CHAPTER 3

MATERIALS AND METHODS

This chapter describes the method and techniques used to product and characterize the Bi_2Te_3 investigated. Bismuth (Bi) and tellurium (Te) powders and the HP sample of Bi_2Te_3 were characterized by X–ray diffractometer (XRD), Scanning electron microscopy (SEM), Energy–dispersive X–ray spectroscopy (EDX) analysis. For the mechanical properties measurement were calculated from elastic constant, and Micro– hardness measured using micro–Vickers hardness tester at room temperature. the theoretical density (TD) of the sample calculated from mass of atoms in unit cell and total volume of unit cell. Thermoelectric properties of Bi_2Te_3 were determined using the measured data of electric resistance, Seeback coefficient measured using ZEM–3 in helium atmosphere and calculated power factor, For the probabilities temperature sensor application.

SAMPLE SYNTHESIS

The basic of experimental procedures were described in our previous study (J.Y. Yang, X.A. Fan, &X.K. Duan, 2006). In brief, Bi and Te powders (<99% purity) were used as stating materials. The powder of Bi and Te were mixed in planetary ball mill 350 rpm for 10 h under argon atmosphere. The hot press (HP) in a cylindrical graphite die (internal diameter of 4 cm) at 673 K under 60 Mpa for 1 h in vacuum (Yong Soo Lim, Won–Seon Seo, Chang–Won Hwang, 2014) (Xi an Fan, Fan Yang, Guangqiang Li, 2015) (Yun Min Kim, R. Lydia, Kyughan Ahn, 2017). The HP specimen were polished by sand water. The crystal structure of the HP was analyzed by using an X–ray diffractometer (XRD–6100 Shimadzu, Japan) at room temperature using Cu K σ radiation (λ = 1.5406 Å) in the range of 2θ –20–70° mode. The sample preparation of HP product and sintered samples are shown in Fig 21.

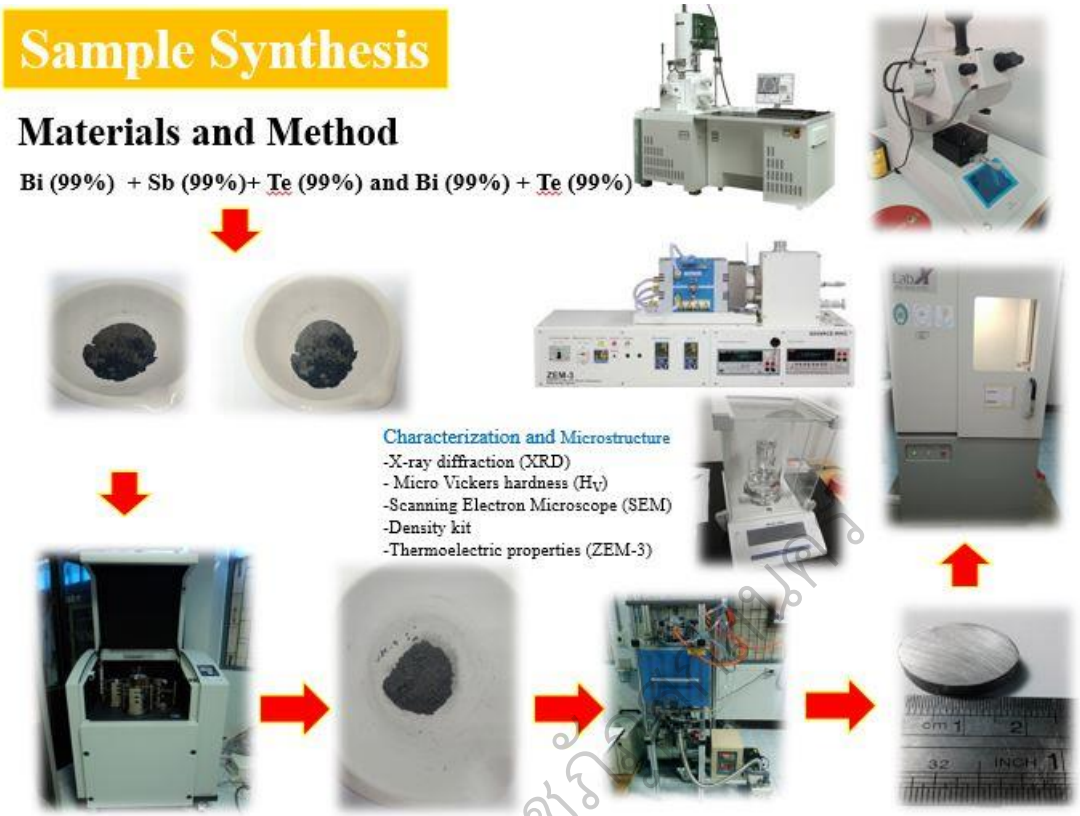

Figure 21 The sample synthesis of HP product and sintered samples

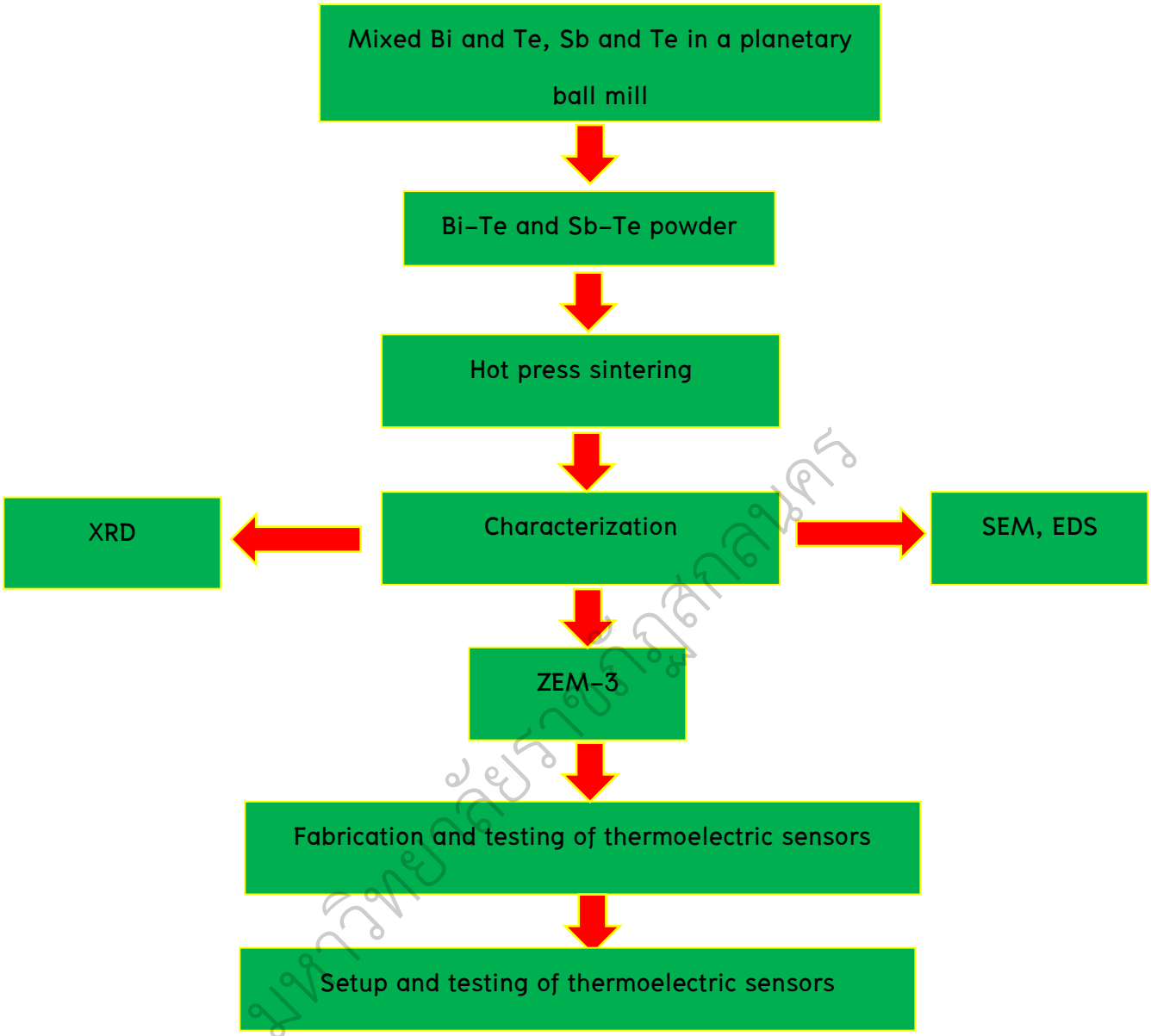

Figure 22 Synthesis and characterization of Bi_2Te_3 and Sb_2Te_3

MICROSTRUCTURE AND CHEMICAL COMPOSITION ANALYSIS

The element compositions of Bi_2Te_3 material were determined using energy-dispersive X-ray spectroscopy (EDX) analysis (at a standard working distance of 8 mm and an accelerating voltage of 15 keV). The following methods were used:

Energy Dispersive X-ray Spectroscopy

Energy Dispersive X-ray Spectroscopy is an analytical technique used for the elemental analysis or chemical characterization. The characteristic spectrum of X-rays emitted by the specimen after excitation by high-energy electrons to obtain information about its elemental composition. For EDX analysis here was performed on a JSM-7800F Prime.

Figure 23 The FE-SEM observations were performed on Scanning Electron Microscope JSM-7800F Prime at National Metal and Materials Technology Center (MTEC)

Scanning Electron Microscopy

The scanning electron microscopy *(SEM)* an important technique for examining the surface microstructure measurement of materials. It is expanding from 20 to 30,000 imaginable, and using electron wave, the properties of the material can be analyzed more than 300 imaginable, compare the normal microscope. This is a good way to analyze the surface of the sample. The sample for measurand SEM is small such as thinner than 20 mm, height not exceeding 80 mm, and clean the sample with a solution. Due to the sample must be in a vacuum, the pressure is lower than 1.3 mPa *(10^{-5} bar)*. If the sample is not electrically conductive, it must be coated with carbon or gold, so that electrons accumulated on the surface of the sample.

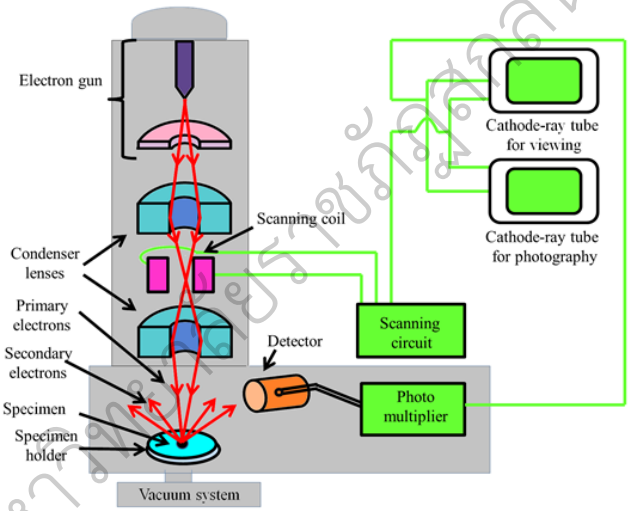

Figure 24 Schematic diagram of the SEM equipment

The working principle of SEM, it consists of the source of electrons, which produce electron for the system. The electrons are accelerated by the electric field source, and electron rays pass through a condenser lens, to get the electron is an electron beam. After that, the electron beam is adjusted focus by objective lens, and the electron beam into the surface of the sample, and the electron beam is grafted onto the surface of the sample, called that *"secondary electron"*. The signal from secondary electron is converted into an electronic signal and was created on a computer screen.

Figure 25 The SEM observations were performed on a Hitachi-S-3400N Scanning Electron Microscope at National Metal and Materials Technology Center (MTEC).

CRYSTALLINE IDENTIFICATION

The sample identifications of a sample were made carried out using the X-ray diffraction (XRD) technique.

X-Ray Diffraction Analysis

X-ray diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline and can provide information on unit cell dimension. In this study, measurements were performed on an (XRD-6100 Shimadzu, Japan), Sakon Nakhon Rajabhat University; Center of Excellence on Alternative Energy at; Thailand by using Cu K α radiation (λ = 1.5405 Å) at room temperature. The characteristic X-ray diffraction pattern generated in a typical XRD analysis provides a unique fingerprint of the crystals present in the sample. When properly interpreted, by comparison with standard reference patterns and measurements, this fingerprint allows identification of the crystalline form. The lattice parameter, unit cell volume and theoretical density of the sample calculated from mass of atoms in unit cell, and total volume of unit cell and

estimated from the XRD result. When the X-rays hit the sample, they are diffracted onto a detector. The X-ray detector then detects the signal and converts signal to a count rate. The angle between the X-ray sample and detector, using the angle between the X-ray tube, sample, and detector (2θ , which can be measured) and the wavelength of a generated x-ray beam (λ , which is known based on materials generating the x-rays). These X-rays are adapted and detect into the sample. The sample and detector are rotated and the reflected X-ray reflector is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg's law,

$$2d_{hkl}\sin\theta = n\lambda \qquad (3.1)$$

where d, θ, λ and n are lattice spacing, diffraction angle, the wavelength of the X-ray, and an integral number respectively. A set of d-spaces' obtained from a single compound will represent the set of planes that can pass through the atoms and can be used for comparison with sets of d-spaces obtained from standard compounds (Overview, 2013).

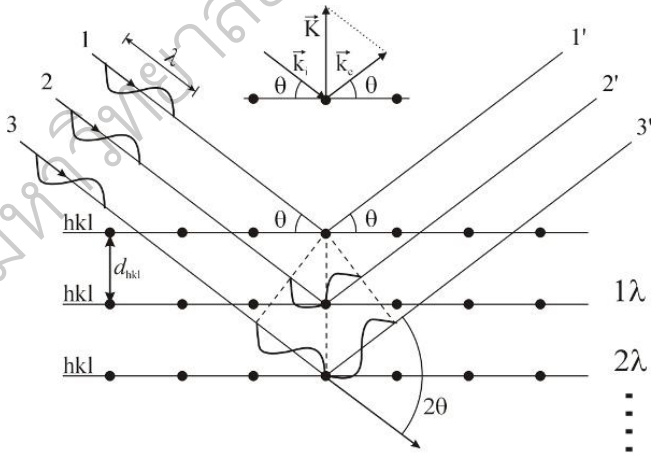

Figure 26 Principle of X-ray diffraction (Oumaïma Gharbi, 2016)

Figure 27 the X–ray diffraction *(*XRD*)* measurement was performed on Center of Excellence on Alternative Energy at Sakon Nakhon Rajabhat University

The density and relative density calculated from lattice by using equation;

$$\rho = \frac{nA}{V_c N_A} \tag{3.2}$$

where *n* number of atoms in unit cell, *A* is atomic weight, V_C is unit cell of volume and N_A is Avogadro's number. The elastic is calculated from the relation:

$$\frac{E}{(1+\nu)} = m^* \sin^2 \psi d_{0(hkl)} \tag{3.3}$$

where m^* is the partial derivative of applied stress with respect to the change in lattice spacing, d_0 is the unstressed lattice spacing and ψ is the range of the angle.

$$K = \frac{E}{(1+\nu)} \frac{1}{\sin^2 \psi} \left(\frac{\cot \theta_0}{2} \right) \frac{\pi}{180} \tag{3.4}$$

The elastic constant E/(1+v) is determined in the direction normal to the (hkl) planes and listed with an uncertainty equal to one standard deviation. The quantity K giving the approximate stress required to produce a one degree, 2θ, shift in the diffraction peak position for a ψ rotation of degrees is calculated from the (hkl) of E/(1+v).

MICRO HARDNESS

The hardness measured by hardness testing for a test performed to materials, and resistance to the transformation of materials. In this research, using the Vickers hardness testing. The Vickers hardness (H_V) is a hardness measurement using diamond head and the feature of the diamond head is similar to the pyramid square shown in Fig 28.

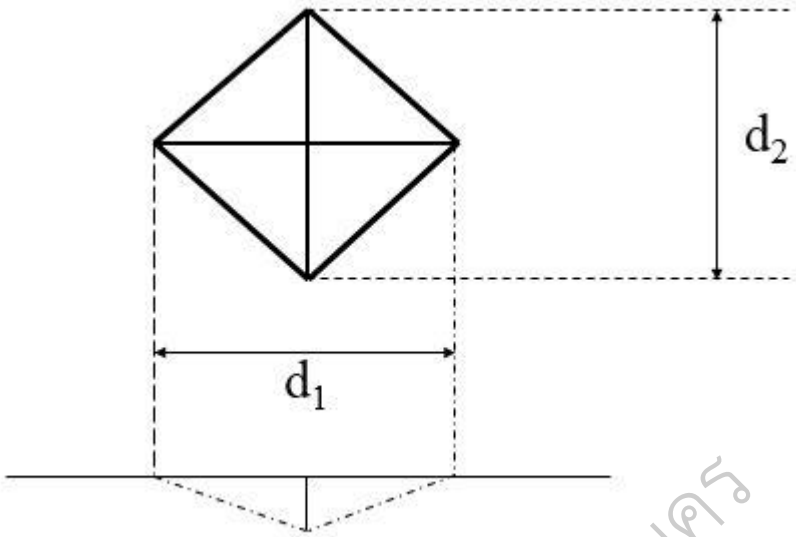

Figure 28 Diagram of the Vickers hardness tester model

The hardness value was calculated from applied load with surface area of the sample. In this research, we measured Bi_2Te_3 at room temperature by micro hardness tester with the applied load of 0.245, 0.490, 0.980, 2.942 and 9.807 N respectively and the loading time of 10 s. and the repeated 3 times for each sample, and the average hardness measured data, and the Vickers Pyramid Number (H_V) indenter into the surface of the specimen, defined by,

$$H_V = \frac{2P_H \sin\theta}{l^2} = 1.8544 \frac{F}{\left(\frac{l_1 + l_2}{2}\right)^2} \qquad (3.5)$$

where l is the average diagonal length of the diamond shaped impression made on the indented surface, P_H is the stress of the indenter and F is applied load (N). The unit of the Vickers hardness can be used GPa, given by eq. (3.5)

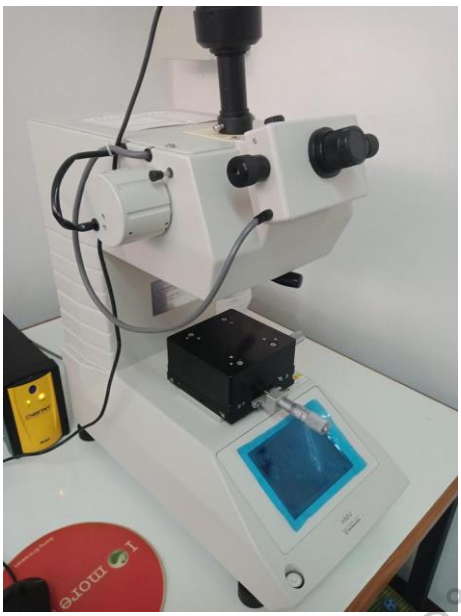

Figure 29 The Vickers hardness tester Model on Center of Excellence on Alternative Energy at Sakon Nakhon Rajabhat University

ELECTRICAL RESISTIVITY AND SEEBECK COEFFICIENT

Electrical Resistivity

The electrical resistivity was measured performed in a helium atmosphere using the thermopower measuring device (ADVANCE RIKO ZEM-3), as shown in Fig. 30. The electrical resistivity is represented by the following equation:

$$\rho = \frac{V_1}{V_2} R \tag{3.6}$$

where V_1 is the measured voltage between two probes on the sample, R and V_2 are a standard resistor incorporated into the equipment and the voltage dropped across the standard resistor.

Seebeck Coefficient

The Seeback coefficient (S) measured the magnitude of an induced thermoelectric voltage in response to a temperature difference of materials, using *(*ADVANCE RIKO ZEM–3*)* in helium atmosphere and over the temperature range of 273–*500* K as shown in Fig. 30. The Seebeck coefficient is represented by the following equation*:*

$$S = \frac{\mathrm{D}V}{T_H - T_C} \tag{3.7}$$

Where ΔV is the Seebeck coefficient voltage development between two points on the sample, T_H and T_C are the measured absolute temperature.

Figure 30 Show ZEM–3; ADVANCE RIKO Technologies apparatus, on Center of Excellence on Alternative Energy at Sakon Nakhon Rajabhat University

THERMAL CONDUCTIVITY

The thermal conductivity measured by used homemade steady state technique, using (TRC thermal) as show in Fig. 31 and over the temperature range of 273–500 K. The thermal conductivity is represented by the following equation (3.8)

$$\kappa = \frac{\dot{Q}}{A\Delta T} \tag{3.8}$$

The κ is thermal conductivity of sample, $\dot{Q}$ is the amount of heat following of the sample, A is the cross–sectional area of the sample, and ΔT are the distance and temperature difference between thermocouple 2 and 3.

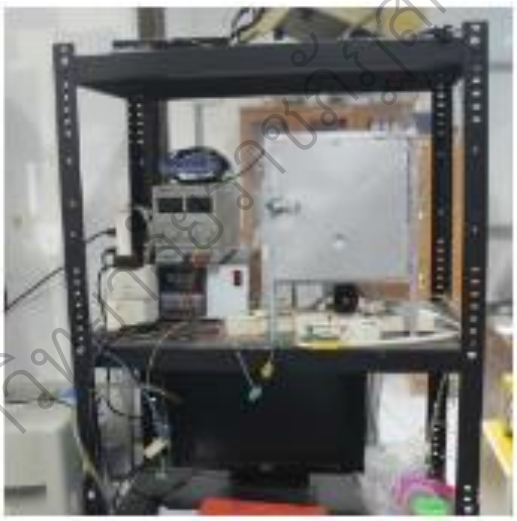

Figure 31 the thermal conductivity *(*TRC Thermal*)*, on Center of Excellence on Alternative Energy at Sakon Nakhon Rajabhat University

DENSITY

The density measured using the standard Archimedes method. The volumetric density was measured of mass of an object divided by its volume.

$$\rho = \frac{A}{|B|} \times (\rho_0 - d) + d \qquad (3.9)$$

Where ρ is density of sample, A is weight in air, B is weight in water, ρ_0 is density of water and d is density of air

Figure 32 Show density Kit on Center of Excellence on Alternative Energy at Sakon Nakhon Rajabhat University

DIMENSIONLESS FIGURE OF MERIT

The dimensionless figure of merit calculated by using the above-mentioned values of the Seebeck coefficient (S), electrical resistivity (ρ) and thermal conductivity (κ) according to the relation;

$$ZT = \frac{S^2 T}{\rho \kappa} \tag{3.10}$$

ELECTRONIC STRUCTURE CALCULATION

The electronic structure calculated using the density functional theory and BoltzTraP simulation. For the Bi_2Te_3 and $Bi_{2-x}Sb_xTe_3$ cluster models were designed by sing space group number 166, lattice parameter a = 4.38 Å, b = 4.38 Å and c = 30.49 Å. The electronic structure was calculated by the density functional theory based on QUANTUM ESPRESSO *(*P. Giannozzi, S. Baroni and R. M. Wentzcovitch 2009*)*. The exchange correlation function, energy convergence limit set as 10^{-8} Ry, and energy cutoff 40 Ry are performed *(*J. P. Perdew, K. Burke and M. Ernzerhof, 1996*)*. The density of states was calculated using 8×8×1 k –mesh and k –points in the Brillion zone. The thermoelectric properties, such as, Seebeck coefficient, electrical conductivity, and thermal conductivity was calculated using Boltzmann transport theory based on BoltzTraP. The equation can be written as;

$$\sigma(T;\mu) = \frac{1}{\Omega}\int \sigma(\varepsilon)\left[-\frac{\partial f_u(T;\varepsilon)}{\partial \varepsilon}\right] d\varepsilon, \tag{3.11}$$

$$v(T;\mu) = \frac{1}{eT\Omega}\int \sigma(\varepsilon)(\varepsilon-\mu)\left[\frac{\partial f_u(T;\varepsilon)}{\partial \varepsilon}\right] d\varepsilon \tag{3.12}$$

$$S = E(\nabla T)^{-1} = (\sigma^{-1})v \tag{3.13}$$

where Ω is unit cell, v is the band velocity, μ is the chemical potential, ε is band energy, f_u is the Fermi function and E is electromotive force. The electronic thermal conductivity has similar outline to electrical conductivity, which is because that the electrical thermal conductivity is connected with electrical conductivity by the Wiedemann–Franz law*:*

$$\kappa_e = \sigma LT = \frac{\kappa_e}{\tau_r} \times \tau \tag{3.14}$$

$$\kappa = \kappa_e + \kappa_L \tag{3.15}$$

where L is the Lorenz number, κ is total thermal conductivity τ is empirical scattering and τ_r is true scattering time

FABRICATION OF THERMOELECTRIC SENSOR

Thermoelectric sensor fabricated from the p–$Bi_{0.4}Sb_{1.6}Te_{3.4}$ and n–Bi_2Te_3 thermoelectric cell. TE materials cut of 2×2×2.5 mm^3 for making TE cell, using copper foil 0.3 mm^3 substrate in order to create a good contact between the element and the metal parts in the cell.

ARDUINO CIRCUITS

In this topic presents materials and equipment for fabricated thermoelectric sensor and program can be support of Arduino circuits.

Equipment of thermoelectric sensor

ESP8226 is an impressive, low cost WIFI module suitable for adding WIFI functionality to an existing microcontroller project via a UART serial connection. The module can even be reprogrammed to act as a standalone WIFI connected device–just add power.

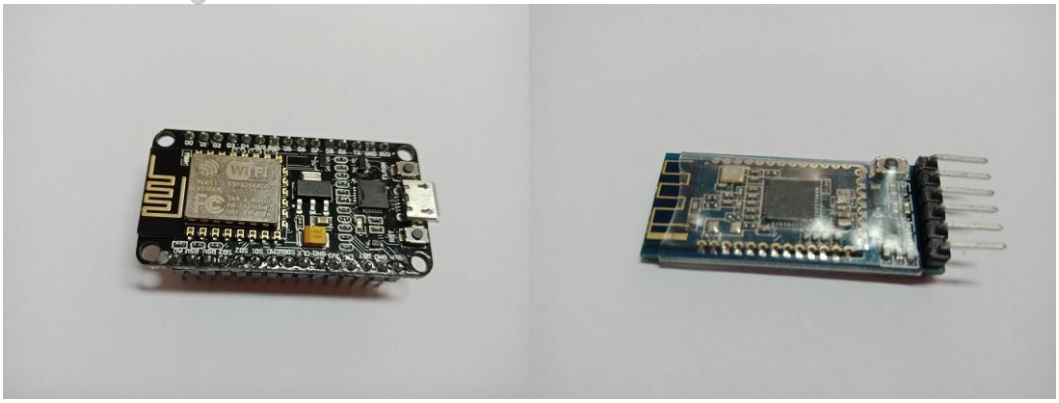

Figure 33 *(a)* Shown ESP8266 circuits, *(b)* Bluetooth 4.0 BLE with logic level translator

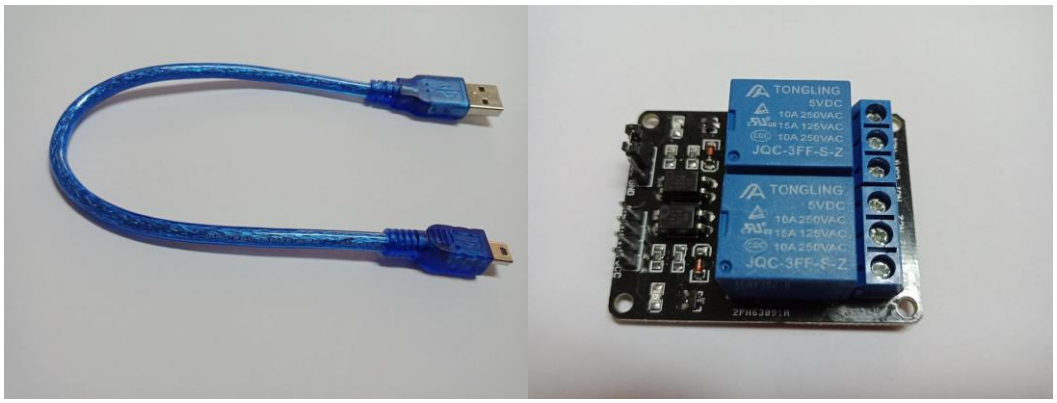

Figure 34 *(a)* Shown MiNi USB, *(b)* 2–channel 5VDC relay

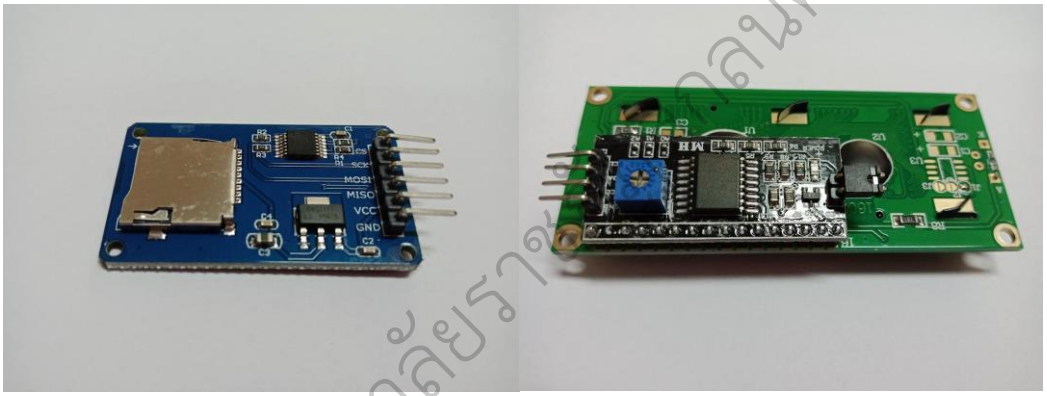

Figure 35 *(a)* Micro sd card module side *(b)* Character LCD module display

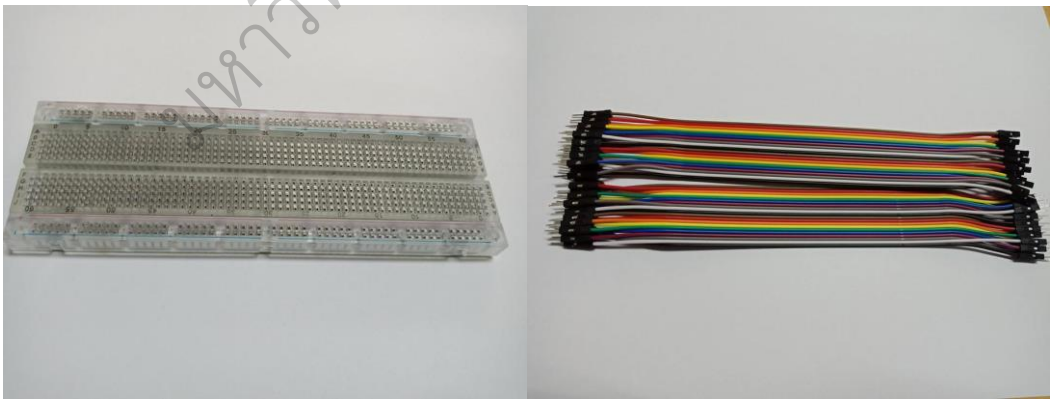

Figure 36 *(a)* Shown 830–point breadboard *(b)* Male to male jumper wire and male to female jumper wire (c) temperature sensor

Connection thermoelectric sensor with Arduino circuits

In this topic, we wanted to present system of Arduino circuits

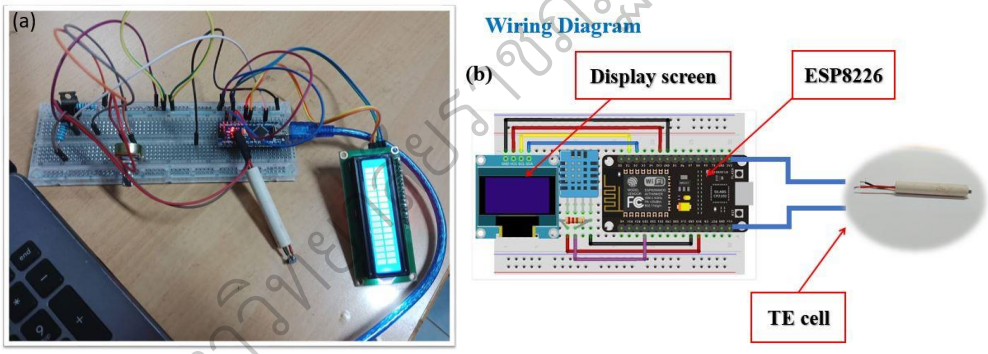

Figure 37 Shown temperature sensor with Arduino circuits

Program and command of thermoelectric sensor

In this topic, we wanted to present a program for support of Arduino circuits and the selection board Arduino for working process of the program shown in Fig. 38.

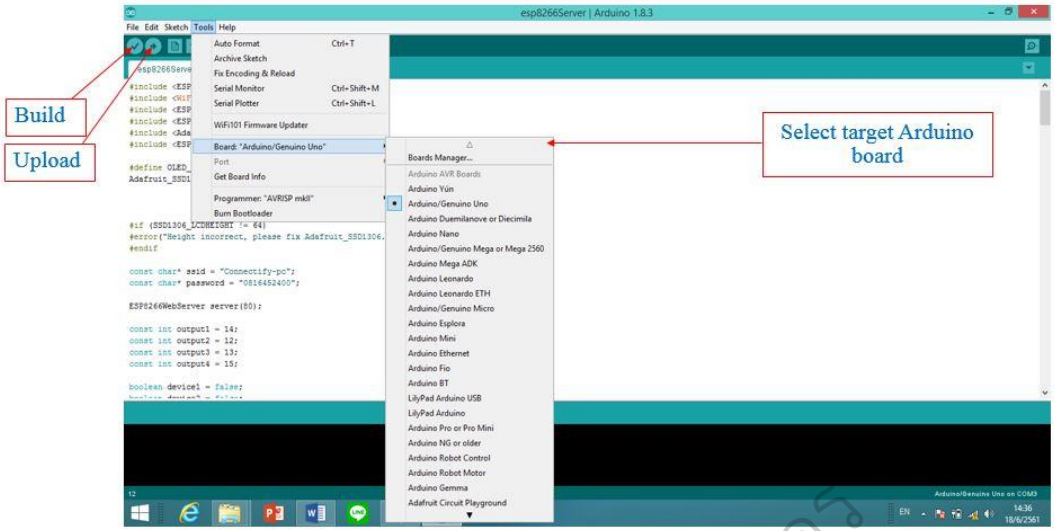

Figure 38 Show the selection board Arduino

```
#include <LiquidCrystal_I2C.h>
LiquidCrystal_I2C lcd(0x27, 16, 2);
#include "HX711.h"
HX711 scaleA(3,4);
HX711 scaleB(6,7);
HX711 scaleC(8,9);
HX711 scaleD(10,11);
float SENSORA=0;
int SENSORB=0;
int SENSORC=0;
int SENSORD=0;
int outA=0;
int SA=30;
int outB=0;
int outC=0;
int outD=0;
float outputValue=0;

void setup()
{
lcd.begin();
Serial.begin(9600);
scaleA.set_scale(2280.f);                  // this value is obtained by calibrating the scale with known weights; see the README for details
scaleB.set_scale(2280.f);
scaleC.set_scale(2280.f);
scaleD.set_scale(2280.f);
}
```

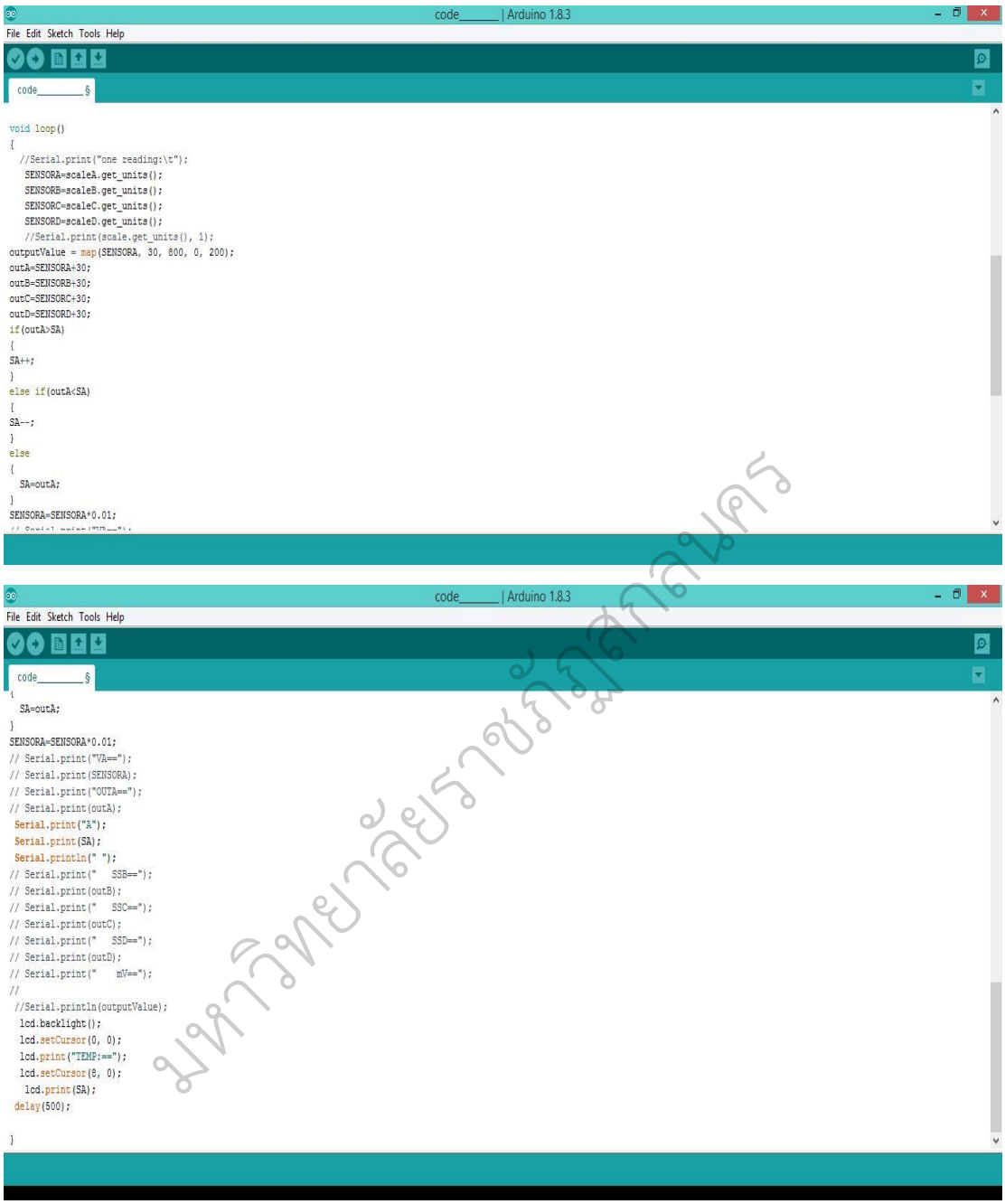

Figure 39 shows the Arduino code for the thermoelectric sensor

Thermoelectric Sensor and Arduino Application

Thermoelectric sensor fabricated from Bi_2Te_3 and $Bi_{0.4}Sb_{1.6}Te_{3.4}$ materials and used Arduino program for support measurement the value of temperature in this work as show Fig. 40.

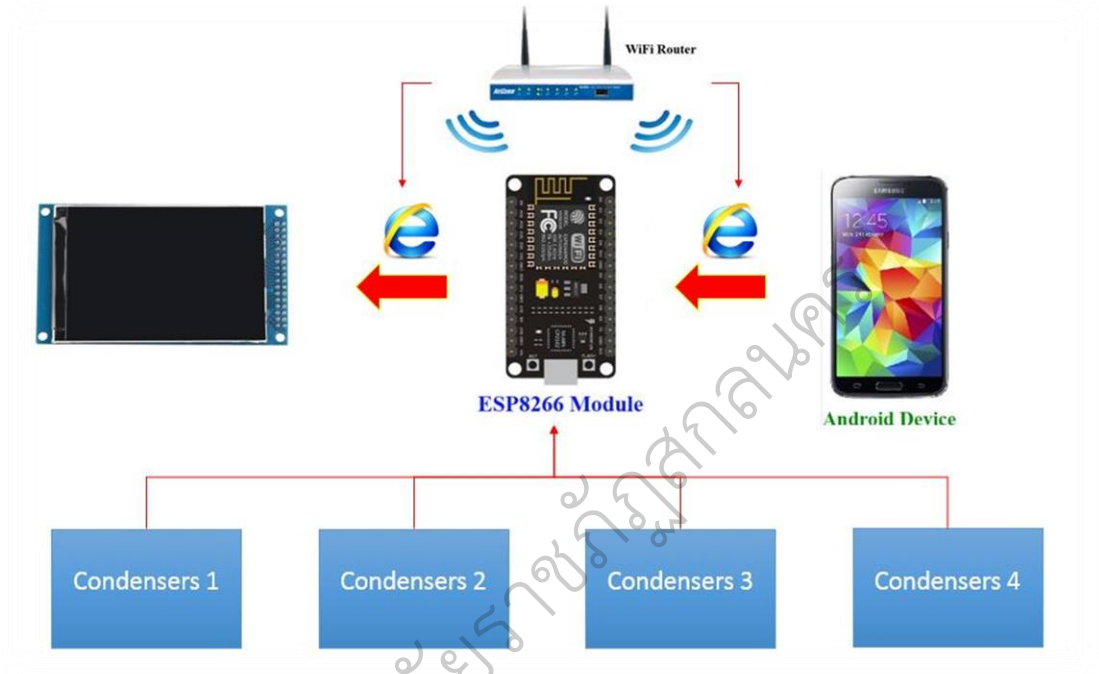

Figure 40 show the system working in Korn Det industry.

The first process presents the thermoelectric materials for temperature sensor and used thermoelectric cell 1 pair p–type and n–type Bi–Te, Bi–Sb–Te for detect temperature. The second process, we fabricated thermoelectric cell and setup to Arduino program, and using WIFI system as a transmitter signal to laboratory. In this work use thermoelectric cell 16 pair for detect temperature and Arduino program 4 system for transmitter signal in Korn Det industry as show in Fig. 41.

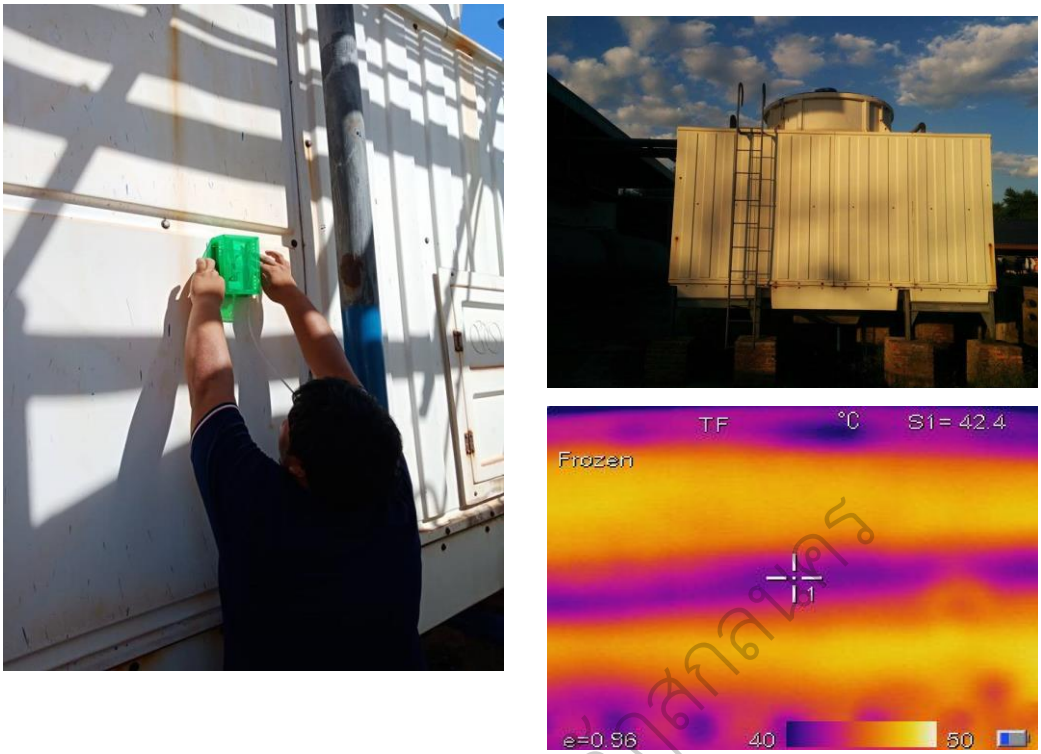

Figure 41 To Setup temperature sensor in Korn Det industry