# CHAPTER 2

# LITERATURE REVIEWS

In this chapter represents 4 topics viz, theorem of thermoelectricity, thermoelectric material, thermoelectric device.

## Theorem of thermoelectricity

### Thermoelectric effect

The conventional flows of heat and electricity in a material and the potentials producing them are nonreversible processes. A classic example of this fact is the production of electrical resistance heat at the rate Q = $I^2R$, regardless of the direction of flow of the electricity; although it is impossible to generate a current (I) in the conductor simplied by supplying the heat (Q) to the resistance volume R. However, there are reversible processes known as the Seebeck effect, the Peltier effect and the Thomson effect.



#### 1. Seebeck effect

The Seebeck effect was discovered in 1823 by Thomas Johann Seebeck results in an emf in a circuit composed of two different homogeneous materials if the junctions of the materials are at different temperatures. For small temperature differences, the emf depends on the temperature difference and function of the material used. The Seebeck coefficient between the materials A and B is $S_{AB}$. $E_{AB}$ and $S_{AB}$ are positive if conventional current flows from A to B at the hot junction (Russche, 1964, pp. 4-5).

$$E_{AB} = S_{AB}\Delta T = \left(S_A - S_B\right)\Delta T \qquad (1)$$

Actually the Seebeck coefficient of a pair of materials is the difference of absolute coefficients.

**2. Peltier effect**

The Peltier effect was discovered in 1832 by Jean Charles Athanase Peltier. Whenever a circuit was composed of two dissimilar materials carries an electric current, heat is absorbed at one junction released at the other at a rate that is proportional to the current. This is called the Peltier effect, and the heat transferred is called the Peltier heat. Resistance heating is exactly nonreversible and proportional to the square of the current. The Peltier coefficient, $\Pi_{AB}$, is positive if current flow is from A to B at the junction where heat is absorbed, and the coefficient is really the difference of the absolute coefficients as in the Seebeck effect (Russche, 1964, pp. 5-6).

$$\frac{dQ_{AB}}{dt} = \Pi_{AB} I = \left(\Pi_A - \Pi_B\right) I \qquad (2)$$

**3. Thomson effect**

W. Thomson studied the Seebeck and Peltier effects, and derived a relation between their coefficients. He also predicted a new effect called the Thomson effect which is related to the reversible absorption or release of heat in a homogeneous conductor carrying a current through a temperature gradient. The rate of heat absorbed per unit length of conductor is equal to the positive coefficient times the conventional current and temperature gradient which are both in the same direction (Russche, 1964, pp. 6-8).

$$\frac{dQ_A}{dt} = \tau_A I \frac{dT}{dx} \qquad (3)$$

Thomson postulated that the first and second laws of thermodynamics could be applied to the reversible thermoelectric processes alone, in the presence of the irreversible resistance heating and thermal conduction. The first law of thermodynamics requires that the work done by the Seebeck effect in conducting a unit charge around the two conductor circuit must be equal to the thermal energy absorbed from the system.

These thermoelectric effects combine to provide useful power generation, heating or cooling. The efficient operation of such a thermoelectric circuit requires the optimization of the circuit and material parameters.

**Thermoelectric figure of merit and the thermoelectric parameter**

In 1949 the concept of a thermoelectric figure of merit, ZT, was developed by Abram Fedorovich Ioffe (Vedernikov, & Iordanishvili, 1998, pp. 37–42). The figure of merit (FOM) presented in Eq.4 describes the relationship between the three quantities determining the thermoelectric proprieties of a material (Ohtaki, 2011, pp. 770–775)

$$ZT = \frac{\sigma S^2 T}{\kappa_{tot}} = \frac{S^2 T}{\rho \kappa_{tot}} \tag{4}$$

where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $\kappa_{tot}$ is the total thermal conductivity, $\rho$ is the electrical resistivity and T is the absolute temperature. In principle z is the thermoelectric figure of merit a material, however since it is temperature dependant it is more meaningful to use it in its dimensionless form ZT.

The ultimate goal is to have as high ZT as possible which implies that a good thermoelectric should possess (i) large Seebeck coefficient, in order to efficiently convert heat into electricity, (ii) high electrical conductivity to minimize ohmic losses and Joule heating due to electrical resistance and (iii) low thermal conductivity to minimize heat losses and maintain the thermal gradient (Molinari, M., Tompsett, D. A., Parker, S. C., Azough, F., & Freer, R., 2014, pp. 14109–14117). The three thermoelectric parameters are functions of the carrier concentration and are interrelated in a conflicting manner.

## Cement thermoelectric

Cement and concrete are ubiquitous materials found and used in huge quantities across the world. Cement and concrete may sound and are frequently treated as synonymous in the everyday language, however, technically they are different. Cement is a finely powdered material that when mixed with water, creates a paste (the cement paste) that hardens via hydration and curing. During this process it is capable of binding rocks and sand (also called aggregates) together in a matrix. All these constituents bound together make concrete. Cement is the key ingredient of concrete. There is an additional distinction between mortar and concrete that is based on the size of the aggregates; if only sand is used, it is called mortar while if bigger stones are also used, it is called concrete.

### Chemistry nomenclature

Cement is such a particular material that has its own chemistry nomenclature (although, of course, obeying the same fundamental physical and chemical rules). In practice all the elements are described in term of oxides as shown in table 1.

Table 1 The element composition of cement

| Cement notation formula | Traditional formula | Name |
|---|---|---|
| C | CaO | Calcium oxide |
| S | $SiO_2$ | Silica |
| A | $Al_2O_3$ | Aluminium oxide |
| F | $Fe_2O_3$ | Iron oxide |
| H | $H_2O$ | Water |
| $ | $SO_3$ | Sulphur trioxide |
| C | $CO_2$ | Carbon dioxide |

In fact, cement powder is “nothing else” other than a combination of oxides of calcium, silicon, aluminium and iron. Using the nomenclature in table 1, the main components of Portland cement are $C_3S$ and $C_2S$ (tri–calcium and dicalcium silicate, also called Alite and Belite); the European standard required for a Portland cement is a $C_3S$+$C_2S$ content of 67%. These are the two phases that develop the main strength during hydration forming a gel like calcium silicate hydrates (C–S–H) and calcium hydroxide ($Ca(OH)_2$ or “Portlandite” or CH): Two other fundamental phases in cement are the C3A and C4AF (calcium aluminates phases and calcium ferrous aluminates phase, also called aluminate and ferrite phases). These react with the calcium sulphate (gypsum, which is added to the ground clinker) to form another two important groups of products: AFm ($Al_2O_3$–$Fe_2O_3$–mono) and AFt ($Al_2O_3$–$Fe_2O_3$–tri), also called monosulfate and ettringite.

**Thermoelectric properties of cement**

SeyedAli Ghahari et al. (SeyedAli Ghahari, et al, 2017, pp. 755–763) were reported the effect of ZnO nanoparticles on thermoelectric properties of cement. The results showed that after adding nanoparticles to the mixture, Seebeck coefficient of cement particles was increased to 17% due to a decrease in the amount of hydration reactions as show in Figure 1. Thermal conductivity was decreased to 9% as show in Figure 2 due to decreased density and crystallinity of materials, and electrical conductivity was increased to 37% compared to that of plain cement paste because of the increased movement of ions as show in Figure 3. The apparent thermoelectric properties in ZnO–cement composites indicated its potential use for thermal energy harvesting in concrete structures and pavements.

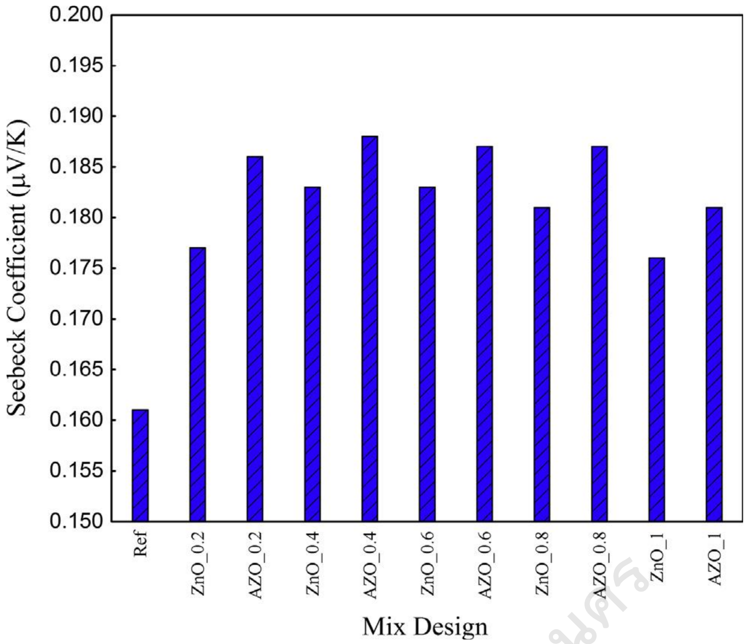


Figure 1 Seebeck coefficient calculated at the age of 28 days

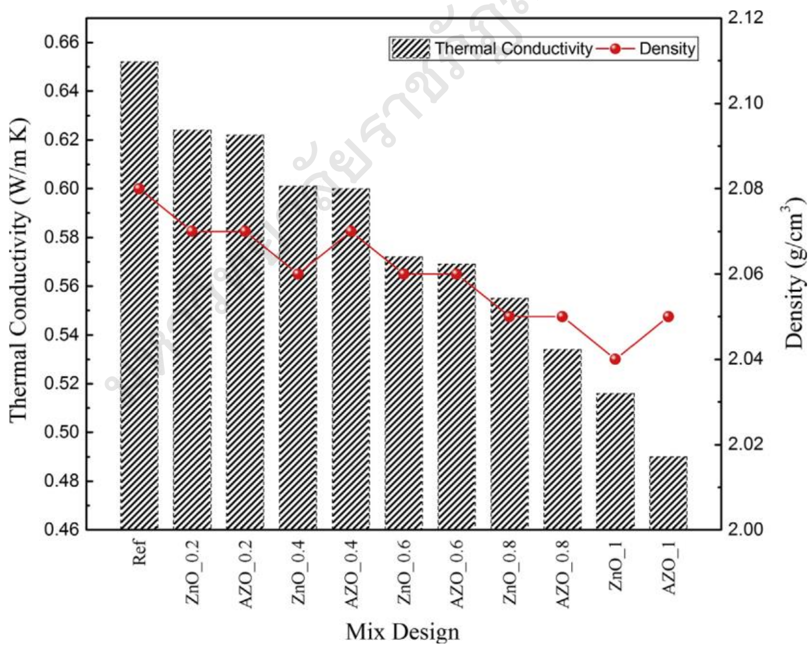


Figure 2 Thermal conductivity of the samples at the age of 28 days

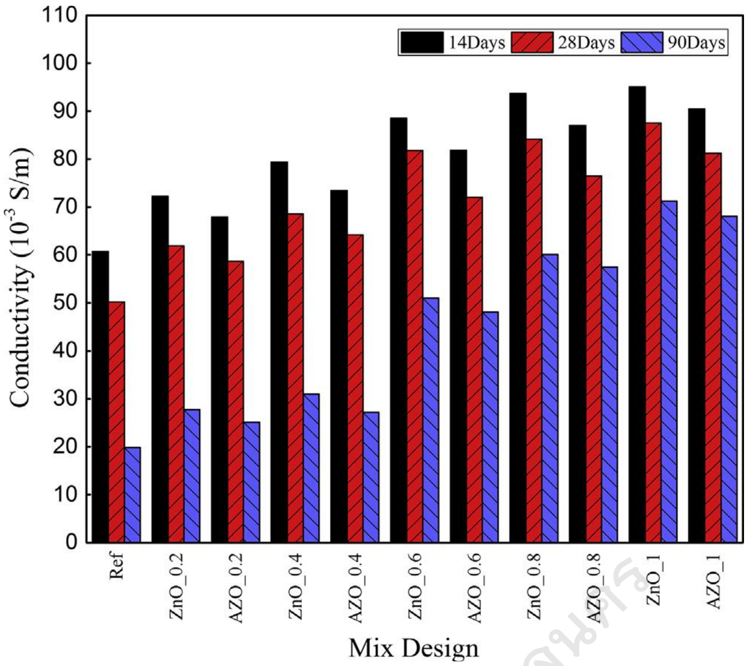


Figure 3 Electrical conductivity vs. ZnO (wt%) and AZO (wt%) at the age of 14, 28, and 90 days

Jian Wei et al. (Wein J., Hao L., He G., Yang C., 2014; pp. 8261–8263) were reported thermoelectric properties of expanded graphite/cement-based composites (EGCC) fabricated by special dry-pressing and curing methods Hall coefficients of the cement-based composites were measured. Results showed that EGCC exhibits a distinct semiconducting electrical behavior, the relatively high Seebeck coefficient at a temperature range of 30–100 °C as shown in figure 4 and extremely high electrical conductivity of 24.8 S/cm for cement-based materials as shown in figure 5. The higher power factor and thermoelectric figure of merit $6.82 \times 10^{-4}$ were then achieved in the case of keeping thermal conductivity of 3.213 $Wm^{-1}K^{-1}$, while the EGCC held ahigh compressive strength (106.51 MPa). The excellent thermoelectric property of EGCC has promising prospects for alleviating the urban heat island effect by harvesting and converting solar radiation thermal energy in large-scale, and thus decreasing cooling energy demand of cities.

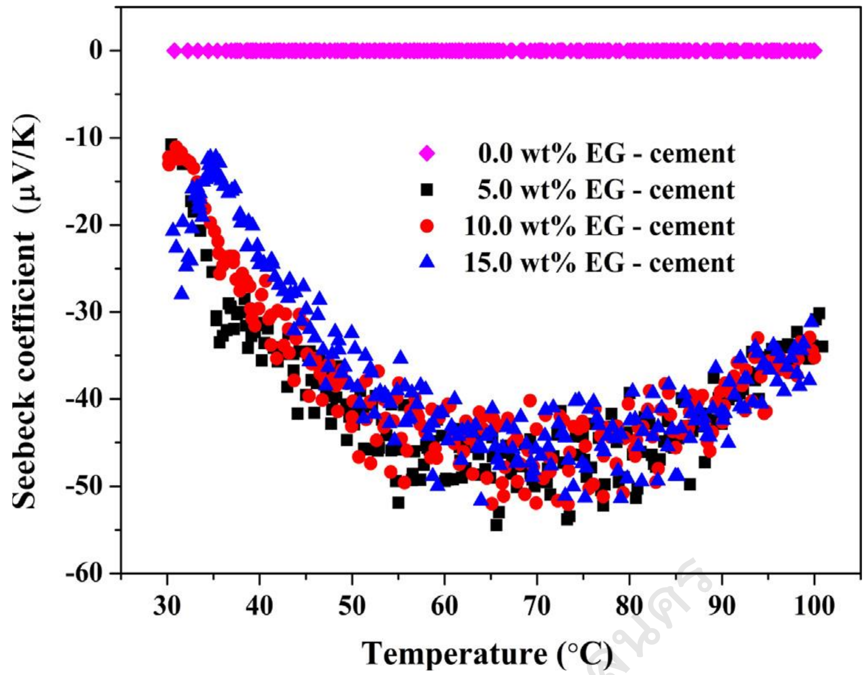


Figure 4 The Seebeck coefficient of EGCC depend on temperature

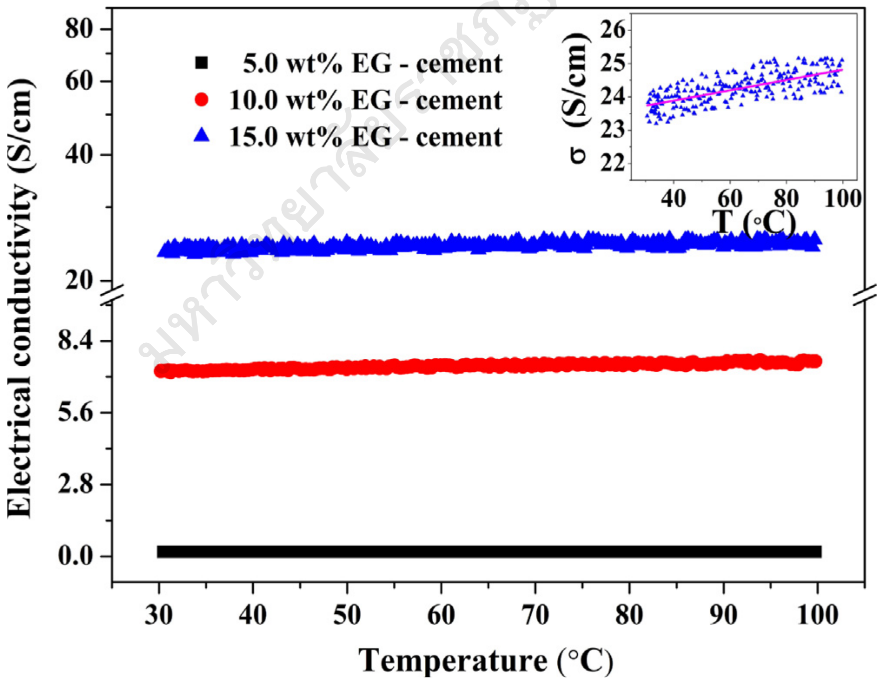


Figure 5 The electrical conductivity of EGCC depend on temperature

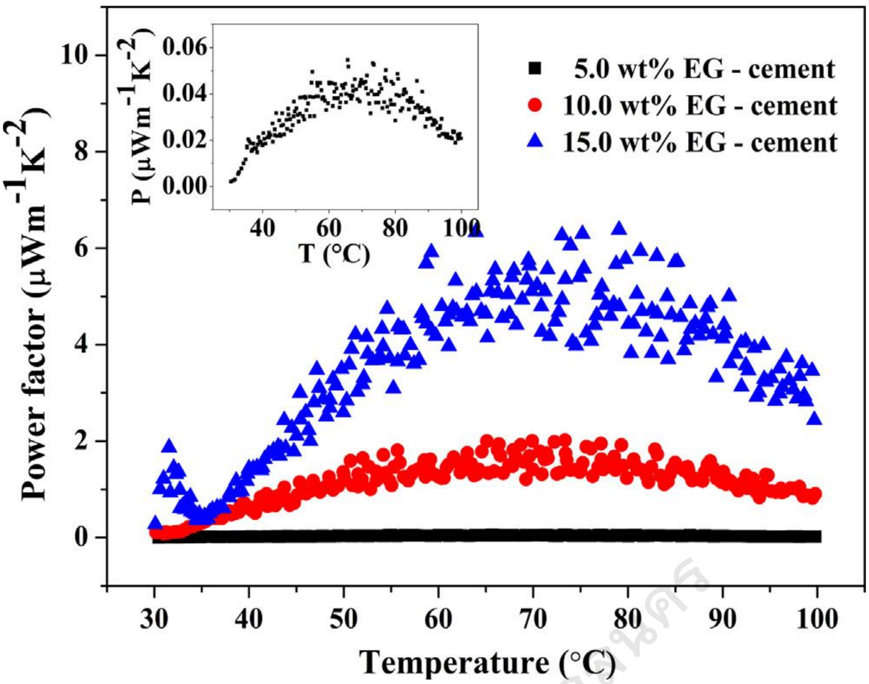


Figure 6 The power factor of EGCC depend on temperature

Jian Wei et al. (Wei J., Zhang Q., Zhao L., Hao L., Nie Zh., 2017, pp. 10763–10769) were added Carbon nanotubes (CNTs) with weight percent of 5.0%, 10.0% and 15.0% into the cement matrix to fabricate CNT reinforced cement-based composites (CNTs/CC) by mixing and dry compression shear methods. Seebeck coefficient, electrical conductivity and thermal conductivity of the as-received CNTs/CC were measured and analyzed. The CNTs/CC exhibits the thermoelectric behavior of p-type semiconductor. CNTs were dispersed uniformly in cement matrix by compression shear stress, which promoted a relatively high electrical conductivity (0.818 S/cm), Seebeck coefficient (57.98 μV/°C) and power factor of CNTs/CC as shown in figure 7, 8 and 9, respectively. Combining with their lower thermal conductivity ranged from 0.734 to 0.947 $Wm^{-1}K^{-1}$, the CNTs/CC shows the highest thermoelectric figure of merit (ZT) has reached $9.33 \times 10^{-5}$, Which is benefit to the applications in large-scale energy harvesting in the buildings and pavements with low cost in the future cities.

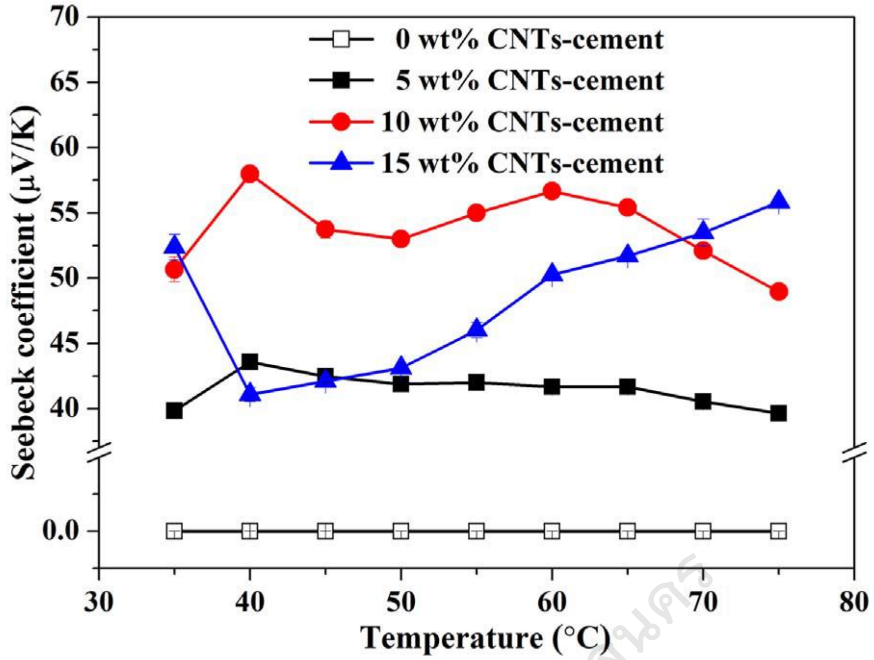


Figure 7 The Seebeck coefficient of CNTs/CC depend on temperature

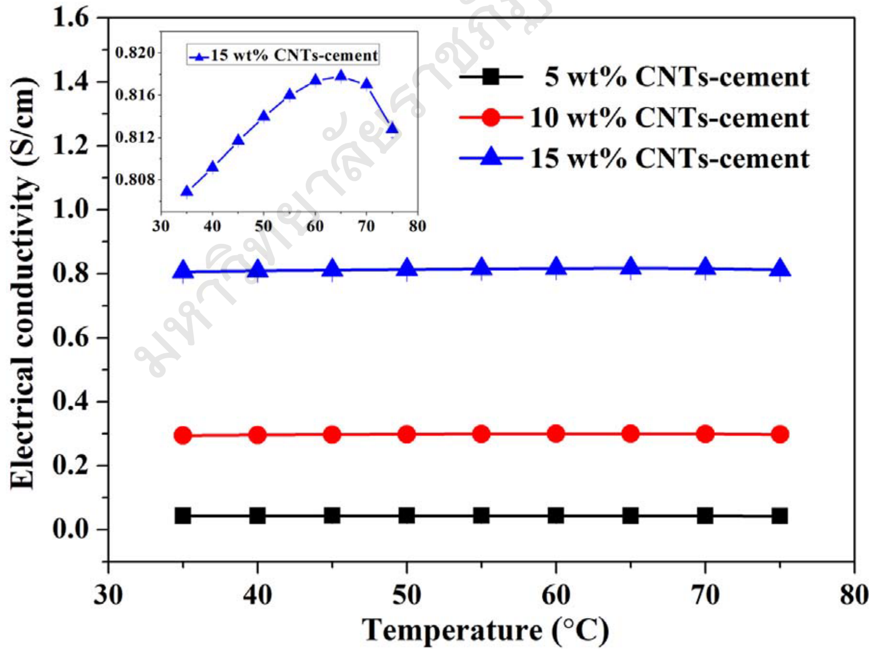


Figure 8 The electrical conductivity of CNTs/CC depend on temperature

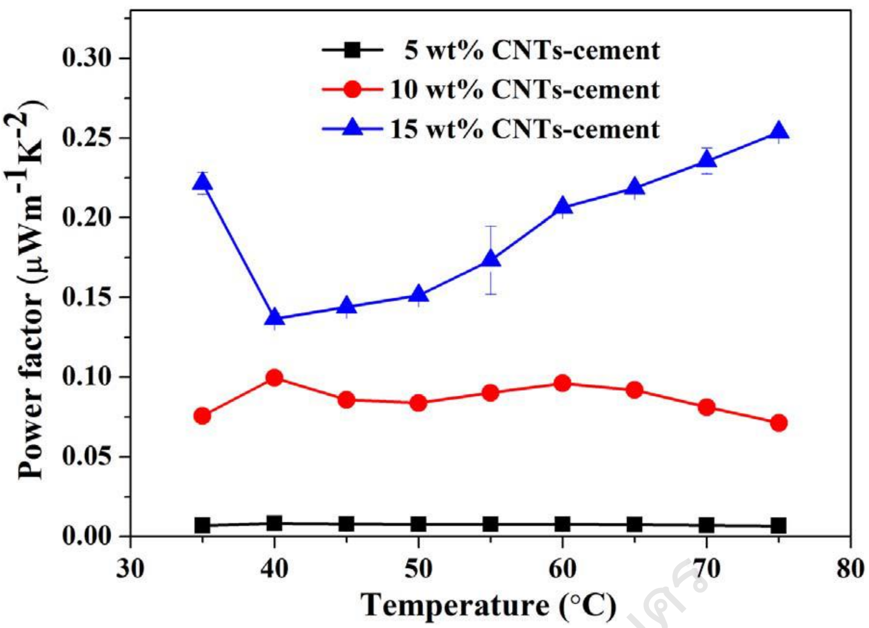


Figure 9 The power factor of CNTs/CC depend on temperature

**Zink Oxide**

Zinc oxide is a typical representative of multifunctional oxide materials. Currently, worldwide production of zinc oxide exceeds one million tons and the range of applications is very broad. Zinc oxide is used as an additive in rubber, in cement and concrete production, as a white pigment in paints, in electronics, in sensors, as a catalyst of some organic reactions, as UV absorption additive in cosmetics, in pharmacy, as a component of food supplements for humans and in many other areas. An important stimulus for the increased interest in zinc oxide was the recent development in nanotechnology leading to nanostructured forms of ZnO (nanoparticles, nanowires, nanolayers, nanocomposites, etc.), expanding the range of potential applications. Reducing particle sizes below 100 nm is associated with significant changes in physical and chemical properties of zinc oxide. This paper provides a comprehensive overview focused on thermodynamic properties of nanostructured ZnO. Within the top-down approach using a simple thermodynamic model, this paper interprets literary data on the influence of ZnO nanoparticle size and shape on the on the structural and chemical stability, solubility in water and aqueous solutions, and mutual miscibility with other oxides of metallic elements. At atmospheric pressure, crystalline zinc oxide is thermodynamically stable in hexagonal wurtzite structure of ZnO (wz) (space group P63mc), for which the lattice parameters have been experimentally and theoretically determined several times. These data do not differ significantly from average values a = 0.325 nm and c = 0.521 nm yielding the unit cell volume V cell= $4.766 \times 10^{-2}$ $nm^3$, molar volume Vm= $1.435 \times 10^{-5}$ $m^3mol^{-1}$ and theoretical density d = 5671.7 kg $m^{-3}$.

The above-mentioned properties of ZnO, its structural and chemical stability, solubility in aqueous solutions, and miscibility with other metal oxides are dependent on the size and shape of the ZnO particles. These experimentally proven dependences were interpreted within the top-down approach using a simple thermo-dynamic model. Numerous simplifications have been used in the calculations, for example, particles were always assumed as surface is otropic spheres, but there are also approaches to approximate the shape of the particles to reality, e.g. using the so-called shape factor. Let us note that these phenomena can be described by other theoretical models within the top-down approach orbased on the theoretical (ab initio) or semiempirical (molecular dynamics) calculations. In addition, there are a number of other physical properties of ZnO that show this size-dependent effect. Using BOLS (top-down approach) the experimentally determined or theoretically calculated dependences of Young's modulus, width of band-gap and Raman shift on the size and shape of ZnO nano-structures have been interpreted. The ability to influence the mechanical, electrical and optical properties of ZnO by controlling the size and shape of their particles extends the application potential and detailed studies of these phenomena will be in focus of both basic and applied material research (Leitnera J., Bartunek V., Sedmidubsky D., Jankovsky O., 2018, pp. 1–11).

Urai Seetawan et al. (Urai Seetawan, et al, 2011, 1599-1603) were reported the effect of annealing temperature on the crystallography, particle size and thermopower of bulk ZnO. The powder of bulk ZnO exhibited good distribution of particles after being annealed below 600 °C and covered with the nanoparticles, while other portions retained the smooth morphology. The particle sizes increased from

73.50 to 79.67 nm with increase in annealing temperatures from 400 °C to 650 °C as show in Figure 10. The bulk ZnO has highest thermopower of −92.99 mVK−1 at room temperature for annealing temperature of 550 °C and indicating that the behavior of the n-type thermoelectric material as show in Figure 11.

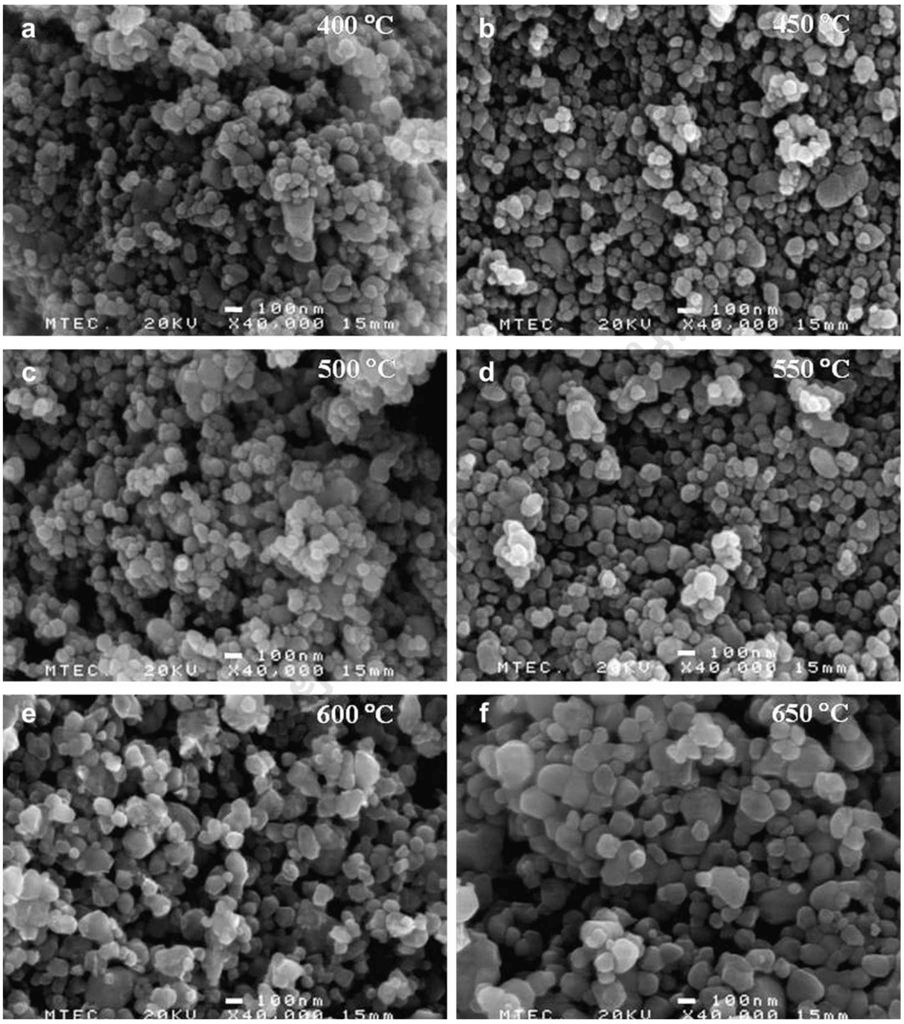


Figure 10 SEM morphology of powder of bulk ZnO after anneling at (a) 400 °C, (b) 450 °C, (c) 500 °C, (d) 550 °C, (e) 600 °C and (f) 650 °C

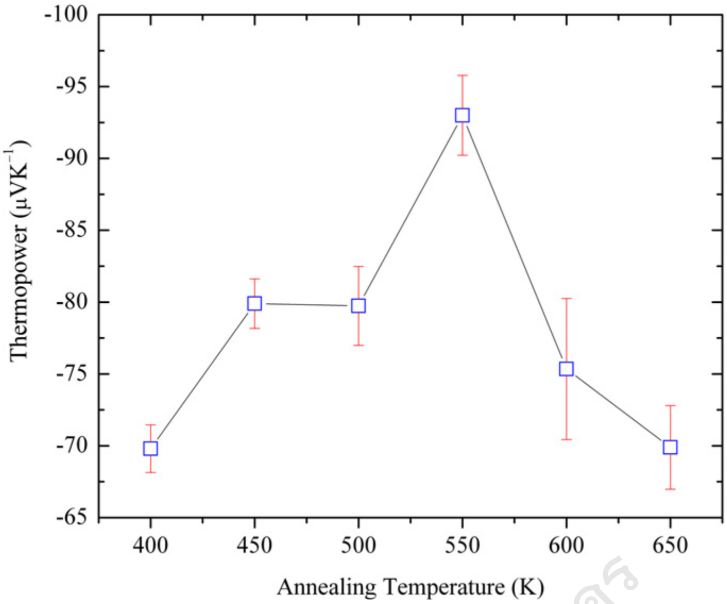


Figure 11 The thermopower depend on annealing temperature