CHAPTER 4

RESULTS AND DISCUSSION

In this chapter represents 7 topics viz, results of thermoelectric materials synthesis, crystal structure analysis, microstructure analysis, thermoelectric properties and power generation of PC thermoelectric devices when temperature difference occurs.

Materials preparation

Portland cement samples

Portland cement samples of PC–A, PC–B, PC–C, PC–D, PC–E and PC–F after drying 48 h show in figure 18 (a), (b), (c), (d), (e) and (f), respectively. All samples have the same color and outward appearance.

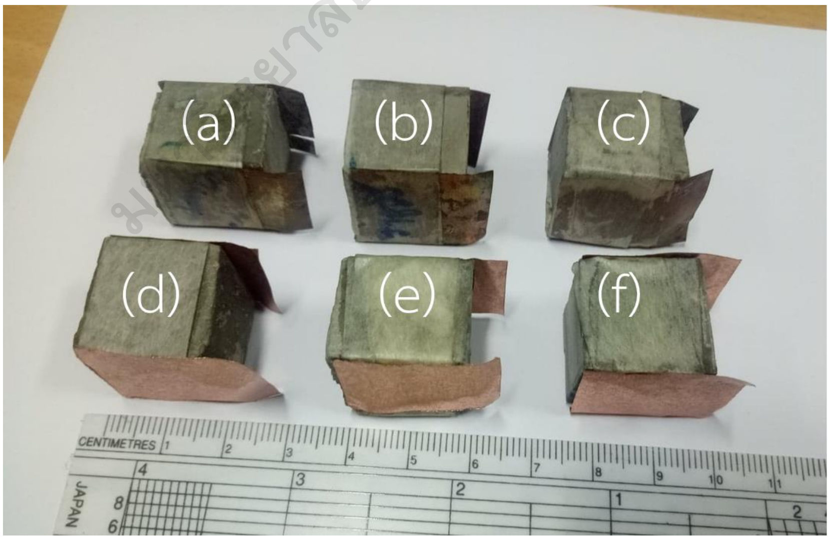

Figure 18 Portland cement samples of (a) PC–A, (b) PC–B, (c) PC–C, (d) PC–D, (e) PC–E and (f) PC–F

Portland cement samples added with nano ZnO (10%, 20%, 30%, 40% and 50%)

The PC-C samples added with nano ZnO 10%, 20%, 30%, 40% and 50% after drying 48 h shown in figure 19 (a), (b), (c), (d) and (e), respectively. The samples showed increased whiteness in accordance with the amount of doping.

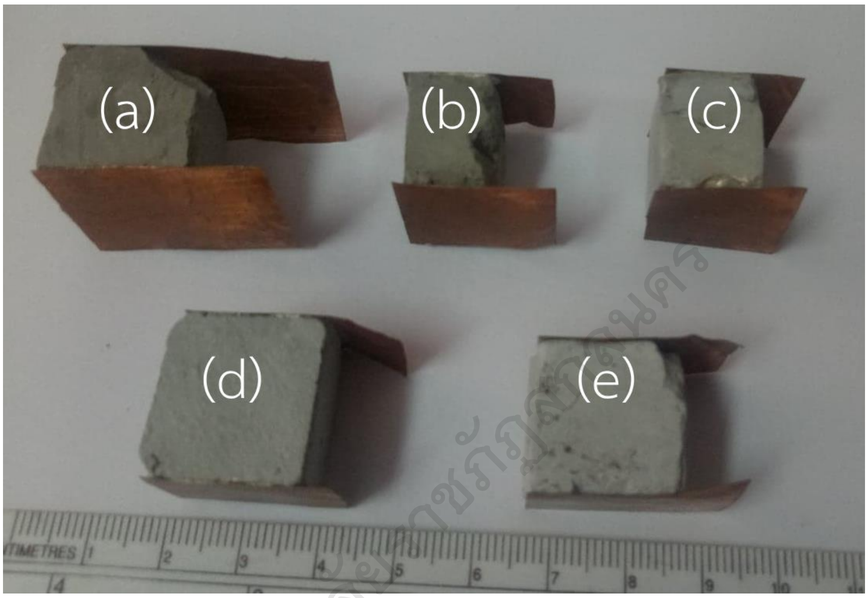

Figure 19 The PC-A samples added with nano ZnO (a) 10%, (b) 20%, (c) 30%, (d) 40% and (e) 50%

Crystal Structure

The XRD patterns of PC-A (green line), PC-B (pink line), PC-C (orange line), PC-D (blue line), PC-E (red line) and PC-F (black line) show in figure 20. All samples agree with ICDD number 00-055-0739 (Ca_3SiO_5) except PC-C due to secondary phase of SiO_2 was observed. The crystal structure of all samples shows monoclinic structure with space group number PC-7. It can be seen that main element of Portland cement included Ca, Si and O. Figure 21 shows XRD pattern of nano ZnO added PC-C (10 – 50 wt%) agreeing with PC-C for main phase and nano ZnO for secondary phase. The nano ZnO patterns were increased with amount of added increasing.

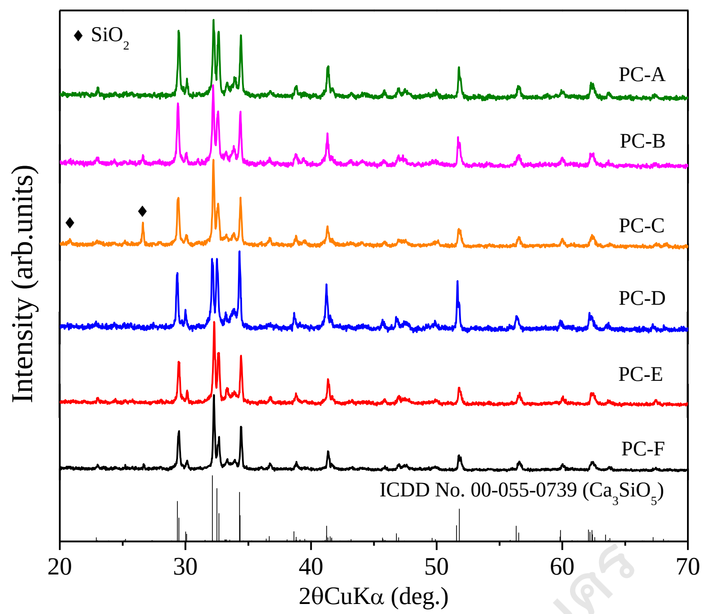

Figure 20 XRD patterns of PC powders samples

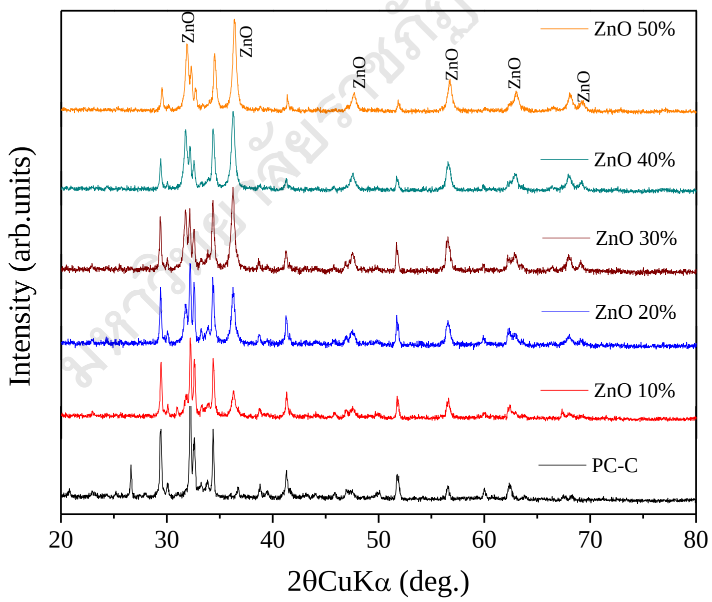

Figure 21 XRD patterns of nano ZnO added PC-C (10–50 wt%) powders samples

Microstructure Analysis

Figure 22 shows SEM images of (a) PC–A, (b) PC–B, (c) PC–C, (d) PC–D, (e) PC–E and (f) PC–F bulk samples. The bulk samples exhibit different particle size about 2 – 10 μm and PC–A show biggest particle size about 10 μm.
The microstructures of 10 – 50 wt% nano ZnO added PC–C show size of particle decreasing when increases nano ZnO content effect to Seebeck coefficient value larger as shown in figure 23. The EDS mapping of 10, 20, 30, 40 and 50 wt% nano ZnO added PC–A is shows in figure 24 (a – e). The element of Zn, Ca, S, Ni, Si, Cu, Cl, Ti, C and O exhibit good distribution indicating that completely mixing method. The intenseness of Zn element (pink color) increased with increasing added content.

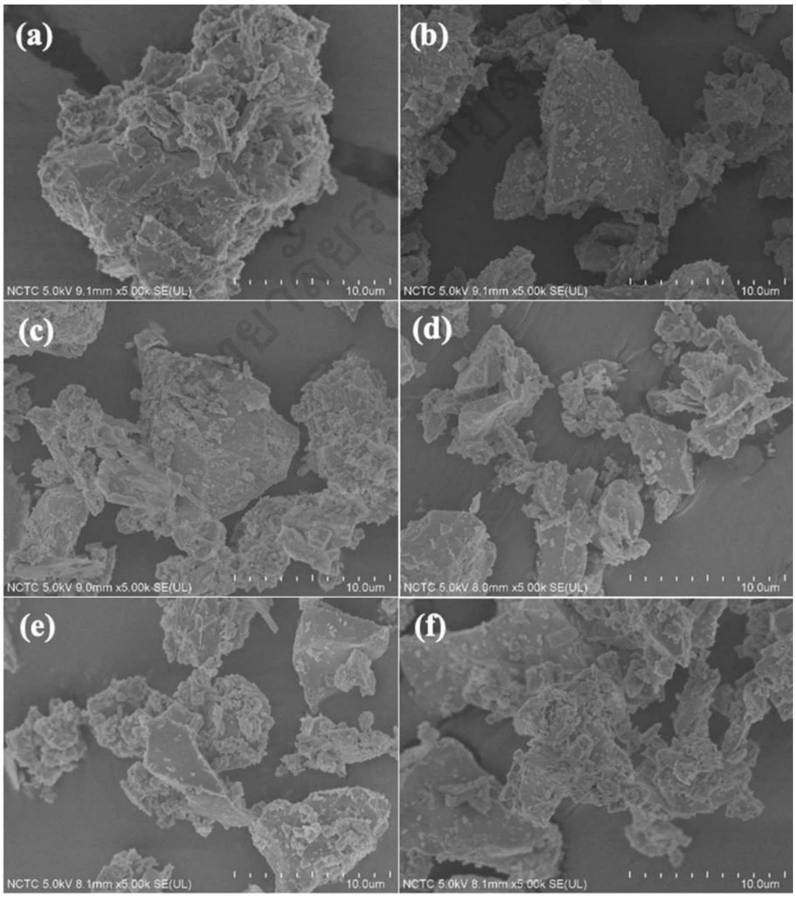

Figure 22 SEM images of (a) PC–A, (b) PC–B, (c) PC–C, (d) PC–D, (e) PC–E and (f) PC–F bulk samples

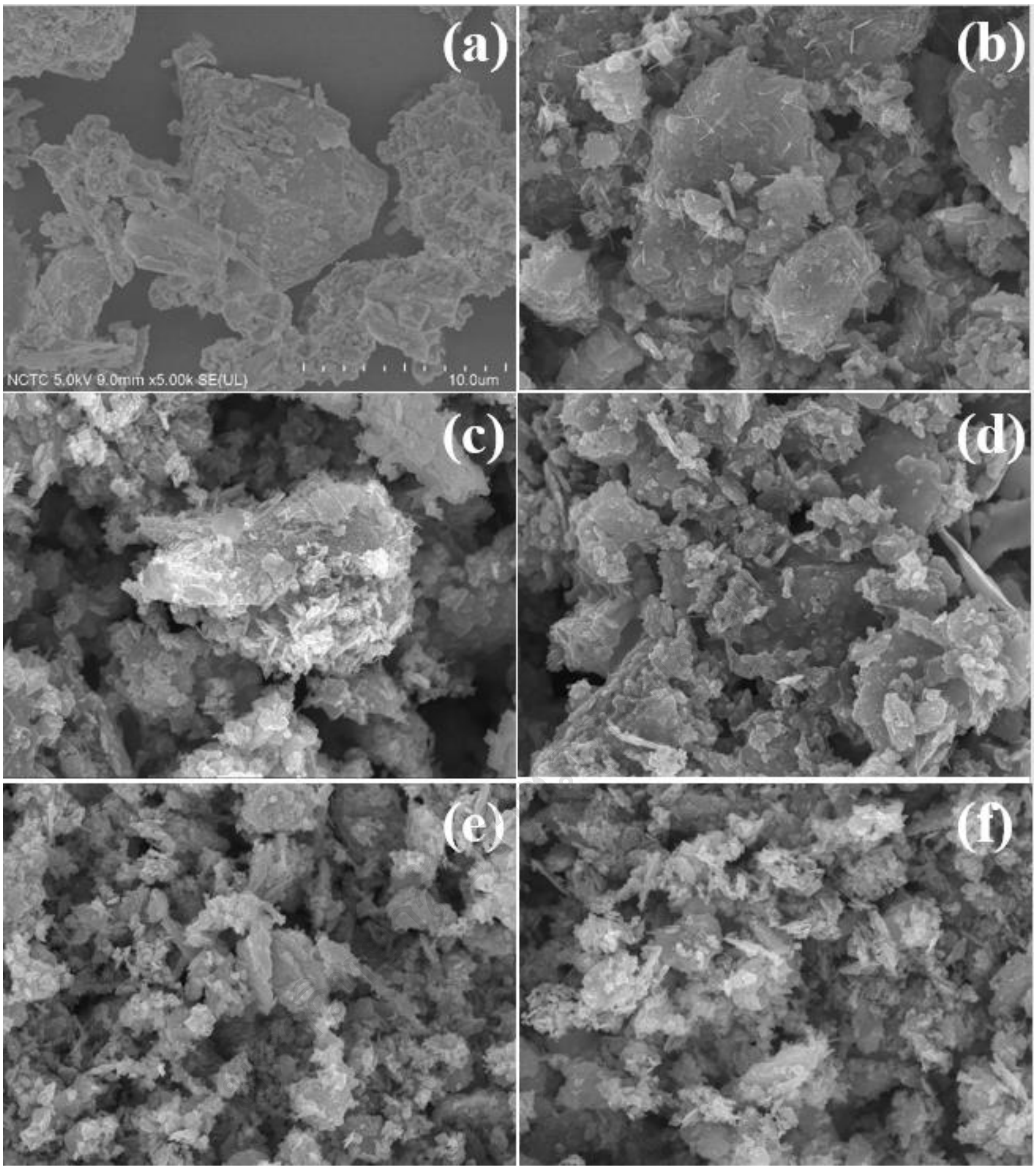

Figure 23 SEM images of (a) 0% nano ZnO added PC-C, (b) 10% nano ZnO added PC-C, (c) 20% nano ZnO added PC-C, (d) 30% nano ZnO added PC-C, (e) 40% nano ZnO added PC-C and (f) 50% nano ZnO added PC-C bulk samples

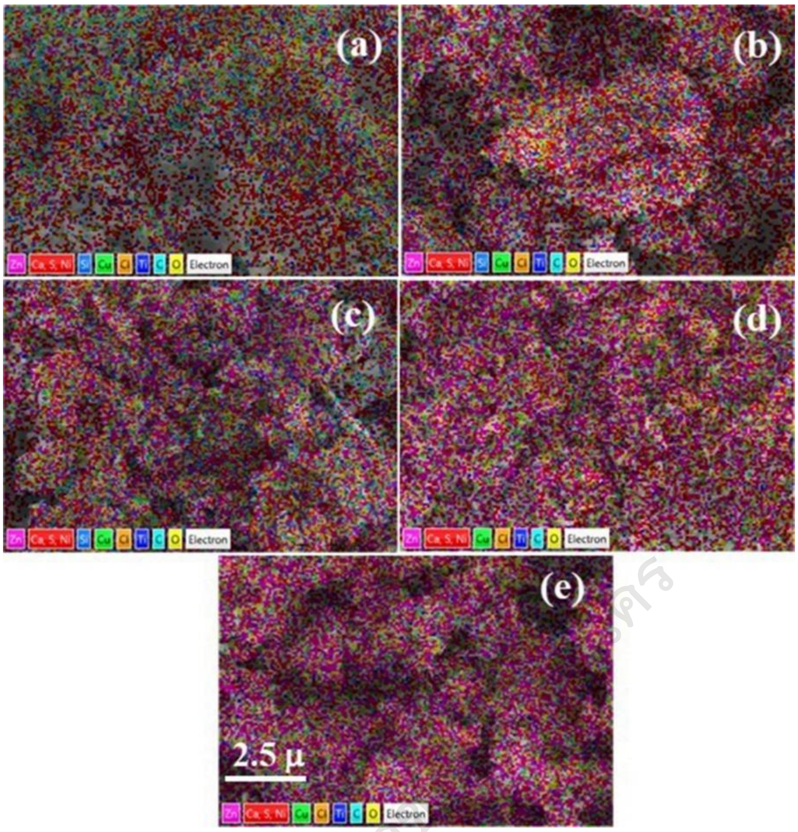

Figure 24 EDS mapping of (a) 10% nano ZnO added PC-C, (b) 20% nano ZnO added PC-C, (c) 30% nano ZnO added PC-C, (d) 40% nano ZnO added PC-C and (e) 50% nano ZnO added PC-C bulk samples

Table 2 EDS result of nano ZnO added 10%

Element	Wt%	Wt% Sigma
C	25.18	1.02
O	31.05	0.89
Si	3.31	0.17
S	1.39	0.13
Cl	0.00	0.10
Ca	19.90	0.51
Ti	0.05	0.16
Ni	0.12	0.35
Cu	1.77	0.89
Zn	17.24	0.68
Total	100.00	

Table 3 EDS result of nano ZnO added 20%

Element	Wt%	Wt% Sigma
C	12.53	1.06
O	28.75	0.89
Si	3.83	0.21
S	0.98	0.14
Cl	0.00	0.12
Ca	21.69	0.57
Ti	0.18	0.19
Ni	0.00	0.46
Cu	2.41	1.08
Zn	29.63	0.87
Total	100.00	

Table 4 EDS result of nano ZnO added 30%

Element	Wt%	Wt% Sigma
C	19.74	1.06
O	22.77	0.71
Si	2.54	0.16
S	0.76	0.12
Ca	12.55	0.36
Ti	0.00	0.16
Ni	0.54	0.36
Cu	1.93	0.98
Zn	39.16	0.89
Total	100.00	

Table 5 EDS result of nano ZnO added 40%

Element	Wt%	Wt% Sigma
C	7.08	1.12
O	21.50	0.73
S	1.29	0.17
Cl	0.15	0.13
Ca	7.02	0.32
Ti	0.12	0.19
Ni	0.00	0.47
Cu	3.43	1.21
Zn	59.39	1.23
Total	100.00	

Table 6 EDS result of nano ZnO added 50%

Element	Wt%	Wt% Sigma
C	2.99	1.10
O	22.21	0.70
S	0.42	0.15
Cl	0.05	0.14
Ca	4.63	0.27
Ti	0.00	0.21
Ni	0.00	0.46
Cu	1.31	1.30
Zn	68.39	1.34
Total	100.00	

Thermoelectric Properties

Thermoelectric properties of PC

The thermoelectric properties including Seebeck coefficient (S) and electrical resistivity (ρ) were measured at room temperature. The schematic diagram of S and ρ shows in Figure 25 (a) and (b), respectively. The S measurement was applied heat on the top and cooling on bottom of PC bulk sample to generate temperature difference from 0 to 10 K then measuring voltage output. The electrical resistance (R) was measured for calculating ρ (ρ = RA/l, where A is cross section area and l is distance of sample) as shown in Figure 24 (b)

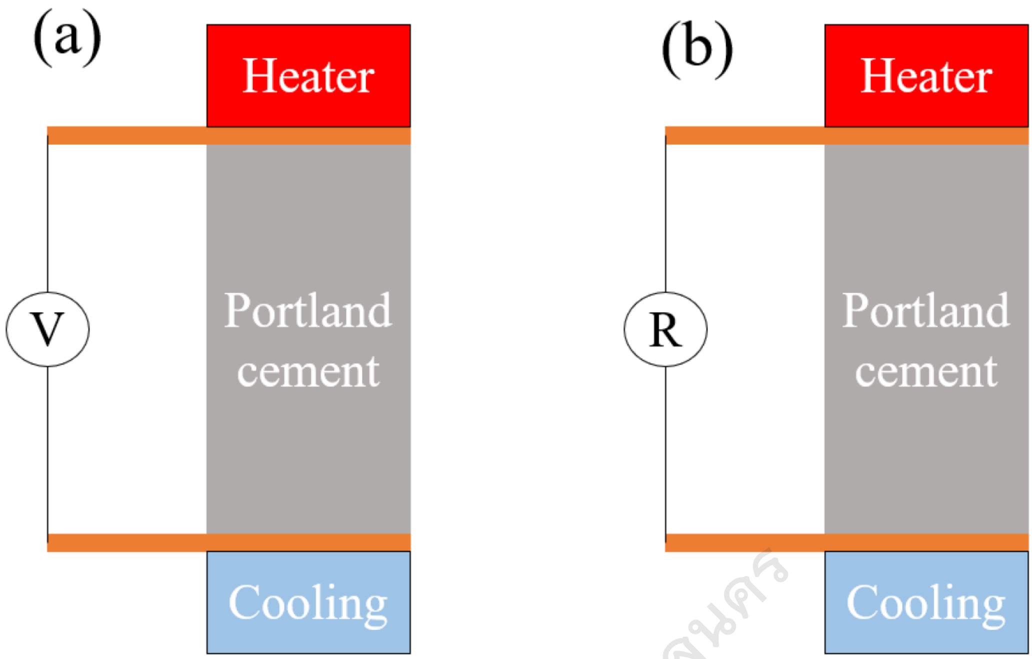

Figure 25 The schematic diagram of (a) Seebeck coefficient and (b) electrical resistivity measurement

The relationship between voltage and temperature difference at room temperature shows in figure 26. The voltage of all samples shows increased with temperature difference increasing due to thermoelectric material behavior (Earl Russcher G., 1964). The slop of graph between voltage and temperature difference is Seebeck coefficient ($S = - DV / DT$, where DV is voltage and DT, temperature difference) as shown in figure 27. The Seebeck coefficient of all samples exhibit positive value indicating that p-type thermoelectric materials and shows higher than literature data (Wein J., Hao L., He G., Yang C., 2014; pp. 8261–8263, Wei J., Zhang Q., Zhao L., Hao L., Nie Zh., 2017, pp. 10763–10769, Earl Russcher G., 1964). The Seebeck coefficient of PC-B bulk sample obtained highest value about 55.43 μV/K while PC-F bulk sample shows lowest value about 49.27 μV/K.

The electrical resistivity dependent on temperature difference of PC bulk samples at room temperature shows in figure 28. The electrical resistivity of all samples excepting PC-C decreased when temperature difference increasing demonstrates being a semiconductor material. The average electrical resistivity of PC-B reveals lowest value about 0.745 Ω m while PC-E obtained highest value about 0.788 Ω m but higher than literature data (Wei J., Zhang Q., Zhao L., Hao L., Nie Zh., 2017, pp. 10763–10769) as shown in figure 29. The power factor of PC bulk samples was calculated from Seebeck coefficient and electrical resistivity ($PF = S^2 s$). It was found that, *PF* of all samples obtained value in the nano scale which is very small value, however the *PF* value of this work shows higher than literature data (Wei J., Zhang Q., Zhao L., Hao L., Nie Zh., 2017, pp. 10763–10769). The PC-C shows highest value about 4 nW/mK^2 at room temperature as shown in figure 30.

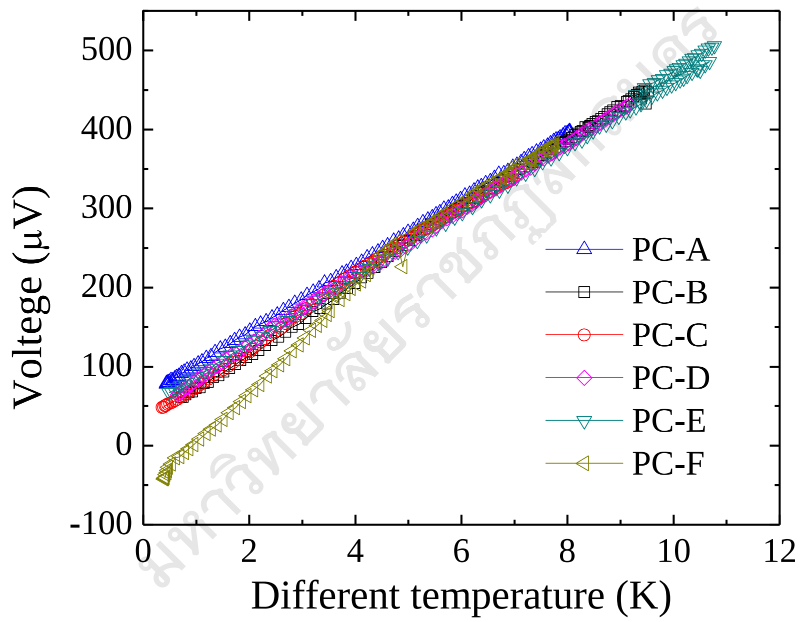

Figure 26 Electrical voltage dependence on temperature difference of PC bulk samples

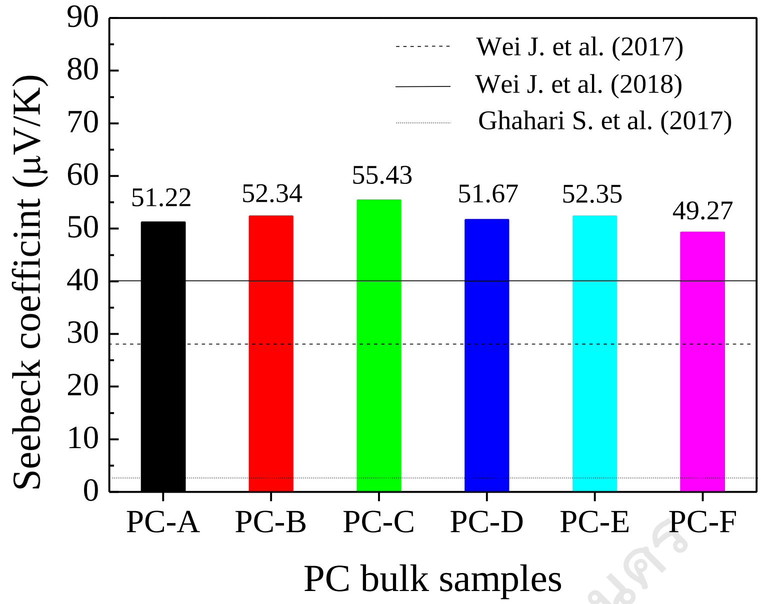

Figure 27 Seebeck coefficient of PC bulk samples

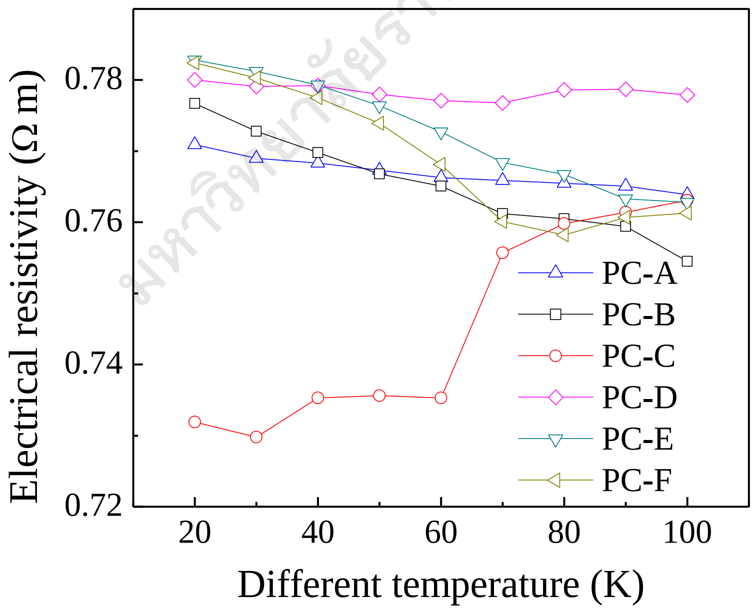

Figure 28 Electrical resistivity of dependence on temperature difference PC bulk samples

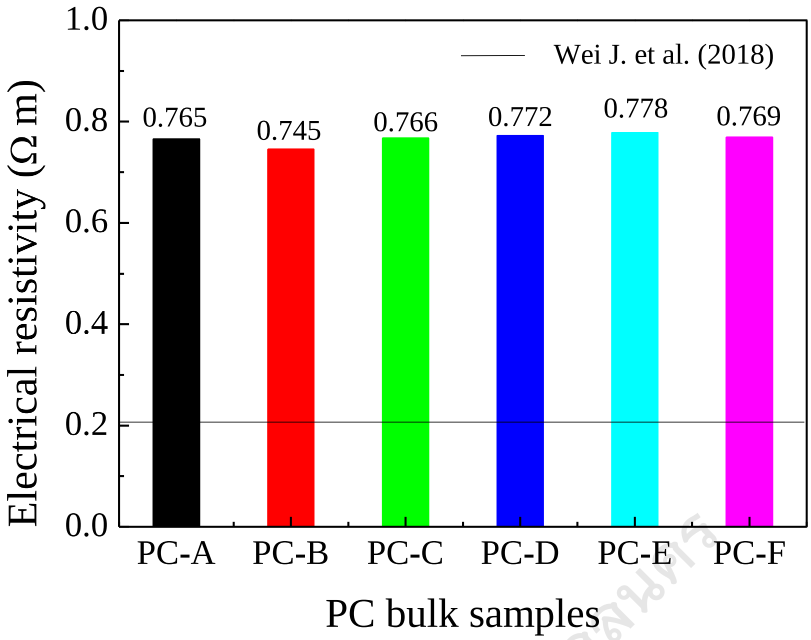

Figure 29 Electrical resistivity of PC bulk samples

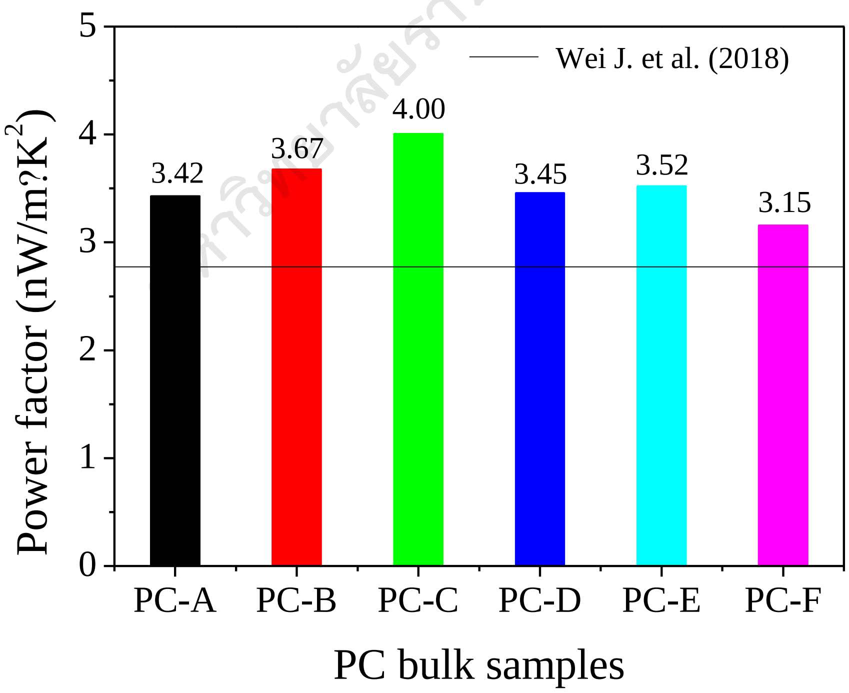

Figure 30 The power factor of PC bulk samples

Thermoelectric properties of nano ZnO-added PC

The Seebeck coefficient of nano ZnO added PC-C show in figure 31. It was found that the Seebeck coefficient show large enhancement value when added with nano ZnO. The positive value of Seebeck coefficient indicate p type thermoelectric materials due to most hole carriers. The Seebeck coefficient of all added sample show higher than un- added indicating that effective carrier mass increasing, which is in accordance with Eq. 14.

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n_H} \right)^{\frac{3}{2}}, \qquad (14)$$

where m^* is effective carrier mass, k_B is the Boltzmann constant, T is temperature, h is the Planck constant, e is the electron charge and n_H is Hall carrier concentration.

The nano ZnO added effected to increasing the Seebeck coefficient until 40% and then decreasing. The 40% of nano ZnO added PC-C obtained highest value of Seebeck coefficient about 278.64 μV/K at room temperature. The electrical resistivity of nano ZnO added PC-C show higher than un- added and increased with nano ZnO increasing namely the carrier mobility decreased as shown in figure 32, which is in accordance with Eq. 15.

$$\rho = \frac{1}{\sigma} = \frac{1}{n_H e \mu_H} \qquad (15)$$

where σ is electrical conductivity and μ_H is Hall mobility. The power factor of added samples shows large enhancement value and increased with nano ZnO until 40%. The power factor of 40% nano ZnO added PC-C show maximum value about 16.87 nW/mK^2 at room temperature which higher than un- added about 4 times as shown in figure 33.

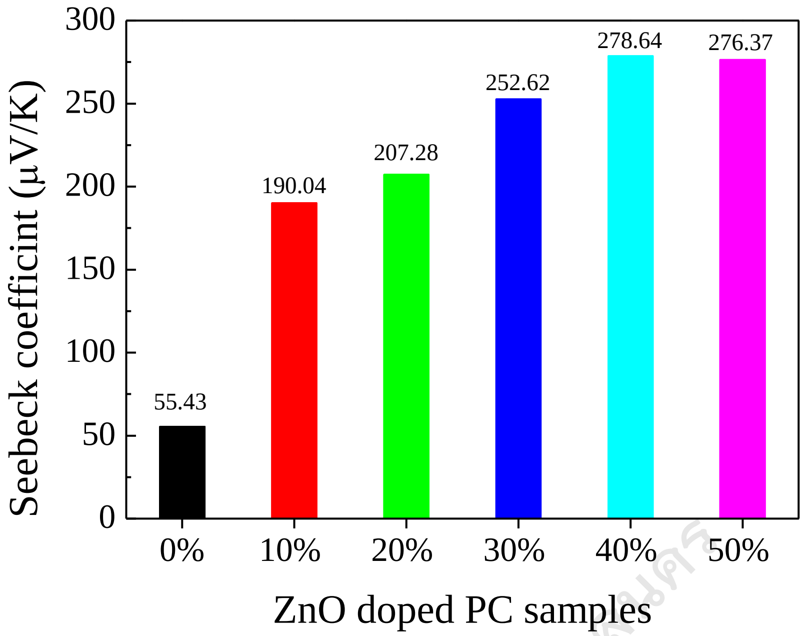

Figure 31 The Seebeck coefficient of nano ZnO added PC-C bulk samples

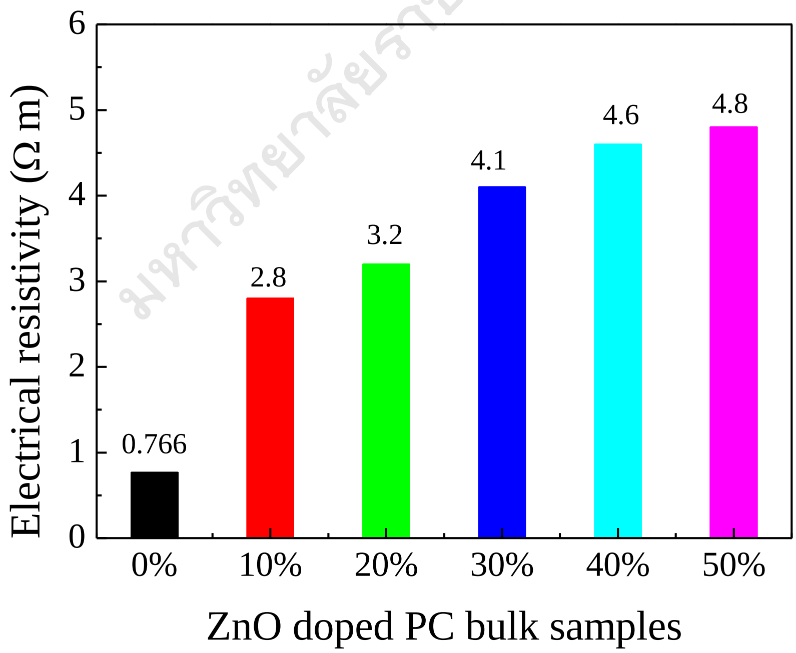

Figure 32 The electrical resistivity of nano ZnO added PC-C bulk samples

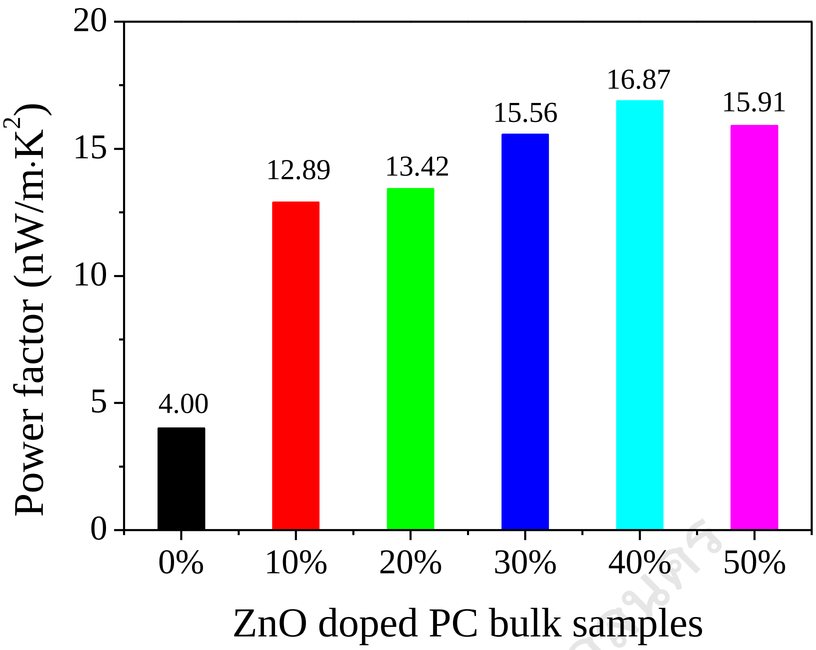

Figure 33 The Seebeck coefficient of nano ZnO added PC-C bulk samples

Power generation of PC thermoelectric Devices

The power generation of PC thermoelectric device were measured by vary load resistance from 10 kΩ to 110 kΩ at different temperature 70 K. It was found that, the voltage and power increased with load resistance increasing while current decreasing as shown in figure 34. The maximum voltage and power were obtained by 110 kΩ of load resistance about 3.5 mV and 0.11 nW, respectively.

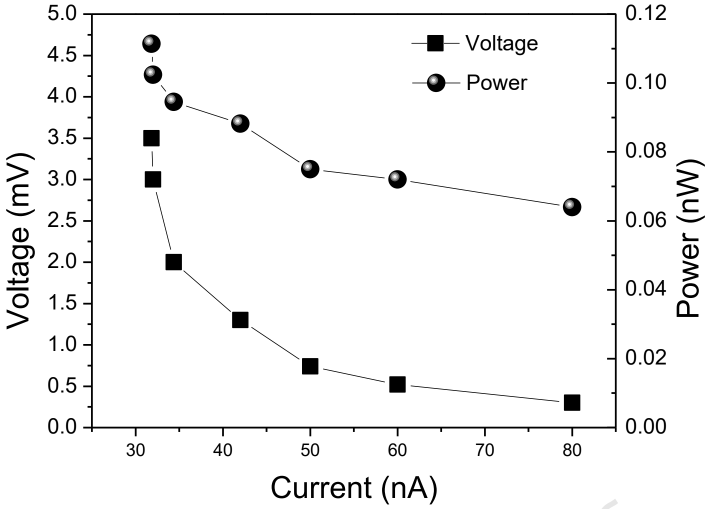

Figure 34 The power generation of PC thermoelectric device depend on load resistance

The voltage of PC thermoelectric devices

Figure 35 shows the open circuit voltage depend on temperature difference of PC thermoelectric devices and open circuit voltage increased with temperature difference increasing showing maximum value about 53.99 mV at 70 K. The voltage of PC thermoelectric device at load resistance 110 kΩ depend on temperature difference shows in figure 36 and obtained the maximum value about 3.65 mV at 69.8 K.

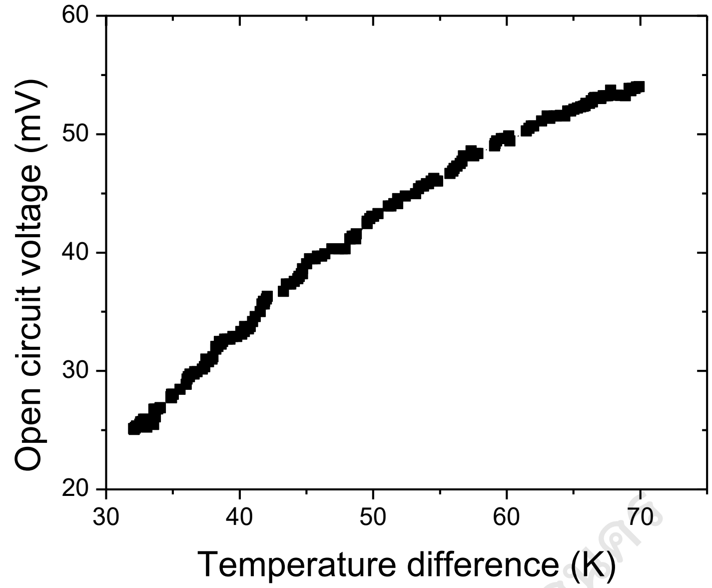

Figure 35 The open circuit voltage dependence on temperature difference of PC thermoelectric devices

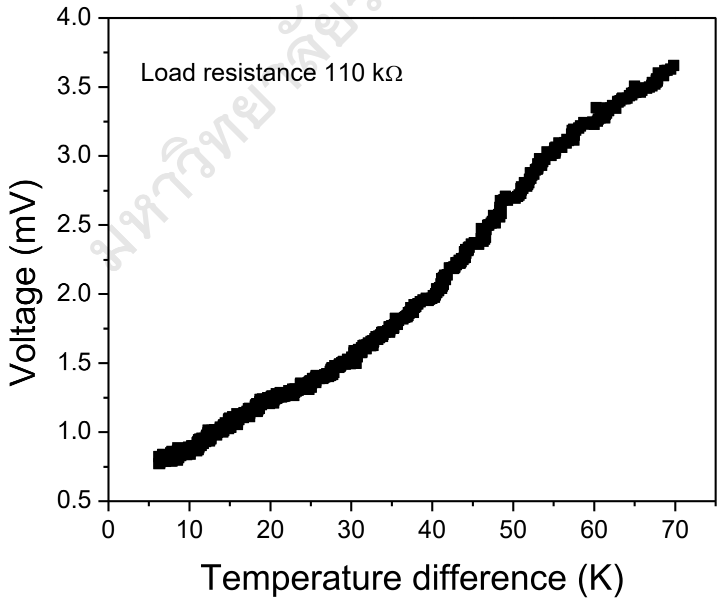

Figure 36 The voltage dependence on temperature difference of PC thermoelectric devices

The current of PC thermoelectric devices

The current at load resistance 110 kΩ depend on temperature difference of PC thermoelectric devices shows in figure 37. The current increased with increasing temperature. The maximum current of PC thermoelectric devices is 33.23 nA at temperature difference of 69.8 K.

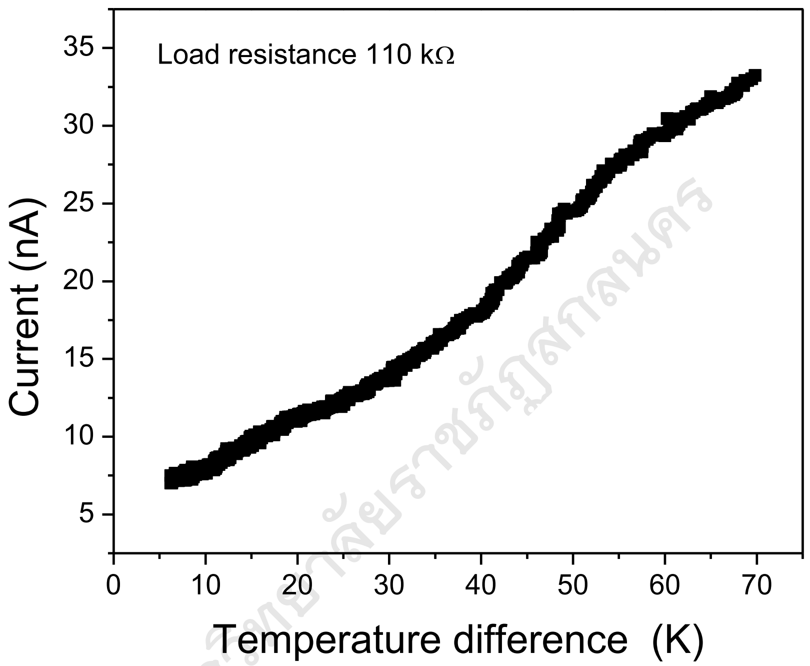

Figure 37 The current dependence on temperature difference of PC thermoelectric devices

The power of PC thermoelectric devices

The power dependence on temperature difference of PC thermoelectric devices shows in figure 38. The measurement power output was used matching load of 110 kΩ. The power of PC thermoelectric devices increased with increasing temperature. The PC thermoelectric devices show the maximum power about 0.12 nW at temperature difference 69.8 K.

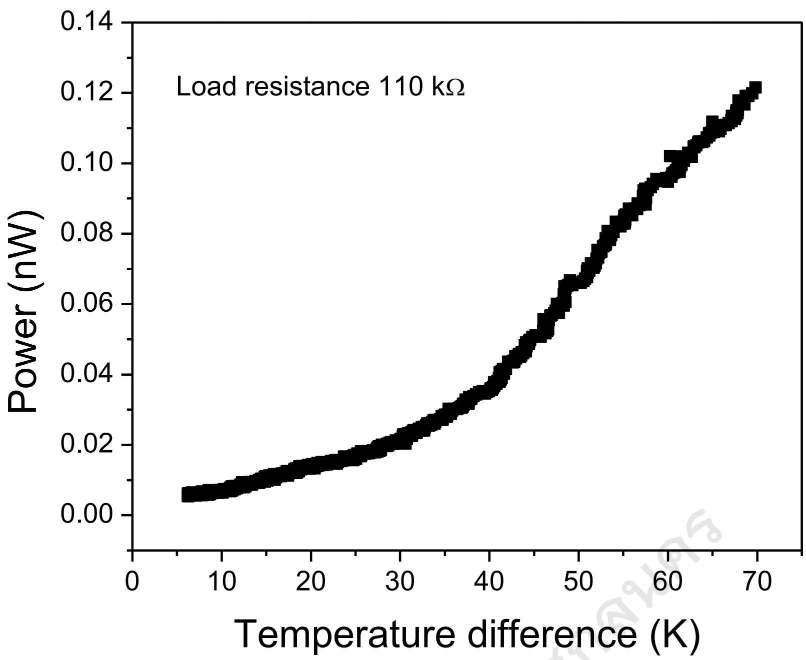

Figure 38 The power dependence on temperature difference of PC thermoelectric devices