Chapter 3

Materials and Methods

In this chapter are presented the thermoelectric materials synthesis, crystal structure analysis, micro structure analysis, thermoelectric properties measurement, thermoelectric device fabrication, thermoelectric power generation and refrigeration measurement. The schematic diagram of methodology as shown in Figure 9.

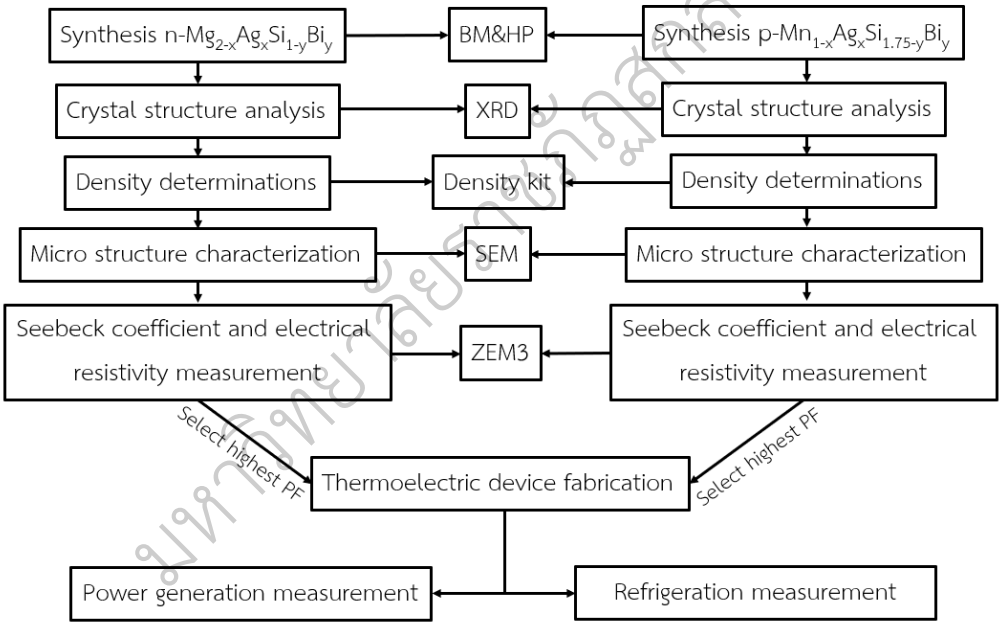

Figure 9 The schematic diagram of methodology

Thermoelectric materials synthesis

Synthesis of $Mn_{1-x}Ag_xSi_{1.75-y}Bi_y$ (x = y = 0, 0.01, 0.02, 0.03, 0.04 and 0.05)

The of p-type $Mn_{1-x}Ag_xSi_{1.75-y}Bi_y$ (x = y = 0, 0.01, 0.02, 0.03, 0.04 and 0.05) materials were synthesized by ball mill and hot press method as follow by:

1. The Mn (Sigma-Aldrich, 99 %), Si (Sigma-Aldrich, 99 %), Ag (Sigma-Aldrich, 99.9%), and Bi (Sigma-Aldrich, 99.9%) powders were used for raw materials and weigh at an atomic ratio as shown in Eq.3.1-3.6 and table 3.

$$Mn+1.75Si \rightarrow MnSi_{1.75} \quad (3.1)$$

$$0.99Mn+0.01Ag+1.74Si+0.01Bi \rightarrow Mn_{0.99}Ag_{0.01}Si_{1.74}Bi_{0.01} \quad (3.2)$$

$$0.98Mn+0.02Ag+1.73Si+0.02Bi \rightarrow Mn_{0.98}Ag_{0.02}Si_{1.73}Bi_{0.02} \quad (3.3)$$

$$0.97Mn+0.03Ag+1.72Si+0.03Bi \rightarrow Mn_{0.97}Ag_{0.03}Si_{1.72}Bi_{0.03} \quad (3.4)$$

$$0.96Mn+0.04Ag+1.71Si+0.04Bi \rightarrow Mn_{0.96}Ag_{0.04}Si_{1.71}Bi_{0.04} \quad (3.5)$$

$$0.95Mn+0.05Ag+1.70Si+0.05Bi \rightarrow Mn_{0.95}Ag_{0.05}Si_{1.70}Bi_{0.05} \quad (3.6)$$

Table 3 Materials balance of $Mn_{1-x}Ag_xSi_{1.75-y}Bi_y$ for 5 g

Materials	Balance (g)	
$MnSi_{1.75}$	Mn = 2.6390	
	Si = 2.3609	
$Mn_{0.99}Ag_{0.01}Si_{1.74}Bi_{0.01}$	Mn = 2.5552	Ag = 0.0507
	Si = 2.2959	Bi = 0.0982
$Mn_{0.98}Ag_{0.02}Si_{1.73}Bi_{0.02}$	Mn = 2.4750	Ag = 0.0992
	Si = 2.2336	Bi = 0.1921
$Mn_{0.97}Ag_{0.03}Si_{1.72}Bi_{0.03}$	Mn = 2.3982	Ag = 0.1456
	Si = 2.1739	Bi = 0.2821
$Mn_{0.96}Ag_{0.04}Si_{1.71}Bi_{0.04}$	Mn = 2.3245	Ag = 0.1901
	Si = 2.1167	Bi = 0.3684
$Mn_{0.95}Ag_{0.05}Si_{1.70}Bi_{0.05}$	Mn = 2.2539	Ag = 0.2329
	Si = 2.0619	Bi = 0.4512

2. The raw materials were mixed by planetary ball mill (Restch, PM 400, Germany). The grinding jar is arranged eccentrically on the sun wheel of the planetary ball mill. The direction of movement of the sun wheel is opposite to that of the grinding jars in the ratio 1:-2.5. The grinding balls in the grinding jars are subjected to superimposed rotational movements, the so-called Coriolis forces. The difference in speeds between the balls and grinding jars produces an interaction between frictional and impact forces, which releases high dynamic energies. The interplay between these forces produces the high and very effective degree of size reduction of the planetary ball mill as shown in Figure 10. The powders of raw materials were loaded into the argat grinding jars with stainless steel ball in size of dimeter at 10 mm. Planetary ball mill with a speed of 350 rpm was performed for 5 h.

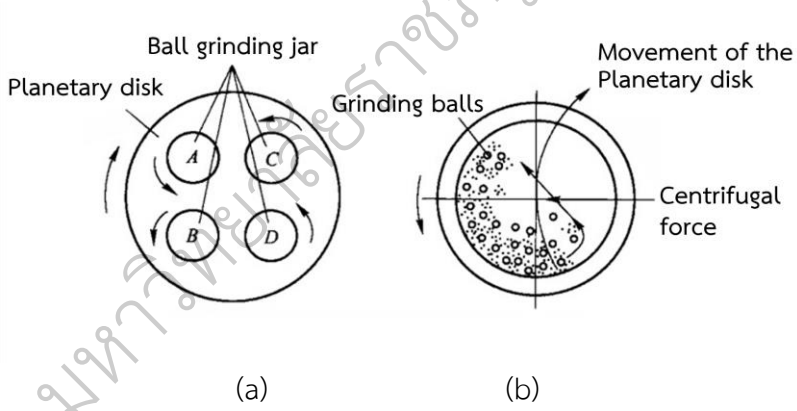

Figure 10 Working principle of planetary ball mill (a) overall layout of planetary disk (b) horizontal section of grinding jar

3. The mixed powder were loaded into cylindrical graphite die with an internal diameter of 10 mm for hot pressing. The graphite die was set up in the hot press machine with temperature profile as shown in Figure 11. The process of hot press was proceeded under pressure 50 MPa for 1 h in argon atmosphere.

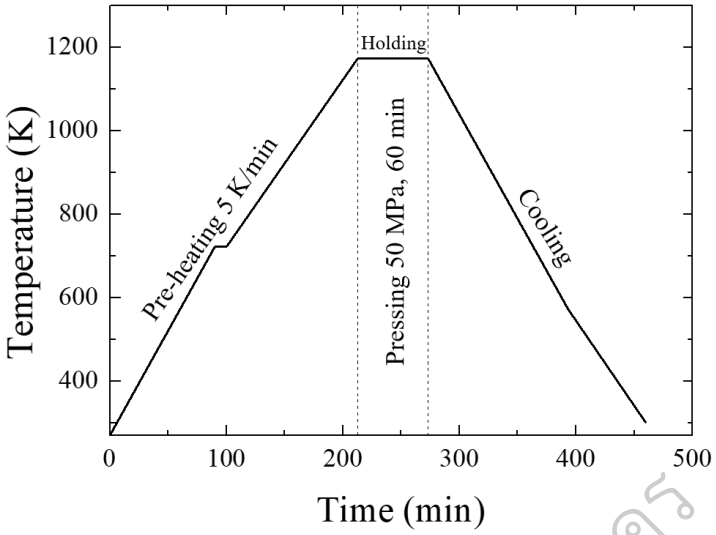

Figure 11 The temperature profile for hot pressing of $Mn_{1-x}Ag_xSi_{1.75-y}Bi_y$

4. The obtained circular pellets from hot press were cut in size of 10×10×1 mm^3 for XRD and SEM, 3×3×15 mm^3 for thermoelectric properties measurement and 2×2×3 mm^3 for thermoelectric device fabrication.

Synthesis of $Mg_{2-x}Ag_xSi_{1-y}Bi_y$ (x = y = 0, 0.01, 0.02, 0.03, 0.04 and 0.05)

The of p-type $Mg_{2-x}Ag_xSi_{1-y}Bi_y$ (x = y = 0, 0.01, 0.02, 0.03, 0.04 and 0.05) materials were synthesized by ball mill and hot press method as follow by:

1. The Mg (Ajax Finechem, 99.99%), Si (Sigma-Aldrich, 99 %), Ag (Sigma-Aldrich, 99.9%), and Bi (Sigma-Aldrich, 99.9%) powders were used for raw materials and weigh at an atomic ratio as shown in Eq. 3.7-3.12 and table 4.

$$2Mg+Si \rightarrow Mg_2Si \quad (3.7)$$

$$1.99Mg+0.01Ag+0.99Si+0.01Bi \rightarrow Mg_{1.99}Ag_{0.01}Si_{0.99}Bi_{0.01} \quad (3.8)$$

$$1.98Mg+0.02Ag+0.98Si+0.02Bi \rightarrow Mg_{1.98}Ag_{0.02}Si_{0.98}Bi_{0.02} \quad (3.9)$$

$$1.97Mg+0.03Ag+0.97Si+0.03Bi \rightarrow Mg_{1.97}Ag_{0.03}Si_{0.97}Bi_{0.03} \quad (3.10)$$

$$1.96Mg+0.04Ag+0.96Si+0.04Bi \rightarrow Mg_{1.96}Ag_{0.04}Si_{0.96}Bi_{0.04} \quad (3.11)$$

$$1.95Mg+0.05Ag+0.95Si+0.05Bi \rightarrow Mn_{1.95}Ag_{0.05}Si_{0.95}Bi_{0.05} \quad (3.12)$$

Table 4 Materials balance of $Mg_{2-x}Ag_xSi_{1-y}Bi_y$ for 5 g

Materials	Balance (g)	
Mg_2Si	Mg = 3.1690	
	Si = 1.8309	
$Mg_{1.99}Ag_{0.01}Si_{0.99}Bi_{0.01}$	Mg = 3.0480	Ag = 0.0679
	Si = 1.7522	Bi = 0.1316
$Mg_{1.98}Ag_{0.02}Si_{0.98}Bi_{0.02}$	Mg = 2.9349	Ag = 0.1315
	Si = 1.6785	Bi = 0.2549
$Mg_{1.97}Ag_{0.03}Si_{0.97}Bi_{0.03}$	Mg = 2.8288	Ag = 0.1911
	Si = 1.6095	Bi = 0.3704
$Mg_{1.96}Ag_{0.04}Si_{0.96}Bi_{0.04}$	Mg = 2.7292	Ag = 0.2471
	Si = 1.5446	Bi = 0.4789
$Mg_{1.95}Ag_{0.05}Si_{0.95}Bi_{0.05}$	Mg = 2.6392	Ag = 0.2994
	Si = 1.4812	Bi = 0.5800

2. The raw materials were mixed by planetary ball mill (Restch, PM 400, Germany). The powders of raw materials were loaded into the argat grinding jars with stainless steel ball in size of dimeter at 10 mm. Planetary ball mill with a speed of 350 rpm was performed for 5 h.

3. The mixed powder were loaded into cylindrical graphite die with an internal diameter of 10 mm for hot pressing. The graphite die was set up in the hot press machine with temperature profile as shown in Figure 12. The process of hot press was proceeded under pressure 50 MPa for 1 h in argon atmosphere.

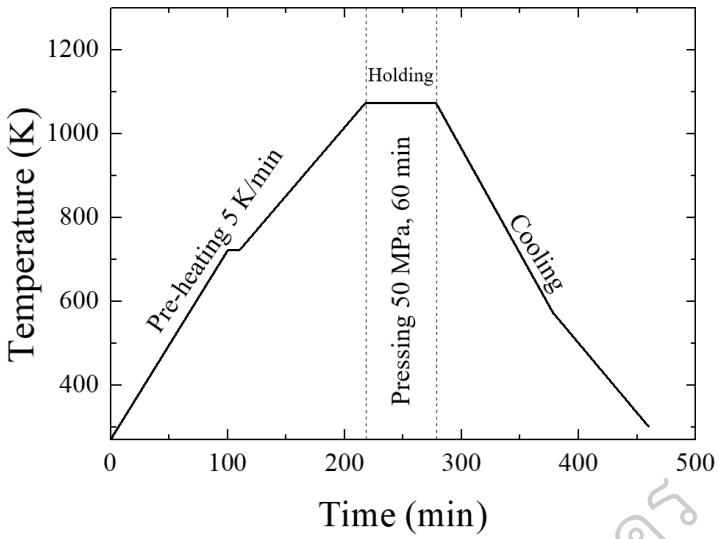

Figure 12 The temperature profile for hot pressing of $Mg_{2-x}Ag_xSi_{1-y}Bi_y$

4. The obtained circular pellets from hot press were cut by Isomet low speed saw (Buehler) in size of 10×10×1 mm^3 for XRD and SEM, 3×3×15 mm^3 for thermoelectric properties measurement and 2×2×3 mm^3 for thermoelectric device fabrication.

Crystal structure analysis

All electronmagnetic radiation is characterized by its wave character λ or by means of photon energy E. The relationship between these quantities can be presented by:

$$\nu = \frac{c}{\lambda} \tag{3.13}$$

$$E = h\nu \tag{3.14}$$

$$E = \frac{hc}{\lambda} \tag{3.15}$$

Where c is speed of light, ν is frequency h is Planck's constant.

$$E = \frac{12.398}{\lambda} \tag{3.16}$$

For CuKα_1 doublet has an energy of 8.046 keV, the wavelength will be equal to 12.398/8.046 = 1.541 Å. The oscillating electric field of a light wave will interact with the electrons in matter to cause coherent scattering knowing since Christian Huygens (1629-1695) that each scattering point may be treated as a new source of spherical waves. If a periodic array of objects each scatter radiation coherently, the concerted constructive interference at specifies angles is called diffraction. Max von Laue first developed the description of the diffraction of X-ray by a crystal. William Henry Bragg and William Lawrence Bragg developed a much simpler way of understanding and predicting diffraction as show in Eq. 3.17.

$$2d\sin\theta = n\lambda \qquad (3.17)$$

Where n is a positive integer, λ is the wavelength of the incident wave and d is the interplanar distance.

The crystal structure was analyzed by X-ray diffractometor (Shimadzu, XRD-6100) in scan rang 20-80 degree of 2θ for 2 deg/min of scan speed with 0.02 of sampling pitch.

The density of bulk samples was determined by density kit (Mettler Toledo, MS-DNY-54) with deionization water for auxiliary liquid. Density determinations are frequently performed by Archimedes' principle, which is also used with the density determination kit for the balances. This principle states that every solid body immersed in a fluid apparently loses weight by an amount equal to that of the fluid it displaces. The procedure for the density determination by Archimedes' principle depends on whether the density of solids or liquids has to be determined.

The density of a solid is determined with the aid of a liquid whose density ρ_0 is known (water or ethanol are usually used as auxiliary liquids). The solid is weighed in air (A) and then in the auxiliary liquid (B). The density (ρ) can be calculated from the two weighings as follows by Eq. 3.18.

$$\rho = \frac{\mathrm{A}}{\mathrm{A}-\mathrm{B}}(\rho_0 - \rho_L) + \rho_L \quad (3.18)$$

$$\mathrm{V} = \alpha \frac{\mathrm{A}-\mathrm{B}}{\rho_0 - \rho_L} \quad (3.19)$$

Where A is weight of the sample in air, B is weight of the sample in the auxiliary liquid, V is volume of sample, ρ_0 is density of the auxiliary liquid, ρ_L is density of air (0.0012 g/cm^3) and α is weight correction factor (0.99985), to take the atmospheric buoyancy of the adjustment weight into account.

Microstructure analysis

The microstructure of bulk samples was analyzed by scanning electron microscope (JEOL, JSM-7600F Prime). The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using EDS).

Thermoelectric properties measurement

The Seebeck coefficient and electrical resistivity were measured by ZEM3 (Advane riko, Inc) in vacuum with the step detail as follow by Figure 13.

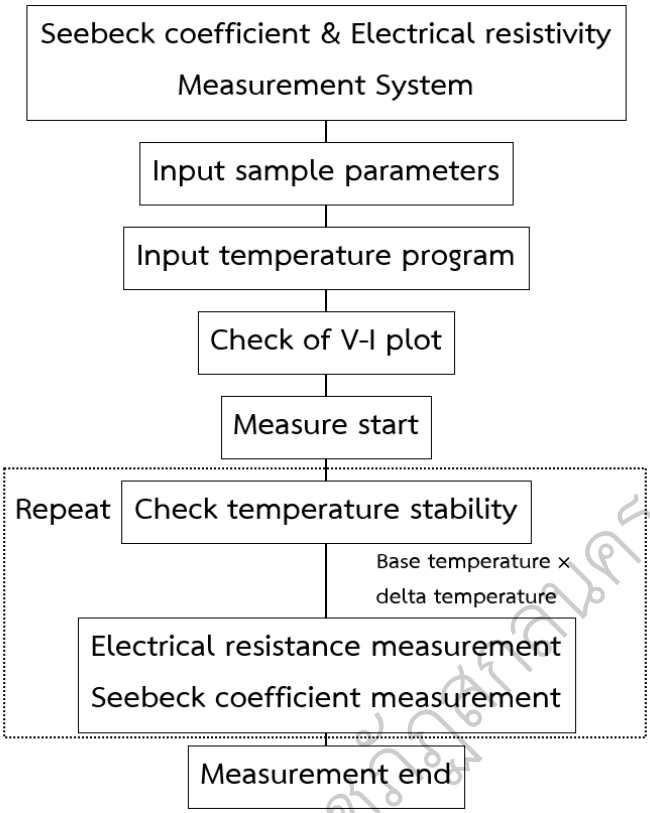

Figure 13 Schamatic diagram of the step detail for Seebeck coefficient and electrical resistivity measurement

A prism sample is set in a vertical position between the upper and lower blocks in the heating furnace. While the sample is heated, and held, at a specified temperature, it is heated by the heater in the lower block to provide a temperature gradient. Seebeck coefficient is measured by measuring the upper and lower temperatures T_1 and T_2 with the thermocouples pressed against the side of the sample, followed by measurement of thermal electromotive force dE between the same wires on one side of the thermocouple. Electrical resistivity is measured by the dc four-terminal method, in which a constant current I is applied to both ends of the sample to measure and determine voltage drop dV between the same wires of the thermocouple by subtracting the thermo-electromotive force between leads as show in Figure 14.

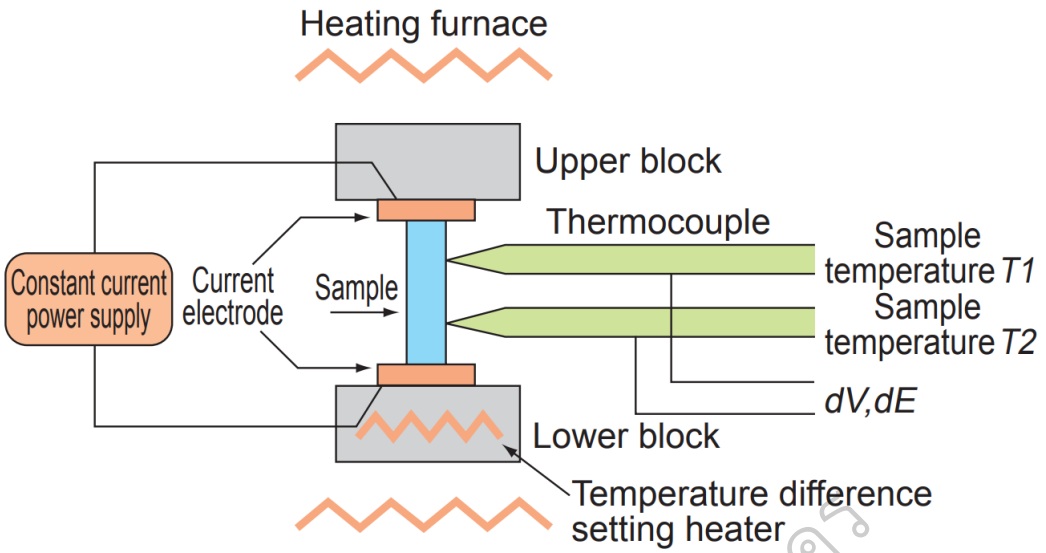

Figure 14 The schematic diagram of Seebeck coefficient and electrical resistivity Measurement

The Seebeck coefficient and electrical resistivity is found by using the following Eq. 3.20 and 3.21, respectively.

Seebeck coefficient (S)

$$S = \frac{\Delta V}{Temp1 - Temp2} \tag{3.20}$$

Where ΔV is Voltage, $Temp1$ is lower probe temperature and $Temp2$ is upper probe temperature.

$$\rho = \frac{RA}{l} \tag{3.21}$$

Where R is resistance value (R=V/I), A is cross section area of sample and l is distance between probes.

Thermoelectric devices fabrication

Thermoelectric devices design

Thermoelectric devices were designed by solid works program and assembly by soldering method. The design of thermoelectric device was stated from assigning the substate size of 10×10×1 mm^3 for 1 pair, 20×22×1 mm^3 for 11 pairs and 25×25×1 mm^3 for 30 pairs. Thermoelectric materials were used in size of 2×2×3 mm^3 and Ni electrode size of 2×5×0.3 mm^3 as shown in Figure 15.

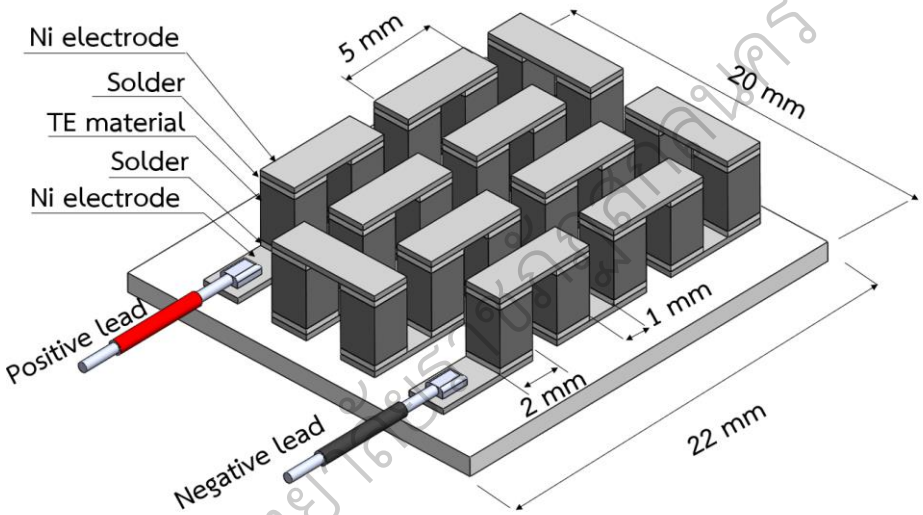

Figure 15 Model design of thermoelecric device configuration

Thermoelectric devices fabrication

The thermoelectric devices fabrication was used highest power factor of $Mg_{2-x}Ag_xSi_{1-y}Bi_y$ and $Mn_{1-x}Ag_xSi_{1.75-y}Bi_y$ materials for thermoelectric element. The Cu plates were stick with alumina substrat by the glue for bottom electrode. The first pellet was started at the left side of thermoelectric device by p-type material and connected by switching n and p continuously on Cu electrode by silver paint. The top of materials between n and p type were also connected with Cu electrode by silver paint. The alumina substrat was sticked again on the top for heat absorption of thermoelectric device. Then the

thermoelectric device was heat at 373 K for drying the glue and silver paint. The red wire was fused on copper electrode at p type side for positive leading and black wire at n type side for negative leading.

Thermoelectric power generation and refrigeration measurement

The power generation was measured using heat source by coil heater on top and water cooling on bottom of thermoelectric device. The electrical voltage and electrical current were measured by Picotest (M3500A 61/2 Digit Multimeter). The schematic diagram of thermoelectric device power generation measurement is shown in Figure 16 (a). In case of refrigeration mensurement, the thermoelectric device was applied by electricity for measuring different temperature between on the top and bottom as show in Figure 16 (b).

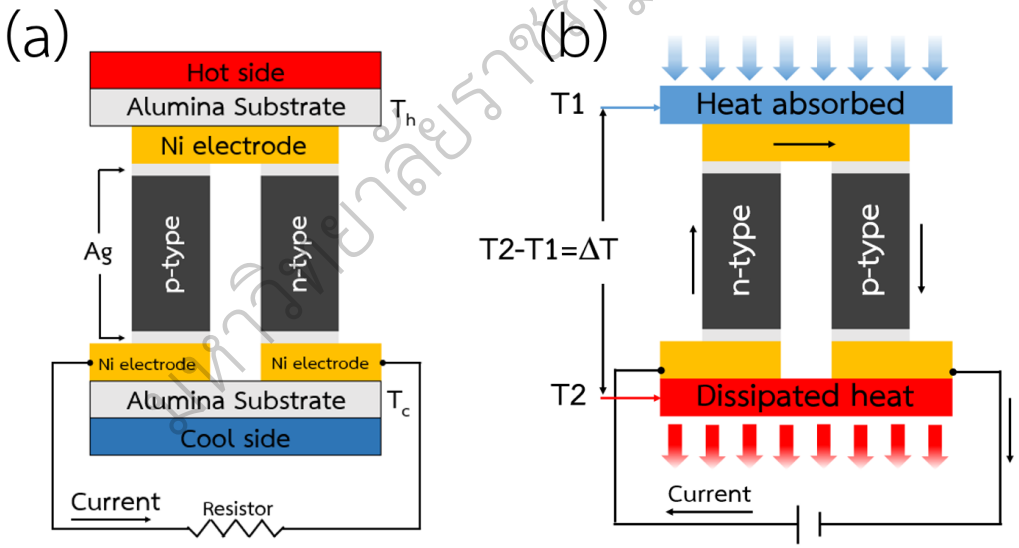

Figure 16 Schematic diagram of (a) power generation and (b) refrigeration of thermoelectric measurement