatometer (NETZSCH DIL 402C) from Department of Materials Science, Faculty of Science, Chulalongkorn University.