

## CHAPTER 3

### MATERIALS AND METHODOLOGY

The polycrystalline samples were synthesized by solid state reaction method which is a most widely used for preparation of polycrystalline solids from a mixing of powder materials. In this work, the precursor powder were mixed by ball milling in ethanol and pressed the powder by hot press method into bulk samples. The bulk sample were analyzed and characterized by equipment for thermoelectric module at high temperature. The thermoelectric module was measured electric power, thermos cycle and application using heat source from brick furnace for turn on LED lamp following by:

#### SYNTHESIS AND PREPARATION THERMOELECTRIC MATERIALS

##### Synthesis $\text{Ca}_{1-x}\text{Bi}_x\text{MnO}_3$ and $\text{Ca}_3\text{Co}_4\text{O}_9$ + Ag 10 wt% powder thermoelectric materials

The solid state reaction (SSR) method is most widely for used synthesis compound because easily mixing solid powder precursor follow stoichiometric ratios. This project was synthesized  $\text{Ca}_{1-x}\text{Bi}_x\text{MnO}_3$  ( $x = 0, 0.01, 0.02, 0.03, 0.04$  and  $0.05$ ) and  $\text{Ca}_3\text{Co}_4\text{O}_9$  + Ag 10 wt% powders by SSR method for successful.

The chemicals powder and equipment for used in this process are shown in Table 1 and Table 2, respectively.

Table 1: List of chemicals used for solid state reaction method their formula, supplier and purity

Chemical	Formula	Supplier	Purity
Calcium carbonate	$\text{CaCO}_3$	QRëC	>99%
Manganese oxide	$\text{MnO}_2$	Fisher Scientific UK	>99%
Bismuth (III) oxide	$\text{Bi}_2\text{O}_3$	QRëC	99.5%
Cobalt oxide	$\text{Co}_3\text{O}_4$	Sigma–Aldrich	99.5%
Silver	Ag	Sigma–Aldrich	99.9%
Ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	QRëC	99.9%

Table 2: List of equipment used for synthesis of powder, preparation of bulk, characterization and measurement of thermoelectric properties together with their model and area of application

Equipment	Model	Application
Ball mill	—	Mixing and milling of powders
Ultra–sonic cleaner	BAKU BK–3350	Cleaning of materials
Hot plate & stirrer	Vision vs–130SH	Drying of wet powders
Weight scale	METTLER TOLEDO	Weighing compound
Furnace	Homemade CEAE	Synthesis, sintering and annealing
Hot press	OTF–1200	Pressing and sintering of pellets
Saw low speed	BUEHLER Isomet	Cutting of materials
Grinder–Polisher	BUEHLER Metaseve 3000	Grinding–Polishing of materials
XRD	SHIMADZU–6100	Study phases composition

Table 2 (continues)

Equipment	Model	Application
FE-SEM	JEOL JMS-7800F prime	Study microstructure and phases composition
Density kit	METTLER TOLEDO MS204	Measure density of materials
Seebeck and Resistivity	TRC-ZTM2	Measure Seebeck coefficient and electrical resistivity of materials
Thermal conductivity	TRC-Thermal	Measure Thermal conductivity of materials
Electric generation	TRC-Efficiency module	Measure voltage, current and Temperature

The  $\text{Ca}_{1-x}\text{Bi}_x\text{MnO}_3$  ( $x = 0, 0.01, 0.02, 0.03, 0.04$  and  $0.05$ ) polycrystalline ceramics were synthesized by SSR method using calcium carbonate powder ( $\text{CaCO}_3$  purity 99%) mixed with manganese dioxide ( $\text{MnO}_2$  purity 99.9%) and bismuth oxide ( $\text{Bi}_2\text{O}_3$  purity 99.5%) in stoichiometric ratios as shown in Table 1. The powders precursor were mixed by ball milling in ethanol by zirconia balls for 12 h. Then mixed powders were kept in a drying hot plate and magnetic stirrer 395 K 4 h for remove ethanol and moisture and then calcined at 1273 K for 24 h in air on alumina cup by using heat rate 5 K/min. After that an intermediate grinding step to powder for prepare bulk TE materials.

The  $\text{Ca}_3\text{Co}_4\text{O}_9 + \text{Ag}$  10 wt% was synthesized by SSR of calcium carbonate powder ( $\text{CaCO}_3$  purity 99%) mixed with Cobalt oxide ( $\text{Co}_3\text{O}_4$  purity 99.5%) and silver (Ag purity 99.9%) in stoichiometric ratios as shown in Table 1. All powder precursor were mixed in ethanol and zirconia ball, then ball milling for 24 h. The mixed powder was dried in hot plate until all the ethanol has been evaporated and after that

calcine power at 1123 K 24 h in air heating rate 5 K/min then calcined powder was grinded. The powder was uniaxially hydraulic pressed at 288 MPa for 1 min in order to obtain green ceramic size ( $25 \times 25 \times 5 \text{ mm}^3$ ). The green ceramics was then sintered in the optimal conditions found in previous works, consisting in one step heating at 1223 K during 12 h with a final furnace cooling.

### Preparation $\text{Ca}_{1-x}\text{Bi}_x\text{MnO}_3$ and $\text{Ca}_3\text{Co}_4\text{O}_9 + \text{Ag}$ 10 wt% bulk thermoelectric materials

Hot pressing sintering (HP) is expected fine increased use to prepare high density and decreased micro-cracking of materials. The schematic view of HP machine and main unit is shown in Figure 18. The system of HP OTF-1200 included furnace for heating unit outside and chamber quartz tube for control atmosphere. The graphite punch up from hydraulic on bottom plate when graphite rods on top of the mold is pulled up and pressed with rods graphite top, it will cause the pressure within the mold to compound powder. The calcined powder of  $\text{Ca}_{1-x}\text{Bi}_x\text{MnO}_3$  was compressed in graphite die diameter 10 mm to pellet

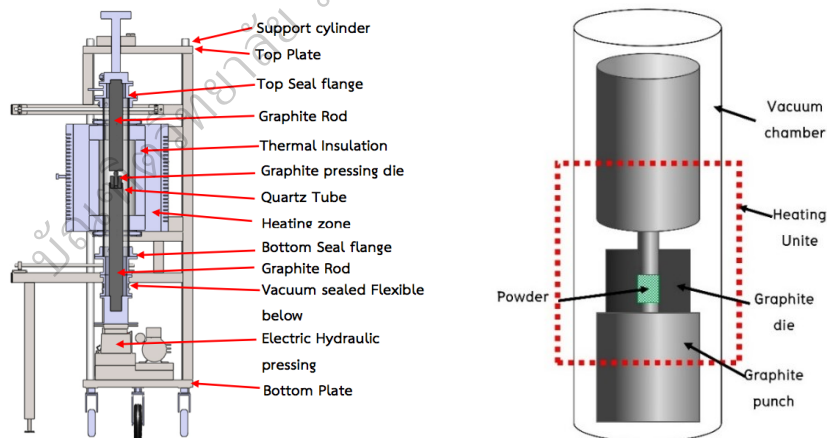


Figure 18 Schematic view of hot press machine and working chamber

In present study, the HP process was carried out using an OTF-1200x-VHP-4 high temperature vacuum hot press. The powder were filled in a cylindrical graphite die with 10 mm inner-diameter and pressed by using two graphite punches

at 60 MPa. Before filling powder into die, a mica was placed bottom the die and filled powder used mica in top powder. The high temperature was used for sintering powder. Then the graphite die with press powder was placed in to graphite punch and install to vacuum chamber.

An atmosphere in the chamber was setting Ar gas for protect graphite die from oxidation 0.08 MPa. The minimum pressure for beginning was applied 10 MPa when temperature increased to peak was increased to 60 MPa. The temperature rate heat and cool was set 5 K/min start at room temperature the holding time at that temperature was 1 h. The sample was cooled down to room temperature by used rate 5 K/min after that to 523 K cooled according to the thermal inertia of the furnace shown in Figure 19. The sample remove from graphite die and co-sintering process for remove carbon from surface and increased density by annealed in furnace 1473 K 36 h in air shown in Figure 20.

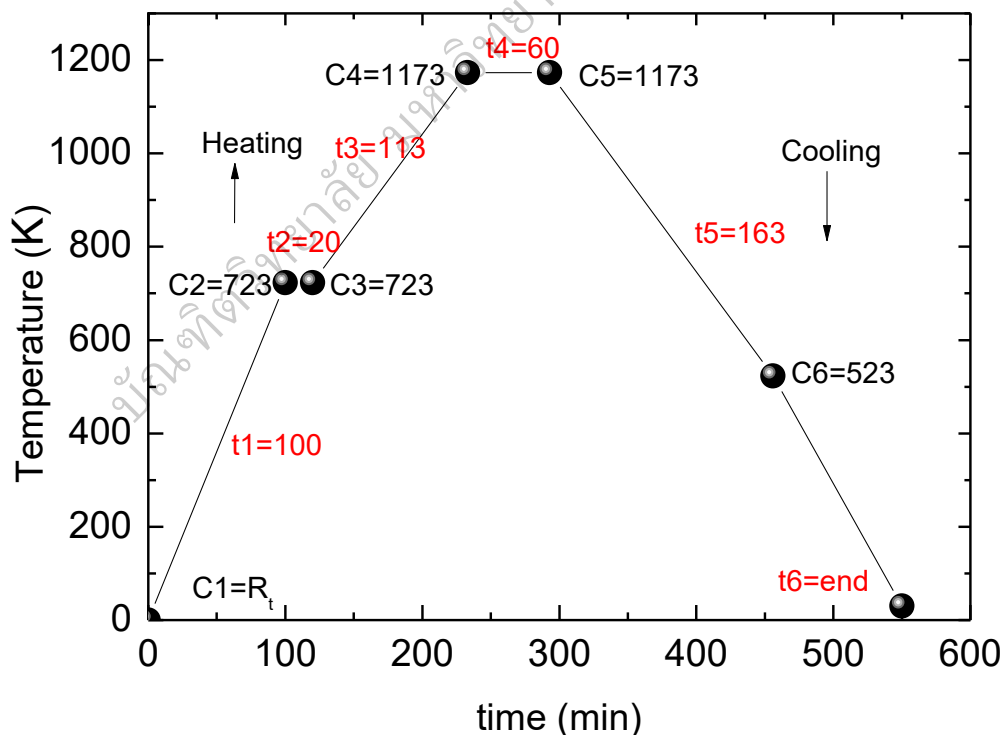


Figure 19 Schematic of heating program for hot pressing of dense bodies used for all samples in Ar gas 0.08 MPa

### Annealing bulk samples

The thermoelectric materials has been hot pressing process require to annealed for remove graphite to achieve a single phase and increased density of sample. A sample from hot pressing was shown mix phase due to carbon from graphite die contaminated to samples. Then the sample was placed in furnace for annealing in air at 1473 K 36 h and using heating and cooling rate 4 K/min in Figure 20. The sample annealed was increased density 9% and sample damage decreased 20 %.

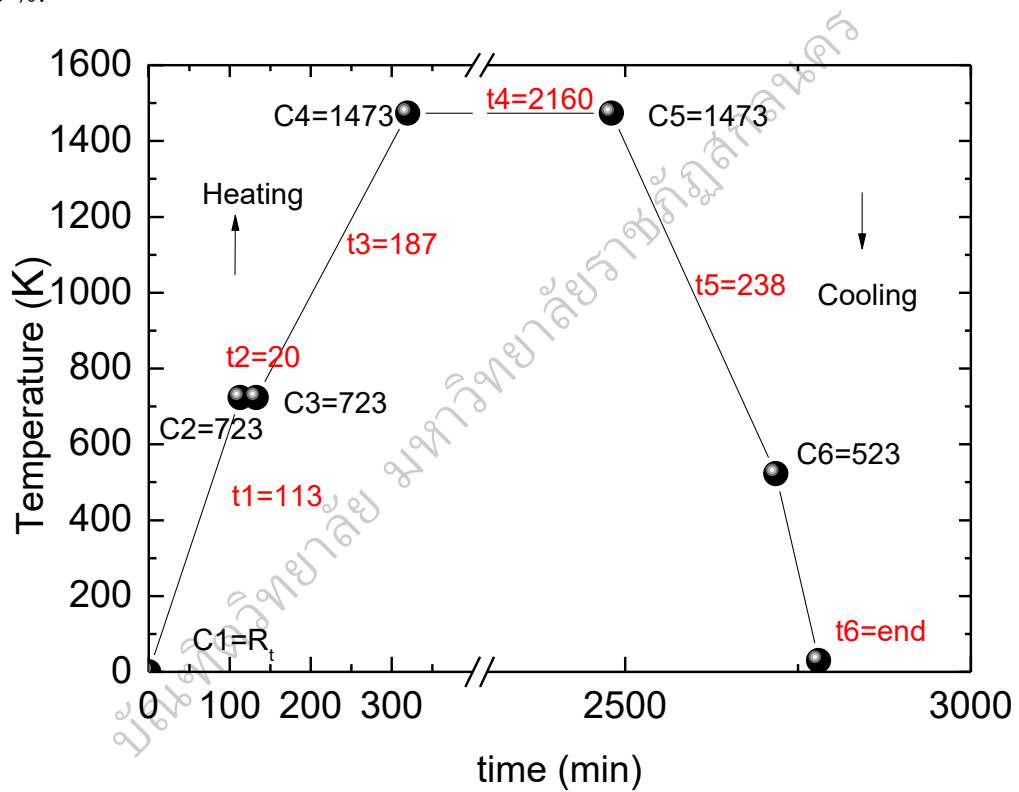


Figure 20 Schematic of heating program used for annealing of the samples with indicated heating /cooling rates in air

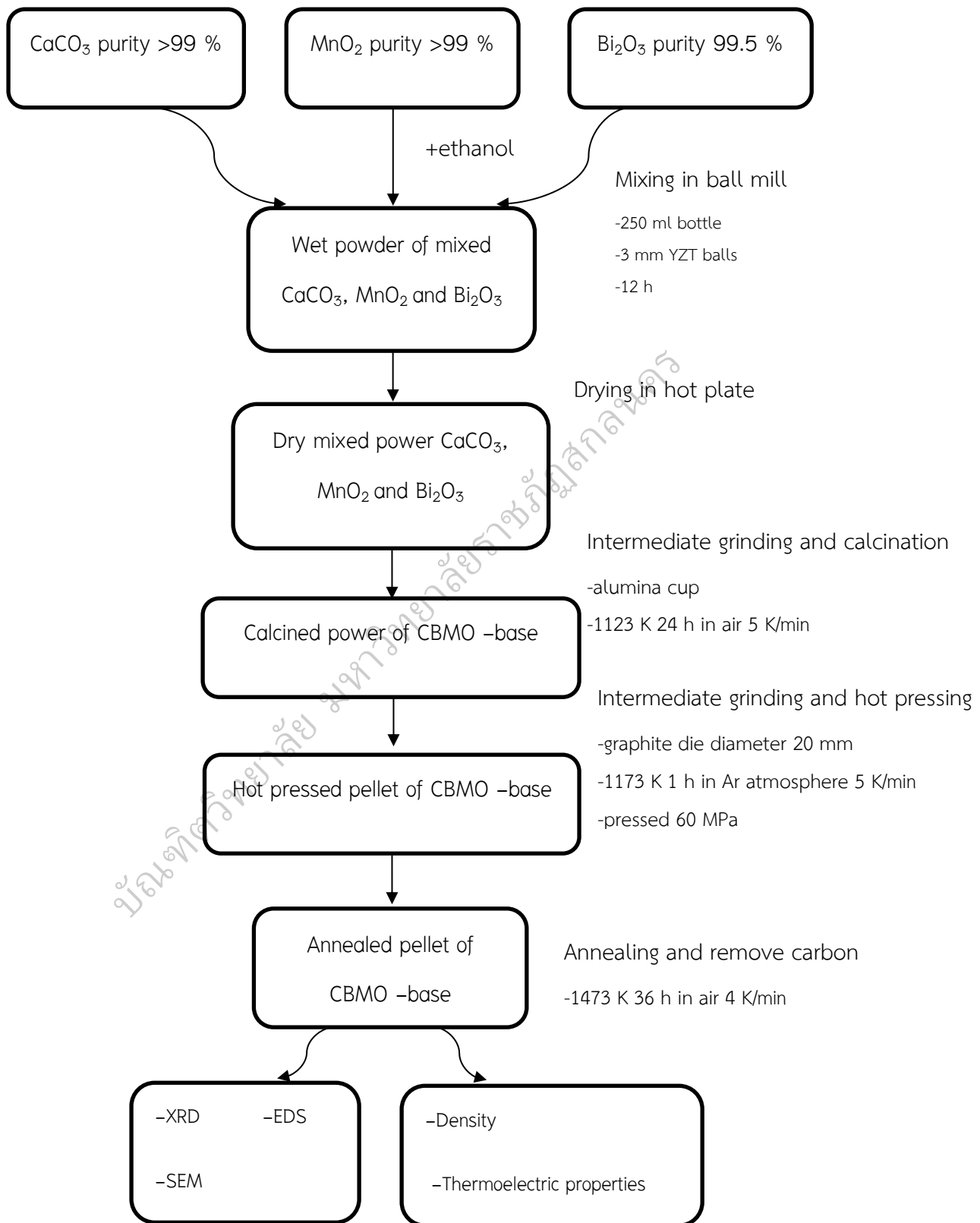


Figure 21 Flowchart illustrating Ca<sub>1-x</sub>Bi<sub>x</sub>MnO<sub>3</sub> (x=0-0.05) synthesis process

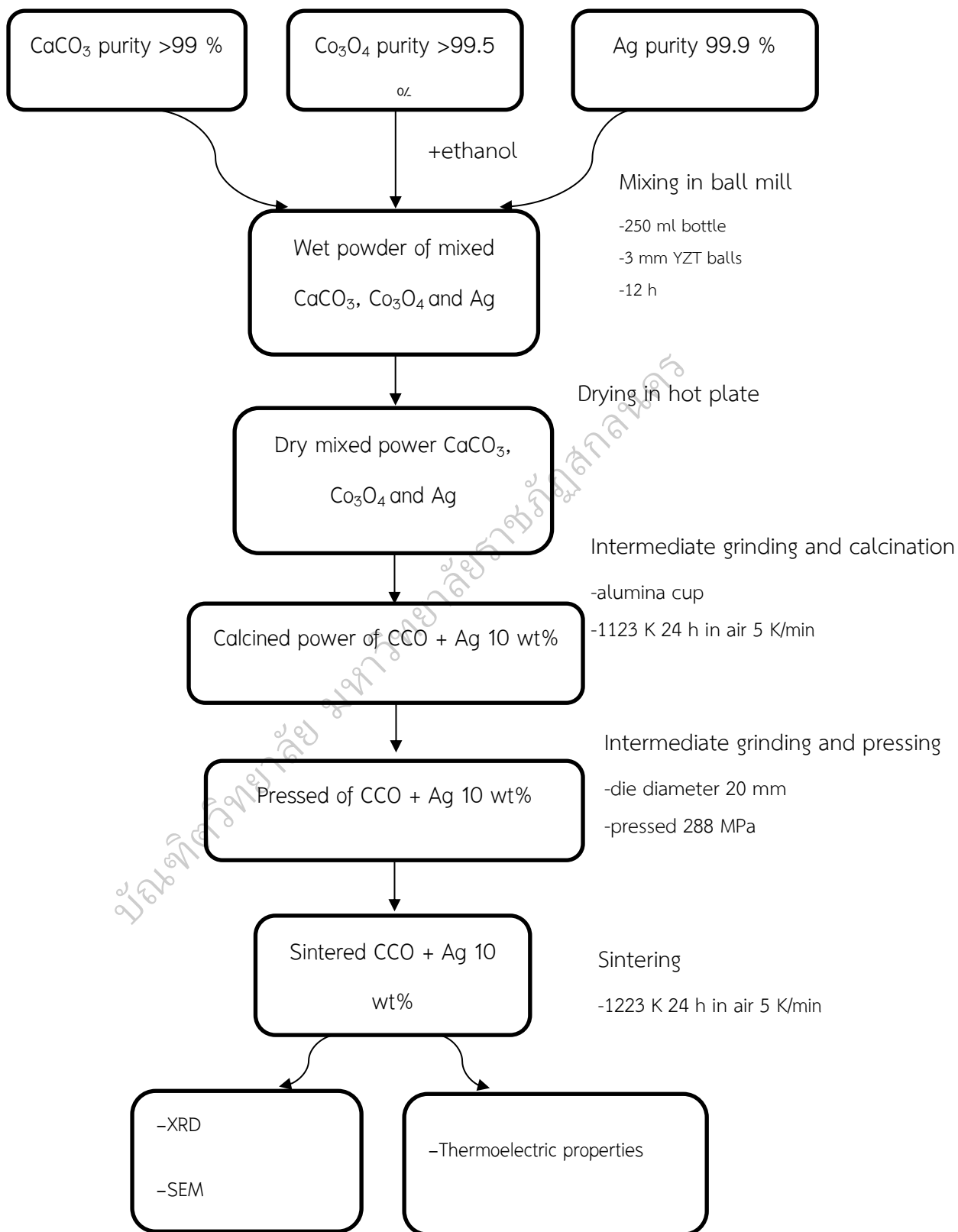


Figure 22 Flowchart illustrating Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> + Ag 10 wt% synthesis process



## CHARACTERIZATION TECHNIQUES

### X-ray diffraction

X-ray diffraction (XRD) analysis was used to establish phase identification for crystalline material and can provide information on crystal structure such as unit cell. XRD used scattering and diffraction technique from x-ray are generated by a cathode ray tube then the x-ray filtered before toward to sample. The diffraction pattern from XRD based on Bragg's law.

$$2d \sin \theta = n\lambda \quad (3.1)$$

Where  $d$  is the lattice spacing in crystal sample,  $\theta$  is the angle between the incident beam and the atomic plane,  $\lambda$  is the wave length of electromagnetic radiation from source,  $n$  is an integer corresponding to order of diffraction. The radiation from sample detected and counted. Due to the random orientation of the sample materials, all possible diffraction directions of the lattice should be attained by scanning the sample through a range of  $2\theta$  angle. Since most materials have unique diffraction patterns, compounds can be identified by using a database of diffraction patterns. All images presented in this thesis were taken with SHIMADZU XRD-6100.

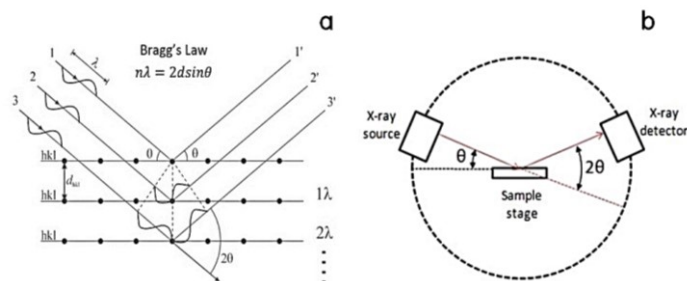


Figure 23 X-ray diffraction (a) and construction of an X-ray diffractometer

(b) (Myers, 1997)

### Scanning electron microscopy

Scanning electron microscopy (SEM) was used to investigate three-dimension of microstructure and sample composition. All images presented in this thesis were taken with JSM-7800F, JEOL. During analysis the electron source is excited by high voltage and the resulting electron beam focused of electron scan at or near the surface of the sample and produce image. This produces several different signals and the ones that were used for analysis. Firstly, secondary electrons (SE) – a result of excitation and replacement of outside shell electrons by the primary electrons enabling us to view microstructure of the sample. Secondly, backscatter electrons (BSE) – in elastically scattered primary electrons. The energy loss is dependent on the weight of surface atoms electrons are interacting with giving an image of phase segregation. Finally, the characteristic x-rays used in energy dispersive spectroscopy (EDS or EDX) – produced from excitation by the primary electron beam and enable us to see the phase composition by determining its chemical composition.

### Archimedes density measurement

Bulk density was determined by Archimedes method via distilled water using the following equations:

$$\rho = \frac{A}{A-B}(\rho_0 - \rho_L) + \rho_L \quad (3.2)$$

$$V = \alpha \frac{A-B}{\rho_0 - \rho_L} \quad (3.3)$$

where,

$\rho$  is Density of the sample

$A$  is Weight of the sample in air

$B$  is Weight of the sample in the auxiliary liquid (distilled water)

$v$  is Volume of the sample

$\rho_0$  is Density of the auxiliary liquid (distilled water)

$\rho_l$  is Density of air ( $0.0012 \text{ g/cm}^3$ )

$\alpha$  is Weight correction factor (0.99985), to take the atmospheric buoyancy of the adjustment weight into account.

The theoretical densities of the samples were calculated using the following formula

$$d_{th} = \frac{4 \times \text{Molecularweight}}{N_A V} \quad (3.4)$$

Where,

$v$  is cell volume obtained from XRD data.

$N_A$  is Avogadro number =  $6.02 \times 10^{23}$  (1/mol)

4 is the number of unite cell in a cell volume

## THERMOELECTRIC PROPERTIES MEASUREMENTS

### Seebeck coefficient and electrical resistivity measurements

The Seebeck coefficient ( $s$ ) and electrical resistivity ( $\rho$ ) measurements were performed with a homemade by using conceptual of ZEM-3 measuring system shown in Figure 24. The TE sample is placed in between two electrodes connected constant current ( $I$ ) source. Hot electrode has built in small heater to generate temperature gradient within surface sample for Seebeck measurement. The K-type

thermocouple A and B in touch with the sample used for measured voltage difference ( $V_{AB}$ ) and temperature difference ( $T_A - T_B$ ) between these two points which depend on distant two probes. The Seebeck coefficients is determined by

$$S = -\frac{V_{AB}}{T_B - T_A} \quad (3.5)$$

Electrical resistivity has been using constant current to sample then the resistance ( $R$ ) determined by  $R = V_{AB} / I$ . The cross sectional area ( $A$ ) of the sample and length between two probe ( $l_{AB}$ ). The Electrical resistivity of the samples were calculated using the following formula

$$\rho = \frac{R \cdot A}{l_{AB}} \quad (3.6)$$

The  $s$  and  $\rho$  in all samples on this work were measured by cutting the sintered pellets in to dimensions of  $3 \times 3 \times 15 \text{ mm}^3$ . A two surface of the sample were flat to get good electrical contact. The distance between the probes was maintained at 4 mm. Samples were measured between room temperature ( $R_T$ ) and 473 K with the interval of 20 K with a temperature gradient of 0.5 – 1 K across the sample. The temperature different between hot and cold point of sample was use K type thermocouple which was measured using a PICOTEST multimeter heating rate was set to be 5 K/min,  $\rho$  and  $s$  were measured three times, corresponding to each temperature gradient.

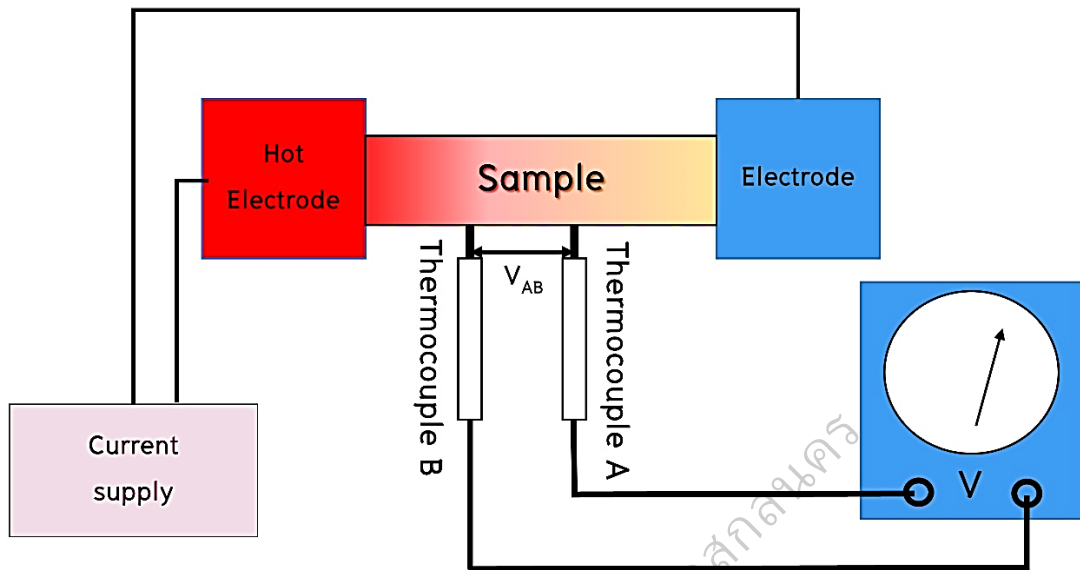


Figure 24 A conceptual diagram of ZEM-3 system

### Thermal conductivity measurement

The thermal conductivity of the samples were determined by using homemade steady state technique (Tan, et al., 2006; Zhao, et al., 2016). The steady state technique is usually used for samples that has a rectangular or cylindrical shape shown in Figure 25. The sample placed in between heater and copper cube connected 4 probe of thermocouple on point 1, 2, 3 and 4 for measured steady state of system in point 1 and 4 then temperature difference 2 and 3 after applied heater on sample. The thermal conductivity of the samples were calculated using the Fourier's law following

$$\kappa = \frac{\dot{Q}}{A \Delta T} \quad (3.7)$$

where,  $\kappa$  is thermal conductivity of sample,  $\dot{Q}$  is the amount of heat flowing through the sample,  $A$  is the cross-sectional area of the sample,  $x$  and  $\Delta T$  are the distance and temperature difference between thermocouple 2 and 3.

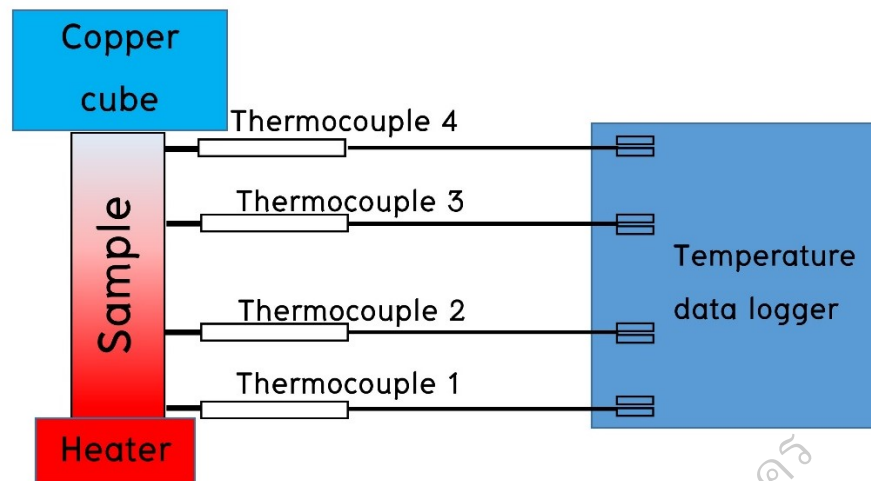


Figure 25 A conceptual diagram of steady state system for measure thermal conductivity

## THERMOELECTRIC SUBSTRATE

Oxide thermoelectric materials were used in high temperature so substrate must be stable in high temperature and low oxidation. With respect to the required high thermal cycling stability ceramic substrates made of alumina with a low thermal expansion and high thermal conductivity are good choice. The active metal brazing (AMB) was used for fabrication TE substrate because this method rapid and made a lot.

### Preparation thermoelectric substrate

Normally thermoelectric substrate was using alumina ( $\text{Al}_2\text{O}_3$ ) metalized with copper for fabrication thermoelectric module, however copper used in high temperature have a big problem in oxidation on surface to increased ohmic contract and module resistant. The manufacturing process most widely in metallized metal to alumina were using direct copper bonding (DCB) and active metal brazing (AMB) which is a different process for fabrication (Fu, et al., 2015; Ali, et al., 2015). The DCB was using eutectic technique for connect metal with interlayer and alumina which

made in eutectic temperature and control atmosphere, however the DCB had been difficult for control atmosphere and samples were poorly so the AMB process used for prepared substrate. The AMB were fabricated from alumina plate size  $50 \times 50 \times 1 \text{ mm}^3$ , metal brazing and silver plate thin 0.05 mm which easily for fabricated in air because silver was low oxidation and good conduction. This process a surface of alumina was cleaning by ultrasonic in acetone 30 minute then silver paste was screening to alumina and dried at 423 K 5 minute after that the silver plate installed on silver paste layer and all part pressed by light brick. The brazing temperature of substrate at 1073 K was dwell 30 minute in air used heating rate 5 K/min cooled according to the thermal inertia of the furnace.

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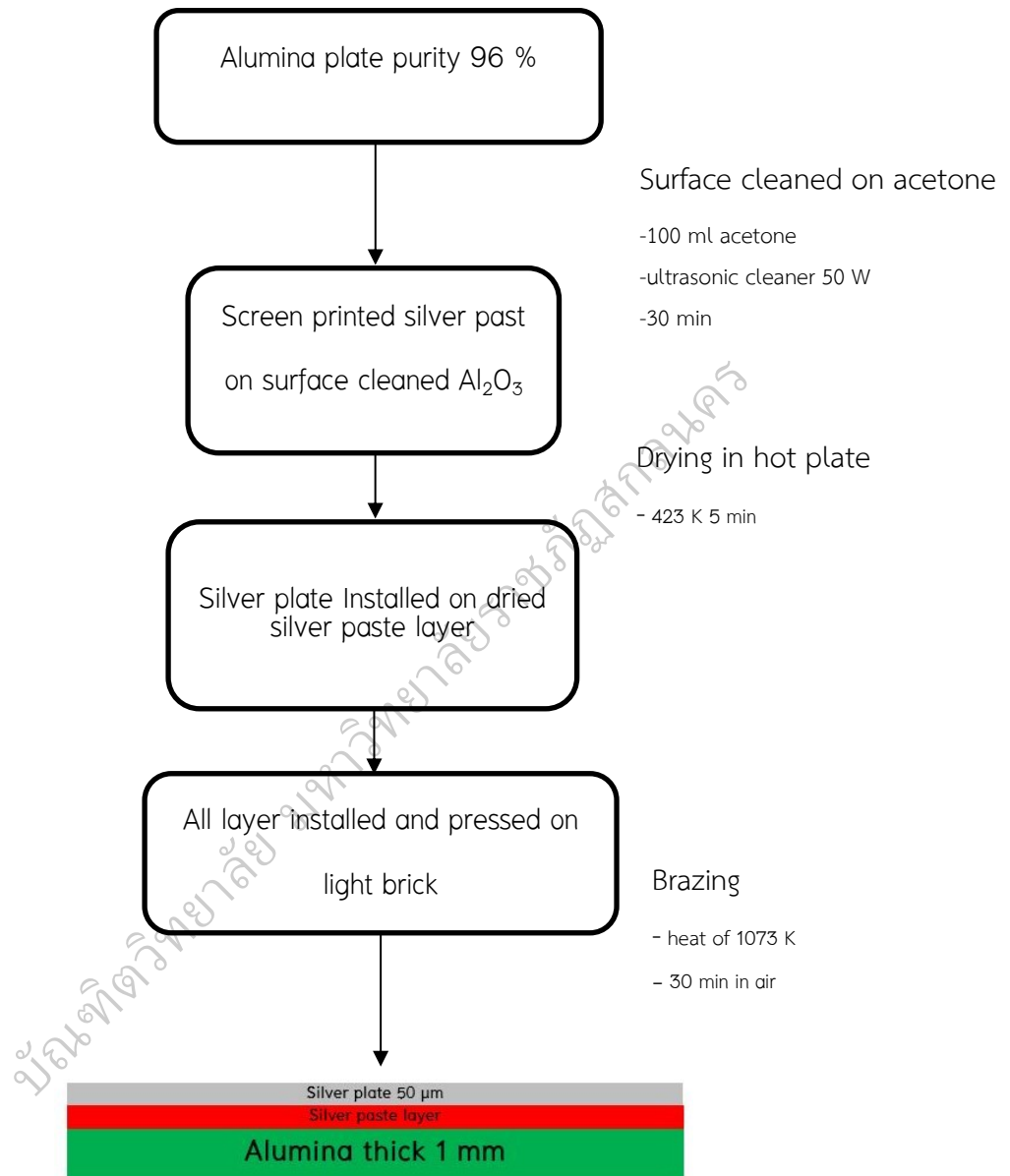


Figure 26 Flowchart illustrating thermoelectric substrate prepared by AMB process



### Etching thermoelectric substrate

Although a substrate size  $50 \times 50 \times 1 \text{ mm}^3$  has been making by AMB process but it also cannot be used the substrate must be etched before use for fabrication thermoelectric module. The etching substrate process on ceramic comprises of four step, Figure 27. First the silver surface is polished for remove all dirty then adhere dry film had covered on surface (Be careful of bubbles), followed a drying step by hot air. The film covered shows already the layout of the later laminated. Place the art work film on the surface and put a clear glass on top so the weight of the glass makes the artwork and the substrate better adhered to each other. Illuminate the UV lamp 18 watt high over 30 cm for approximately 5 minutes. The substrate illuminated was cleaning in developer solution by using sponge to gently rub all over the substrate until the artwork completely showed up. Make sure there is no any unwanted dry film left behind. Rinse the substrate with water and wait until it is dry. The substrate dried pat the substrate into a bowl of nitric acid 65%. Slowly shake the bowl until the excessive (unwanted) silver is completely etched. The substrate cleaned with water then the substrate removed cover film by using acetone and ready for fabrication module.

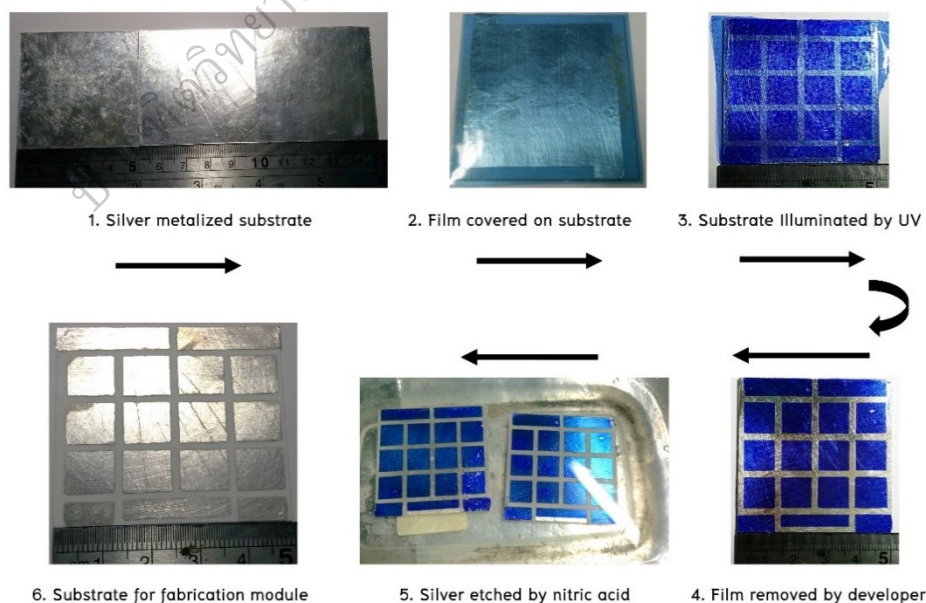


Figure 27 Process of thermoelectric substrate etched by nitric acid

## FABRICATION THERMOELECTRIC CELL AND MODULE

The oxide thermoelectric (TE) cells and modules were according for used at high temperature rang so fabrication process required stable at high temperature. For cell and module construction silver metallized ceramic substrates were made by brazing silver plates. In addition, within the electric contract between substrate and thermoelectric materials silver paste metallized brazing can be used as well.

### Fabrication thermoelectric cell

The process for fabrication thermoelectric cell shown in figure 28. The bulk thermoelectric materials were cut into of  $4 \times 4 \times 6 \text{ mm}^3$  rectangular legs; n-type  $\text{Ca}_{0.97}\text{Bi}_{0.03}\text{MnO}_3$  and p-type  $\text{Ca}_3\text{Co}_4\text{O}_9 + \text{Ag } 10\text{wt}\%$ , then the materials were painting by silver paste on top and bottom then annealed of 1073 K for 30 minute in air heating and cooling used 5 K/min. The two couple annealed p and n legs has been attached to substrate size of  $25 \times 25 \times 1 \text{ mm}^3$  which etched two column by using silver paste then the silver plate attached on top for joint p and n legs to  $\Pi$ -shape. The  $\Pi$ -shape TE cell was drying on hot plate 10 minute for dried silver paste then the TE cell metallized of 1073 K 30 minute in air heating and cooling used 5 K/min. When the cell cooled at room temperature connected red and black wire for positive in p and negative in n legs, respectively then test power and failure temperature for limit temperature used for TE cell and module.

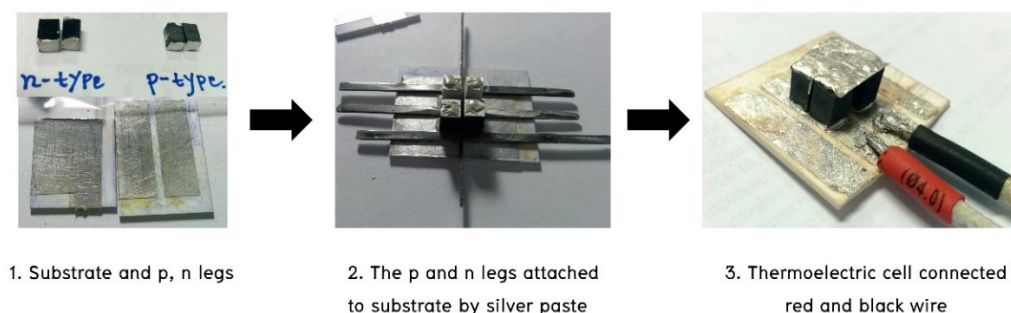


Figure 28 Process of fabrication thermoelectric cell

### Fabrication thermoelectric module

The TE modules with legs size  $4 \times 4 \times 6 \text{ mm}^3$  rectangular were constructed. Figure 29 shows a typical schematic diagram of a module. Basically, the TE modules were assembled using two pairs of p and n thermoelectric legs. The 32 pairs thermoelectric element are electrically connected in double series by thin silver plate of 0.05 mm using silver paste as bonding agent. The assembled is placed all legs to etched metallizing substrate on alumina and fix the position with egg crate which made by using stainless steel so that stand thermally in parallel and act as hot and cold ends for thermoelectric legs. The assembled TE module were annealing of 1073 K for 30 minute in air heating and cooling used 5 K/min for metallized all part at the junction. This resulted in low Ohmic contract and stable thermal contracts and mechanical strength for the TE module (Funahash, et al 2004 & 2006).

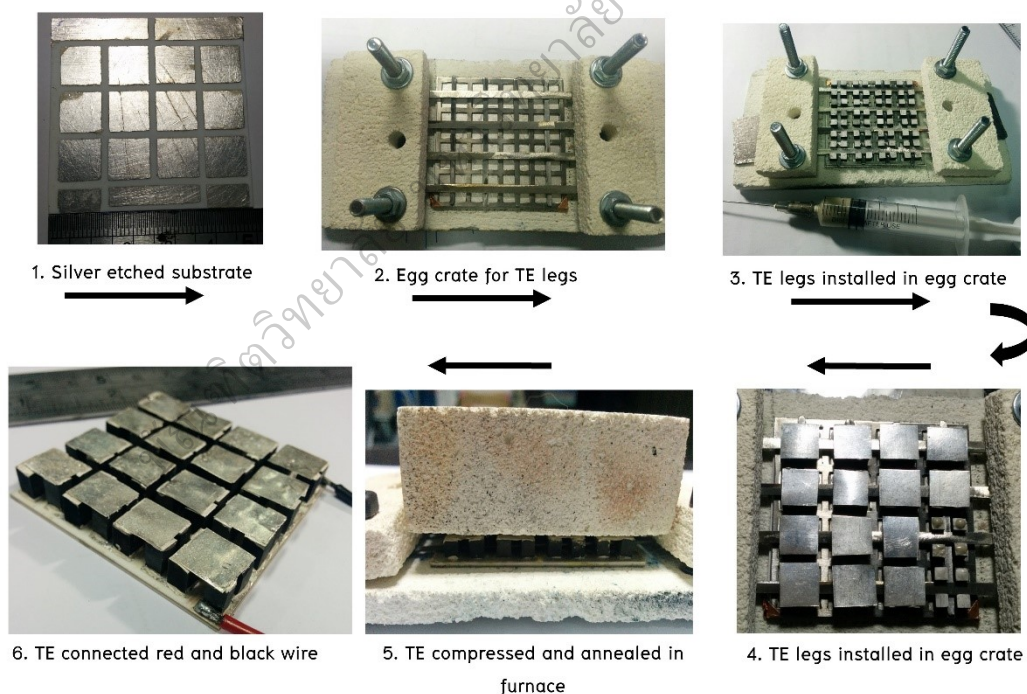


Figure 29 Process of fabrication thermoelectric module.

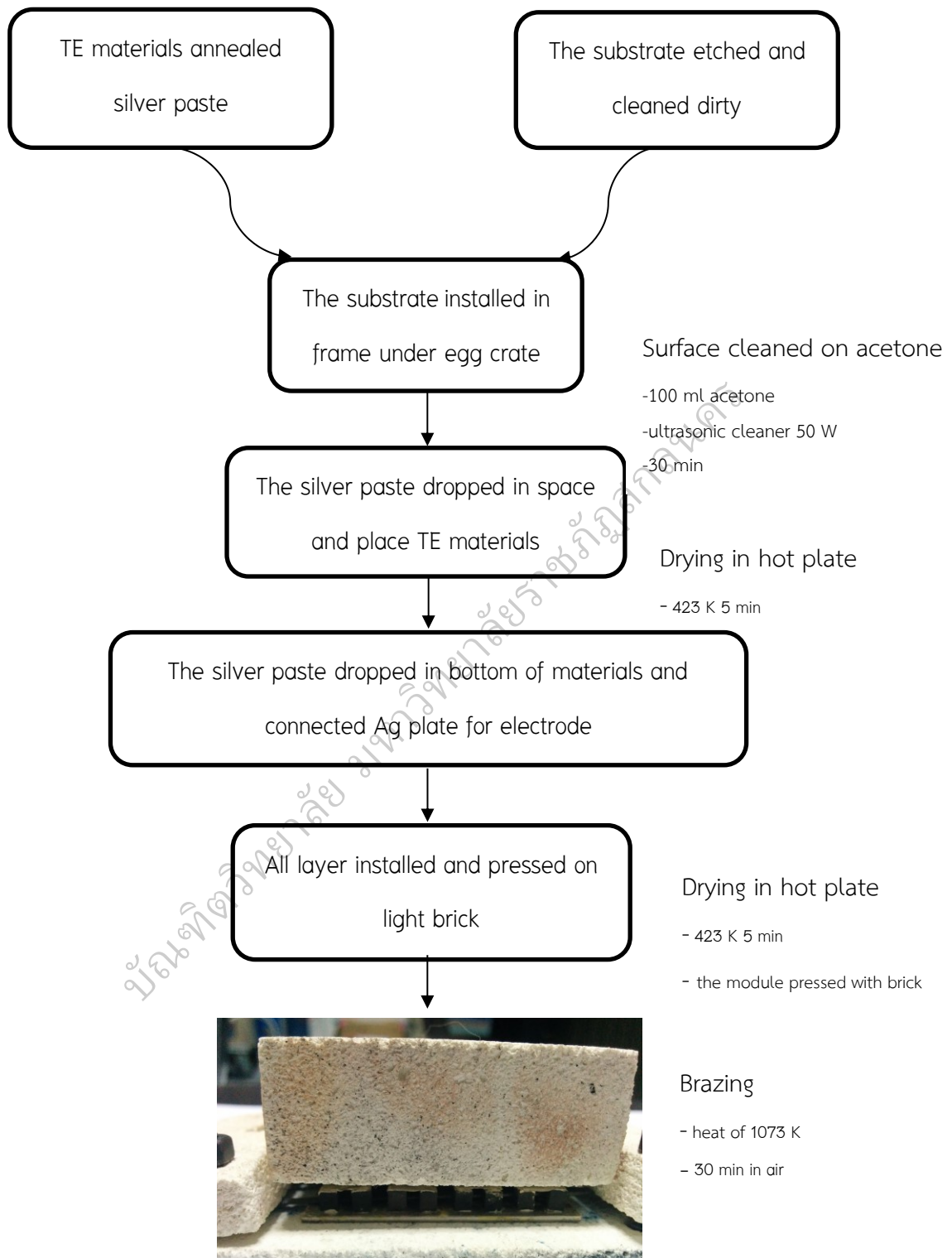


Figure 30 Flowchart illustrating fabrication of thermoelectric module.

## POWER GENERATION MEASUREMENT OF THERMOGENERATOR

The power generation of thermogenerator described above were installed over a heater, and a water cooling was placed over the module. To measure the temperatures of hot and cold side temperatures, the two K-type thermocouples were attached on the thin mica plate of high temperature and low temperature sides using an alumina substrate, respectively. A photograph of output power measurement of thermoelectric module is shown in Figure 31. The output power (W) was calculated by the output voltage (V) and current (I) caused by changing a resistor.

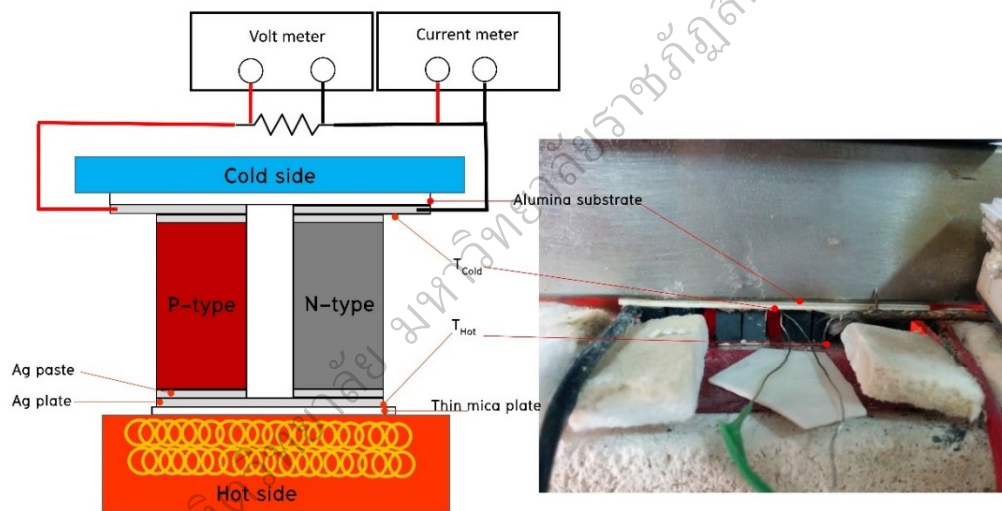


Figure 31 Power generation measurement of thermogenerator

## THERMOGENERATOR APPLICATION

The thermogenerator installed to brick furnace heat source for generate electricity. The thermogenerator system consist of 5 module connected series on aluminum hot plate and a water cooling was placed over the module in Figure 32.

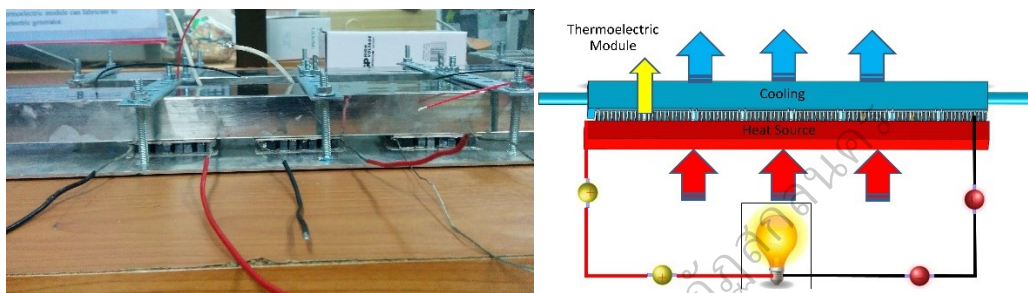


Figure 32 Thermogenerator and cooling water

Thermogenerator were using generated direct current electricity for tern on LED lamp 3 watt then a water cooling used 3 volt pump for running water. The highest temperature difference at was generated maximum power at 0.15 watt continues. The joule thief circuit was using for up the dc voltage from module, due to the LED lamp used high voltage. The light used for refill a husk and firewood in brick furnace.

Unfortunately, oxide thermoelectric module on thermogenerator system were generated not enough for load 15 W so that the commercial thermoelectric module was used for increasing electric power for load and charging battery 12 V. The commercial thermoelectric 5 module were constructed to thermogenerator system for lighting system shown in Figure 33. A brick product from furnace exhibited good color and structure for use shown in Figure 34.

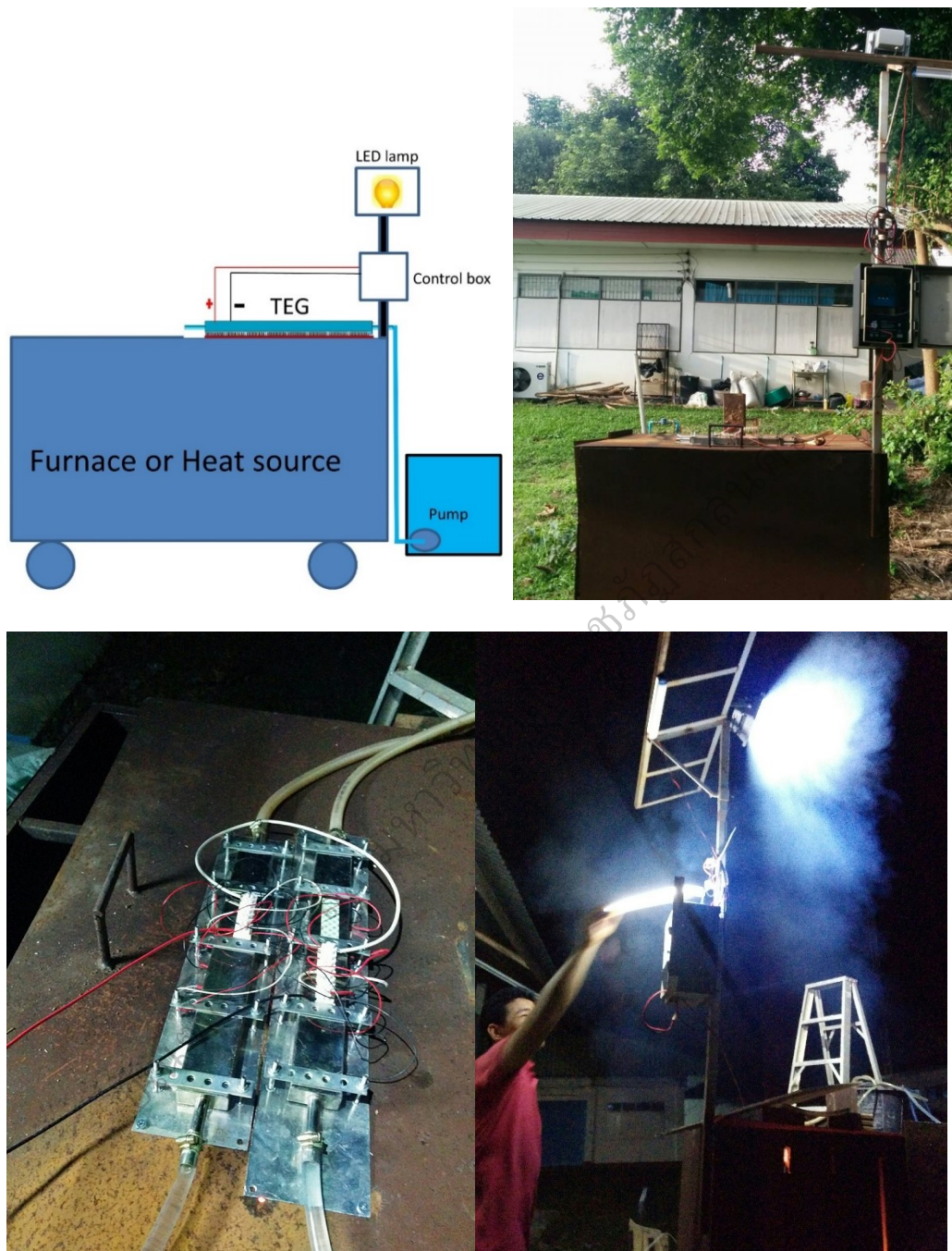


Figure 33 Thermogenerator system for furnace heat source



Figure 34 Brick before firing (left) and Brick before firing (right)

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