



Faculty of Sciences

Department of Physics and Astronomy

**SEMICONDUCTOR METAL OXIDE – POLYMER COMPOSITE
SUPERLATTICE-LIKE THERMOELECTRIC DEVICES**

by

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DECLARATION REGARDING THE WORK AND COPYRIGHT

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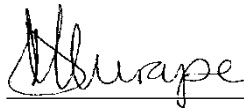
CERTIFICATION

The undersigned certifies that they have read and hereby recommends for acceptance by the Faculty of Sciences a Thesis titled: Semiconductor metal oxide – Polymer composite superlattice-like thermoelectric devices, in fulfilment of the requirements for the degree of Master of Science in Physics (MSc Physics) of the Botswana International University of Science and Technology.

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ABSTRACT

The ultimate success in the drive towards a greener and sustainable global environment can only be achieved if a significant portion of the 70 % waste energy that is lost as heat from various industrial and commercial devices is recovered and is converted into useful applications. This ambitious goal requires more efficient and affordable thermoelectric devices that operate in the lower midrange (150 – 300 °C) temperatures. This work focuses on contributing to the development of non-toxic semiconductor and conducting polymer composite thermoelectric device arranged in mixture form and in a layered structure (superlattice-like) to meet the desired goal. Through morphology manipulation at nanoscale and conducting polymer addition, the figure of merit (ZT) of thermoelectric devices was manipulated to produce high performing devices that operate in the lower midrange temperature where most of the commercial devices are used.

This study achieved this goal by using CuO since it has high Seebeck coefficient (S), and it is a cheap and environmentally friendly material. The figure of merit of CuO was enhanced by lowering thermal conductivity through: (1) nano-structuring, by varying the precursor concentration from 1: 0.2 M to 1: 0.8 M and (2) morphology manipulation by varying the decomposition temperature from 95 °C to 135 °C, and (3) combining CuO and polyaniline to form a composite material. CuO powders were synthesized using hydrothermal method and structural properties were studied using X-ray diffraction (XRD) and scanning electron microscopy (SEM) characterization analysis, which showed that crystalline size increased with temperature and decreased with increase in precursor concentration. Surface morphology changed from ellipsoidal to nanorods when decomposition temperature was increased. Furthermore, the synthesized CuO powders were mixed with 5.6wt% polyaniline (PANI) and were sintered into pellets using spark plasma sintering and ultimately the thermoelectric properties of pellets were studied.

The influence of morphology manipulation on the thermoelectric parameters of CuO nanoparticles was investigated. Thermal conductivity of CuO was lowered when morphology changed from nanorods to ellipsoidal. Thermal conductivity below 10.4

W/mK was reached for CuO with ellipsoidal morphology. Crystal size increased slightly from 16.05 nm to 18.60 nm when decomposition temperature increased from 100 °C to 135 °C. This change in crystal size affected the electrical conductivity of the metal oxide. High values of electrical conductivity were recorded for CuO with crystal size of 16.05 nm. The influence of adding PANI to the CuO was also investigated. Thermal conductivity reduced to below 8.8 W/mK, and electrical conductivity was improved by 10^6 times when PANI was mixed with CuO, however the Seebeck coefficient reduced by a factor of 10^2 . Maximum ZT of $\sim 5 \times 10^{-4}$ was achieved at 200 °C for CuO mixed with PANI compared to maximum ZT of $\sim 2 \times 10^{-5}$ for CuO without PANI. This study has opened opportunities for development of CuO based polymer composites at low temperature for thermoelectric applications.

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DEDICATION

This research work is dedicated to my family, who have been my pillar of strength, and who continually provide their moral, spiritual, emotional, and financial support.

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LIST OF ABBREVIATIONS AND SYMBOLS

°C - Degrees Celsius

CuO – Copper oxide

M – Molarity

wt% - Weight percentage

XRD – X-Ray diffraction

SEM – Scanning electron microscope

PANI – Polyaniline

W/mK – Watts per meter kelvin

ZT – Figure of merit

HCFCs – Hydrochlorofluorocarbons

UV – ultraviolet

TED – Thermoelectric device

S – Seebeck coefficient

σ - Electrical conductivity

k – Thermal conductivity

T – Temperature

ZnO – Zinc oxide

emf – Electromotive force

TEC – Thermoelectric cooler

DC – Direct current

h – Plank’s constant

W/A – Watts per ampere

k_B – Boltzmann’s constant

m^* - Effective mass

μ – Mobility of charge carrier

E_G – Energy band gap

l – Mean free path

P_{ret} – Return probability

k_e – Electronic thermal conductivity

k_l – Lattice thermal conductivity

L_0 – Lorentz’s factor

PEDOT: PSS – Poly (styrenesulfonate)

SPS – Spark plasma sintering

FAST – Field assisted sintering technology

λ – Wavelength

FWHM – Full width at half maximum

EDS – Energy dispersive

V/K – Volts per kelvin

S/m – Siemens per meter

CHAPTER 1

1.0 Introduction

Energy is defined as the capacity to carry out a task[1]. It exists in different forms such as light, heat, chemical and electrical energy etc[2]. A large percentage of energy generated today is from fossil fuels such as petrol, diesel, coal, etc. However, these energy sources are harmful to the environment as they release greenhouse gases, moreover, they will get depleted which poses a major challenge in the future [3]. Emission of greenhouse gases like carbon dioxide, methane, nitrous oxide, and nitrogen oxides from burning fossil fuels in industries and during transportation and various industrial applications, pollute the air in the atmosphere, see Figure 1.1a and b [4].



Figure 1.1: Images showing (a) Air pollution due to greenhouse gases from industry, (b) Air pollution caused by greenhouse gases from car exhausts, and (c) Rise in sea level due to global warming caused by environmental pollution.

Greenhouse gases, such as carbon dioxide, in the atmosphere keeps the planet at a suitable temperature for the development of life by trapping thermal radiation emitted by the Earth's surface after being heated by the sun, however, an increase in the amount of these gases in the atmosphere as a result of air pollution causes them to trap more heat causing global warming resulting in climate change. As the Earth's temperature rises due to greenhouse gases, water heats up and expand causing sea levels to rise [5]. Figure 1.1c shows flooding caused by the rise in sea level resulting from an excessive amount of heat on earth.

The ozone layer protecting us from ultraviolet (UV) rays from the sun is destroyed by hydrochlorofluorocarbons (HCFCs), allowing more UV rays to reach the earth and this leads to skin cancer, reduced crop yields and impaired immune systems [6].

To mitigate the above challenges, requires a shift towards the use of renewable energy sources like solar, wind and hydropower as the alternative sources of energy [4].

In most industrial machinery today, a large amount of energy (about 70%) is lost in the form of heat from various heat sources like exhaust gases, cooling equipment, and hot equipment surfaces [7]. As a way to try to recover this waste energy, the use of efficient thermoelectric generators has been proposed. Thermoelectric generators (TEG) are devices that can directly convert thermal energy into electrical energy, and they are made from a pair of *n*-type and *p*-type semiconductors which are connected electrically in series and thermally in parallel. These semiconductors use the principle of thermoelectric effects to generate electricity from a temperature gradient. The application of thermoelectric devices (TEDs) will result in a low carbon environment by recovering and re-using this thermal heat, this will in turn reduce energy costs [7]–[9].

The thermoelectric effect is a term that explains the physical principle whereby there is direct conversion of heat energy into electricity or electricity into heat based on the flow of charge carriers (electrons or holes) because of a temperature gradient. When the ends of a material are placed at different temperatures, hot and cold, charge carriers

redistribute in the material and this redistribution of charge carriers creates a voltage. This effect is called the Seebeck effect. The reverse of the Seebeck effect is called the Peltier effect, where a temperature difference is created in a material due to an electric current. The Seebeck effect is used for electric power generation applications while the Peltier effect can be used in refrigeration applications [10].

Thermoelectric devices have other applications in photovoltaic (PV) cells where they can be used to provide additional electric power from waste energy lost from PV cells. One junction of a thermoelectric generator (TEG) is kept at room temperature, while the other is placed in thermal contact with the back of a solar cell (hot side). Electric power is generated from the temperature difference between the two junctions of the TEG. On the other hand, the efficiency of a solar cell is improved. As the temperature increases from room temperature to 100 °C, the efficiency of solar cell is reduced by about 25 %. By using a thermoelectric device which is coupled with a solar cell for a hybrid photovoltaic thermoelectric system, efficiency of the photovoltaic module can be increased [11]. This is another novel application of thermoelectric devices.

1.1 Problem statement

Thermoelectric devices have many advantages over conventional energy conversion systems, they are easy to build and have low maintenance costs as they have no moving parts. Their main shortfalls or disadvantages comes from their low energy conversion efficiency [12], and they are made mostly from toxic materials. The performance of a thermoelectric material is evaluated by the thermoelectric figure of merit, denoted as ZT . At present, the material with the highest ZT is the thin film Heusler alloy of $Fe_2V_{0.8}W_{0.2}Al$ which was prepared by magnetron sputtering. The approximated ZT of this material reached a value nearly 5 in a temperature range of 350 - 400 K, which makes it the best performing material in that temperature range. However, the material has highly toxic elements like tungsten, and it requires more care for thermoelectric applications [13].

Many other attempts so far, including some of the thermoelectric devices available in the market have a ZT value below 5, see Figure 1.2. The best commercially available thermoelectric device is a PbTe based TED with ZT of 2.2 [14]. A lot of research work is currently on going to improve and develop new thermoelectric materials that are not harmful to the environment, are of low cost and have a higher ZT . The above challenges motivated this work.

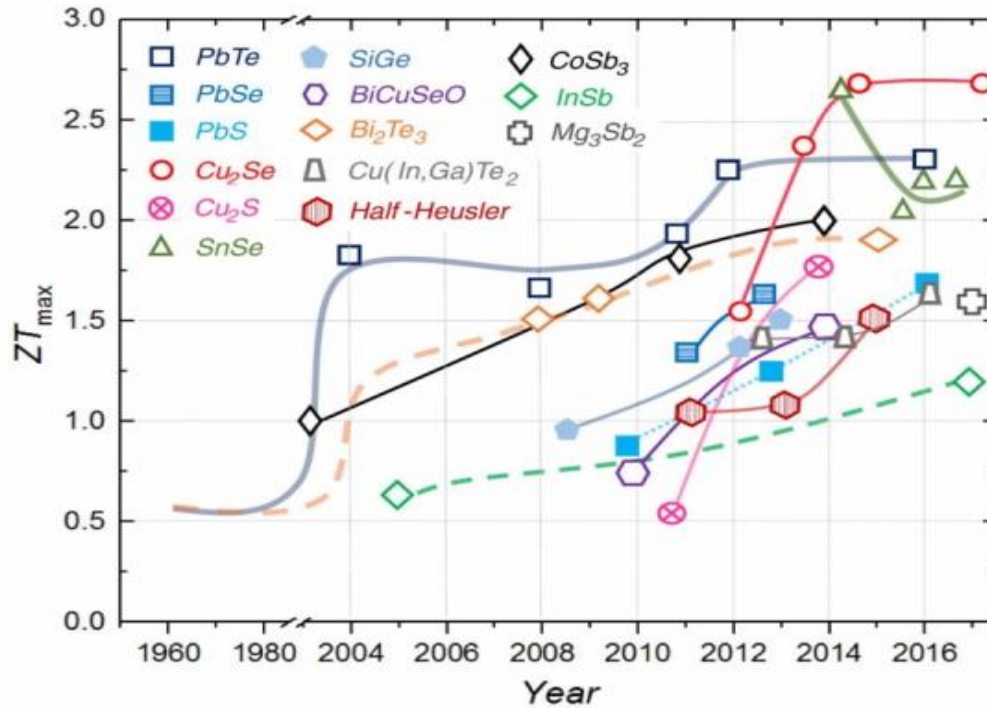


Figure 1.2: Shows ZT of several thermoelectric materials developed over the years [15].

1.2 Objectives

The purpose of this study was to develop low cost and environmentally friendly thermoelectric device with an efficiency higher than what is currently available in the market. As highlighted above most of the best performing thermoelectric devices are not

environmentally friendly. There is therefore a need for novel TEDs that are not toxic and if possible, even renewable. This project aimed at addressing this by developing a thermoelectric material using metal oxides since they are friendly to the environment and of low cost due to their abundance on earth. Copper oxide (CuO) was chosen for this study because it has a higher Seebeck coefficient and lower band gap which are ideal good thermoelectric properties. However, the primary challenge with CuO is the high thermal conductivity which reduces its thermoelectric performance as it cannot sustain a large temperature gradient. This study focused on manipulating the thermoelectric properties by making a copper oxide – polymer composite superlattice-like structure as illustrated in Figure 1.3. A superlattice-like is a structure where two different materials are grown to a specific thickness in alternating layers.

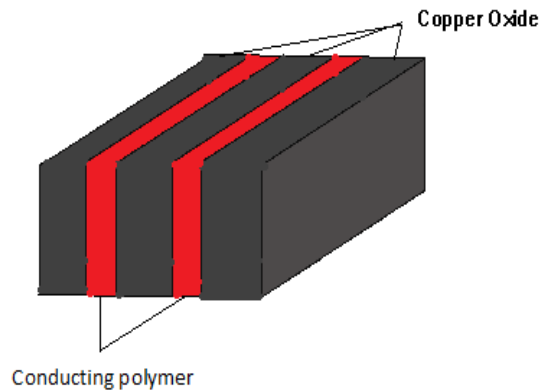


Figure 1.3: *illustration of a copper oxide – polymer composite superlattice-like structure.*

In this structure electrical transport can be maintained and phonon transport be altered. The interface of a super lattice structure is slightly not perfect because of formation of steps or mixing of atoms and for this reason phonons get scattered at these boundaries [16]. This enables the control of all the key parameters in the figure of merit which is defined mathematically as

$$ZT = \frac{S^2 \sigma}{k} T. \quad (1)$$

S is the Seebeck coefficient, σ is electrical conductivity, and k is the thermal conductivity. Lowering the thermal conductivity while maintaining the higher electrical conductivity

and Seebeck coefficient in a layered structure such as the one shown in Fig.1.3, was the hypothesis behind this work.

To achieve the above objective this project explored the idea of morphology manipulation to tune the thermal conductivity of the metal oxide using platelet formations. Nanostructuring has been demonstrated as an effective way to enhance the thermoelectric properties of several materials. Research on controlling thermal properties in nanostructures by manipulating particle morphology has shown interesting results. Research by A. Angayarkanni et al, reported a decrease in thermal conductivity when morphology was changed from nanorods to nanospheres in Al_2O_3 particles [17]. Another study by Li Han et al reported higher ZT values for Al-doped ZnO sample with platelet morphology than the sample with rod like morphology [18]. These studies have shown that thermal conductivity is lower for particles with a shape that has a large surface area as phonons are scattered at the surface boundary.

1.3 Layout of Thesis

This thesis is divided into five chapters, Introduction, Literature review, Methodology, Results and Discussions, Conclusion and Recommendations.

Chapter 1: This introduction, gave a brief background on the importance and disadvantages of current sources of energy on our society. The use of efficient thermoelectric devices in thermoelectric generators to recover waste thermal energy is also explained. It also outlined the motivation, aims and objectives of the study.

Chapter 2: Literature Review, details the theory of thermoelectricity and history of thermoelectric devices. It mainly covers a review of the status of research in enhancing thermoelectric properties of materials through altering the electronic and phonon transport.

Chapter 3: Methodology, gives a detailed description of the methods and techniques used for synthesis, characterization, sintering and thermoelectric measurements of the materials.

Chapter 4: Result and Discussion, presents results obtained from structural and morphological characterization of the materials. Furthermore, the electrical conductivity, Seebeck coefficient and thermal conductivity results will also be given and discussed.

Chapter 5: Conclusion and Recommendations, gives a summary of the project giving the main achievements of the project and some few recommendations for future work.

CHAPTER 2

Literature review

2.0 Theory of thermoelectric devices

2.1 Thermoelectricity

Thermoelectricity is a phenomenon in which a flow of electric charge is generated by temperature difference in a solid material, or a temperature difference is generated by passing electric charge in a material. The two processes involved in thermoelectricity are named after people who discovered them and hence are called Seebeck effect which occurs when electric charge is generated from temperature gradient and Peltier effect which occurs when temperature difference is generated from electric current. Electrons are the elementary charge carriers of electric charge in solids, but unfortunately, they also carry heat energy, which complicates the process of manipulating the figure of merit ZT as it is directly proportional to electrical conductivity and inversely proportional to thermal conductivity as seen earlier in chapter 1 [12].

2.2 Thermoelectric Effects

2.2.1 Seebeck effect and electric power generation

In 1821, Thomas Johann Seebeck observed a deflection of a magnetic needle when placed near a closed circuit of two different metallic conductors, where one of the junctions is being heated. The angle at which the needle is deflected is proportional to the

temperature difference between hot and cold junctions. Seebeck then related this to thermomagnetism, but later Oersted provided a correct explanation that the electric current in the circuit is because of heat and hence he named this phenomenon thermoelectricity. Consider a circuit of two different conducting materials A and B connected as shown in Figure 2.1.

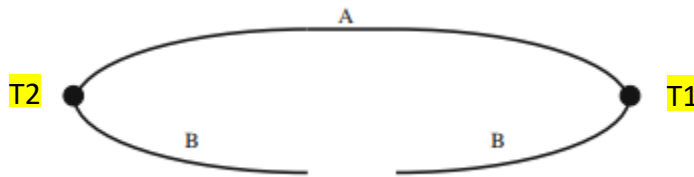


Figure 2.1: *Schematic of a basic thermocouple.*

If one of junction is heated to maintain a temperature difference, an electromotive force (emf) V will be produced. This is due to the fact that when a metallic material experiences a temperature difference ΔT ($T_1 - T_2$), a proportional potential difference, voltage ΔV is developed:

$$\Delta V = S \Delta T, \quad (2)$$

Where S is the proportionality coefficient called Seebeck coefficient and its units are expressed as $V.K^{-1}$. The Seebeck coefficient can either be negative or positive depending on majority of charge carriers, negative for negatively charged carriers (electrons) and positive for positively charged carriers (holes) [12].

Using Seebeck effect, thermal energy can be converted to electrical energy and that is thermoelectric power generation. Figure 2.2 shows that when one junction of the thermocouple is heated, a thermoelectric voltage is induced in proportion to the temperature difference. If a load is connected to the thermocouple, the electric power is consumed at the load and the thermoelectric material acts as a battery, where thermoelectric power corresponds to electro motive force (emf), and resistivity corresponds to internal resistance [12].

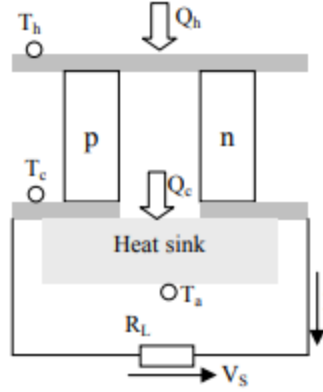


Figure 2.2: *The schematic picture of thermoelectric heating.*

If the emf V_s is closed by a resistive load R_L , then the generated electric power P is expressed as

$$P = I^2 R_L = \left(\frac{V_s}{R_L + R_I} \right)^2 R_L. \quad (3)$$

where R_I is the internal resistance of the thermoelectric couple [19]. This project's work is mainly focused on the Seebeck effect, however a brief discussion about the opposite of Seebeck effect, which is the Peltier effect is given for completeness.

2.2.2 Peltier effect and thermoelectric cooling

A few years later after the discovery of Seebeck effect, Jean Charles Athanase Peltier found in 1834 the reverse of Seebeck effect and named it the Peltier effect. Peltier found that when electric current is passed through two different conducting materials, heat is absorbed at the other junction and emitted at the other junction. From Figure 2.2, if the resistive load R_L is replaced by voltage V , electric current I will flow around the circuit and one junction will be heated to Q_h while the other junction is cooled to Q_c . The ratio of I to Q is the Peltier coefficient (π) given by:

$$\pi = I/Q. \quad (4)$$

The Peltier coefficient is positive when T_h is greater than T_c and its units are watts per ampere, W/A or volts, V [12].

More electricity is required to meet the demand of refrigeration worldwide in the field of air conditioning, food preservation, medical storage etc. To reduce the use of electricity, thermoelectric cooling and heating can be used as new alternative for refrigeration.

Thermoelectric cooling devices are based on Peltier effect as already alluded to earlier, and they are made up of semiconductor placed in between two conducting materials, copper is usually used. Semiconductors are chosen because they can be optimized for pumping heat and because the type of majority charge they carry can be chosen. The semiconductor is connected to the two-conducting material, so when voltage is applied heat is transported in the direction of current flow. Thermoelectric cooler (TEC) has n -type and p -type semiconductor junctions connected by conducting strips which are electrically in series and thermally in parallel (Figure 2.2). When DC power is applied to the thermoelectric cooler, one junction gets heated, and the other junction is cooled as heat is transferred from one side of the TEC to the other [20].

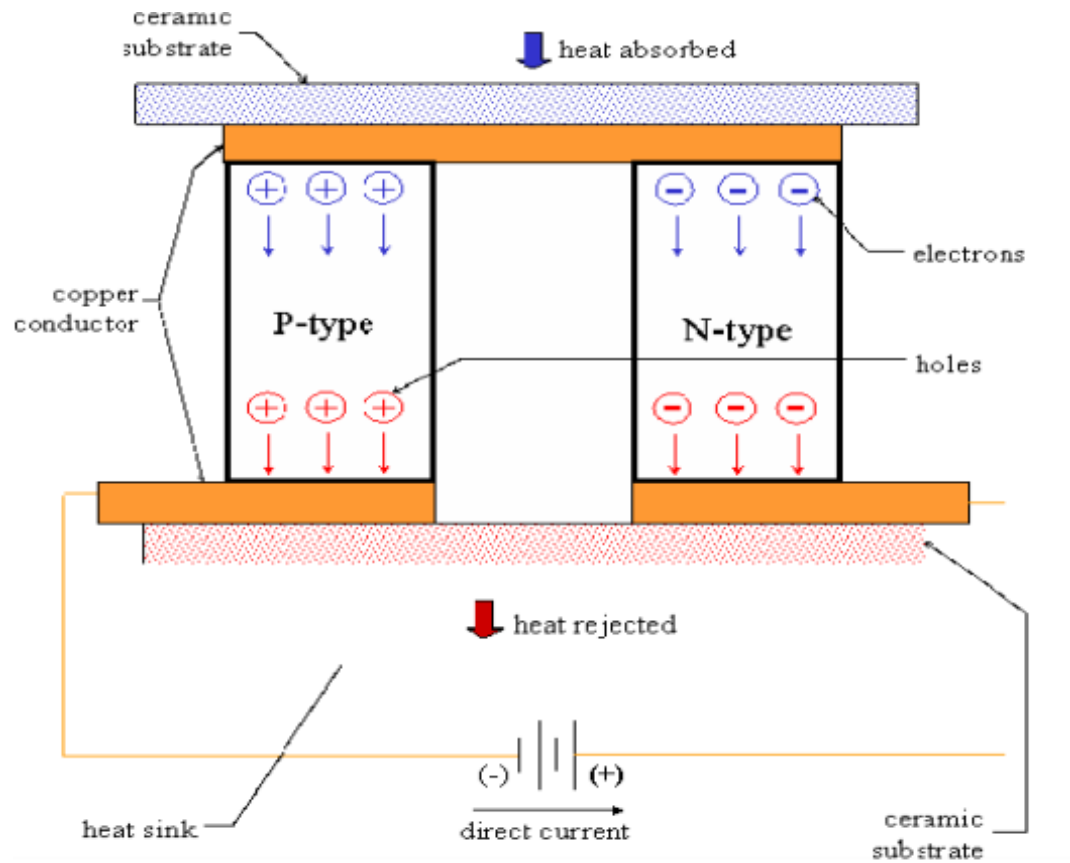


Figure 2.3: A schematic diagram of thermoelectric cooler [20].

2.2.3 Thomson effect

Another related effect was discovered by William Thomson later known as Lord Kelvin in 1851. He found out that there is a relationship between the descriptions of the Seebeck effect and Peltier effect, he found out when doing theoretical analysis that there is an additional effect from the relationship between the two effects and named that effect, the Thomson effect. When electric current is passed through a conducting material subjected to a temperature gradient ∇T , heat Q is generated or absorbed along the conductor. The rate at which heat is absorbed or generated is given by

$$\frac{dQ}{dt} = -\tau j \cdot \nabla T, \quad (5)$$

Where τ is the Thomson coefficient and j is the current density. Thomson found that the three coefficients governing the effects described above are related [12], [21]:

$$\pi = ST \quad (6)$$

$$\tau = T \frac{dS}{dT} . \quad (7)$$

2.3 THERMOELECTRIC DEVICES

2.3.1 Thermoelectric generators

As mentioned earlier a thermoelectric generator is a device that convert heat into electricity. It is manufactured using two thin ceramic plates and a series of n -type and p -type semiconductor materials sandwiched between the plates as shown in the Figure 2.4. Ceramic plates add rigidity to thermoelectric generator and conduct heat well, they have high electrical resistance. The n -type semiconductor material has an excess of electrons while the p -type semiconductor material has an excess of holes. One p -type and one n -type make a thermocouple. A generator can have one to several thousands of thermocouples. The thermoelectric couples are connected electrically in series and thermally in parallel as mentioned earlier [22].

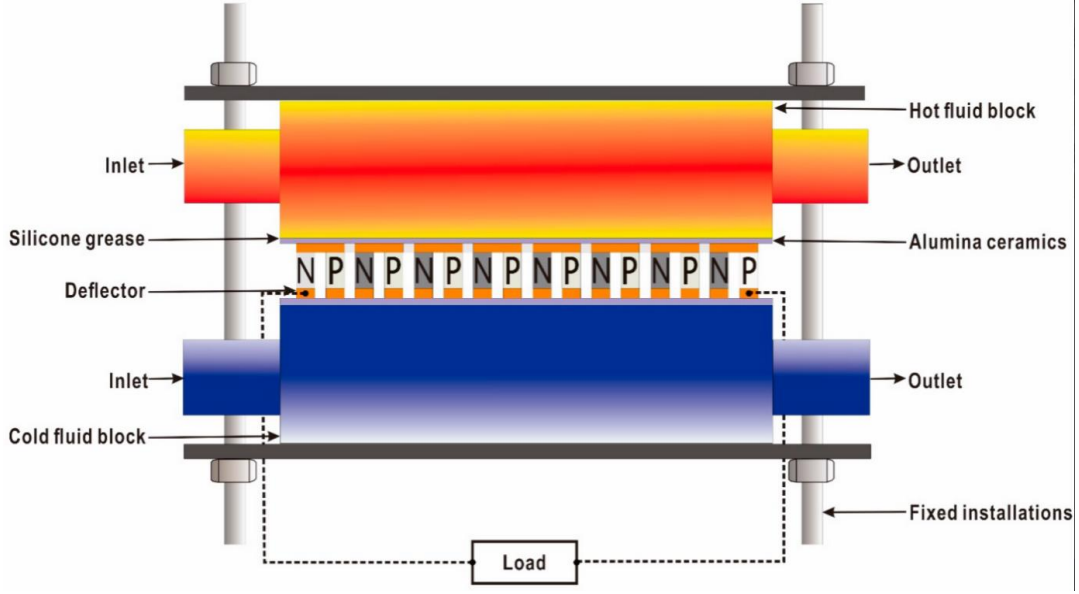


Figure 2.4: *Thermoelectric generator [22].*

The maximum efficiency η of the thermoelectric generator with its cold and hot sides maintained at temperature T_H and T_C is given as

$$\eta = \frac{T_H - T_C}{T_H} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_C}{T_H}} \quad (8)$$

Where ZT is the thermoelectric figure of merit and T_C and T_H are temperatures at cold and hot junctions respectively [12].

2.4 THERMOELECTRIC FIGURE OF MERIT

The efficiency of a thermoelectric material is determined by the dimensionless figure of merit ZT as shown in equation 1. The numerator $S^2\sigma$ is known as the power factor which must be high for a more efficient device. However, this is not easy to achieve as increasing sigma (σ) also usually means an increase in thermal conductivity. This is because these parameters are interdependent on each other primarily because charge carriers are also carriers of heat as shall be explained in later sections [23].

2.4.1 Seebeck coefficient

The Seebeck coefficient of the material is the ratio of generated thermoelectric voltage to the temperature difference across the material. A good thermoelectric material usually has the Seebeck coefficient in the range of hundreds of $\mu V/K$, and is given by:

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{2/3}, \quad (9)$$

Where k_B is the Boltzmann's constant, m^* is the effective mass of the carrier, e is the carrier charge, h is the plank's constant, T is the temperature, and n is the carrier concentration. From the equation 9, it can be seen that, at a given temperature the Seebeck coefficient is directly proportional to the effective mass and inversely proportional to the carrier concentration, the other parameters are constants. That is

$$S \propto \frac{m^*}{n^{2/3}}. \quad (10)$$

For the material to have a high Seebeck coefficient, it should have a higher effective mass and a lower carrier concentration, this aspect shall be discussed later in Chapter 4 during the discussion of the results [24].

2.4.2 Electrical conductivity

The electrical conductivity σ is the measure of the ability of the material to conduct electric current. The inverse of the electrical conductivity is the electrical resistivity ρ , and electrical conductivity is defined as

$$\sigma = \frac{1}{\rho} = ne\mu, \quad (11)$$

Where n is the carrier concentration, e is the charge carrier, and μ is the mobility of charge carrier and is given by:

$$\mu = \frac{e\tau}{m^*}. \quad (12)$$

where τ is the average time between the collisions and m^* is the effective mass[24]. In this discussion on the material development a lot of attention shall be considered of this parameter.

2.4.3 Electrical transport mechanism in semiconductor materials

To fully understand the behavior of thermoelectric devices or materials, some in-depth look at the possible transport mechanism is needed.

In semiconductors, with small energy bandgaps charge carriers get thermally excited to the conduction band where they are free to move hence taking part in conduction governed by a thermally activated mechanism known as Arrhenius behavior. Conductivity in semiconductors is given as

$$\sigma = \sigma_0 \exp\left(-\frac{E_G}{2k_B T}\right), \quad (13)$$

Where E_G is the energy band gap, σ_0 is a constant and k_B is Boltzmann's constant[24].

In a layered, super lattice or composite structure, the electrical conductivity can be complicated because of dissimilar materials, it means several conduction mechanisms such as hopping or weak localization can be significant.

Hopping conduction mechanism often occurs at low temperatures in a disordered system where the disorder causes localization of electron states. In this system charge transfer takes place in a localized energy region within the energy gap of the material and not in the conduction band, and here a charge is transported by hopping of the charge carriers from one localized site to another [25], [26]. There are different types of hopping conduction mechanisms which are Mott's variable range hopping and Efros-Shklovskii variable range hopping [27].

The variable range hopping conduction in general, can be characterized as

$$\rho(T) = \rho_0 \exp[T_0/T]^{1/\rho} \quad (14)$$

where $\rho(T)$ is electrical resistivity, ρ_0 is a prefactor, and T_0 is a characteristic temperature.

In Mott's variable range hopping theory, the parameter ρ in equation 14 is 4, for a constant density of states at the fermi level in a 3D system. However, in Efros-Shklovskii's theory the parameter is expected to be 2 because at low temperatures the density of states around the fermi level is not constant in all dimensions [27]. At high temperatures the nearest -neighbor hopping model dominates.

Transport of electrons in a solid can be classified by 1; the electron mean free path l , which is the average distance an electron can travel before being scattered, 2; The phase coherence length l_ϕ , which is the average distance an electron moves maintaining its phase coherence, and 3; the size of the sample L . In a ballistic transport regime, electrons can travel through the material without being scattered if $l \gg L$, and if $l \ll L$, electrons get scattered and diffuse through the material, resulting in diffusive transport regime. This diffusive transport can be classified into two forms: (1) semiclassical diffusion ($l_\phi \leq l$) which is defined by the Drude conductivity. If $l_\phi \gg l$, electrons maintain their phase coherence after being scattered and this is referred to as (2) quantum diffusive regime. In this regime, coherent backscattering of electrons leads to weak localization effect which lead to a correction in the conductivity [28]. The expression for weak localization correction can be obtained through evaluating the return probability of all paths an electron can travel. The coherent return probability P_{ret} at zero magnetic field can be given as

$$P_{ret} = \frac{1}{4\pi D} \ln \left(\frac{\tau_\phi}{\tau_e} + 1 \right), \quad (15)$$

Where D is the diffusion constant, τ_e is the short time cut-off, below which no elastic scattering occurs, and τ_ϕ is the phase coherence time cut-off, beyond which phase coherence is lost. If $\tau_\phi \gg \tau_e$ at low temperatures, then it leads to logarithmic weak localization correction of the conductivity which is expressed as

$$\delta\sigma = -\left(\frac{4e^2D}{h}\right)P_{ret} \cong -\left(\frac{e^2}{\pi h}\right)\ln\left(\tau_\phi/\tau_e\right), \quad (16)$$

where h is the plank's constant [29].

Weak localization conduction mechanism occurs at low temperatures and its effect is revealed by a decrease in conductivity at low temperatures [30]. It is found in thin metallic films, alloys and composites such as Cu-CuO, $Al - Al_2O_3$, it is also found in heavily doped semiconductors [31].

2.4.4 Thermal conductivity

Another important parameter to consider when dealing with thermoelectric device is the thermal conductivity. This is the ability of the material to transfer heat from its hot region to cold region. The transfer of heat in the material is either through electrons and/or lattice vibrations also known as phonon vibrations. It can be expressed as

$$k = k_e + k_l \quad (17)$$

Where k_e is thermal conductivity due to electrons and k_l is thermal conductivity due to lattice vibrations, the two parameters are defined as

$$k_e = \frac{\pi^2 n^2 k_B^2 T \mu}{e}, \quad (18)$$

$$k_l = \frac{Cvl}{3}. \quad (19)$$

Where C is phonon heat capacity per unit volume, v is the average phonon velocity, and l is the phonon mean free path. Thermal conductivity due to phonons increases as temperature decreases. This is so because when temperature decreases few phonons gets excited hence phonon mean free path becomes high. On the other hand, k_e is proportional to temperature. It is this difference in the two components of k which this project explored.

Thermal conductivity and electrical conductivity are related by Wiedemann law.

$$k_e = L_0 \sigma T, \quad (20)$$

Where L_0 is constant called the Lorentz's number, and its value is $2.4 \times 10^8 J^2 K^{-2} C^{-2}$ [24].

2.4.5 Thermal transport mechanisms

In a solid material, electric current is carried only by charge carriers, whereas thermal transport is due to both charge carriers and phonons. The electronic thermal conductivity dominates over the lattice thermal conductivity in materials that has large electron density like in pure metals such copper. The heat conduction occurs through the electron carrier transport, while the lattice thermal conductivity dominates in materials with less or no free electrons to carry heat like semiconductors and insulators [32]. Lattice thermal conductivity is referred to as heat conduction in solids through vibrations of the lattice ions. The Debye model describes a classical gas where heat is transferred by phonons and phonons are treated as gas particles. In a classical gas, phonon mean free path is limited by the collisions between phonons themselves or phonons with lattice imperfections, unlike in an ideal gas where there is no collision between the particles and if this was the case for a classical gas where phonon mean free path is not limited by any collisions then the lattice thermal conductivity will be infinite. Lattice thermal conductivity in classical model proposed by Debye is given as

$$k_l = \frac{C v l}{3} \quad (219)$$

where symbols have their usual meanings. As mentioned earlier the phonon mean free path is limited by collisions between phonons themselves and collisions between phonons and lattice imperfections. It is assumed that these mechanisms are additive, and the total mean free path can be expressed as

$$\frac{1}{l_{tot}} = \frac{1}{l_{ph-ph}} + \sum \frac{1}{l_{ph-def}} \quad (21)$$

where l_{ph-ph} is phonon mean free path limited by collisions between the phonons and l_{ph-def} is the one limited by collisions between phonons and defects in the material [33].

The phonon mean free path is dependent on temperature however the thermal conductivity expression in equation 19 does not show the temperature dependence of thermal conductivity. This dependence is discussed based on Figure 2.5 showing four stages (A, B, C, and D) of thermal conductivity with temperature. Where θ_D is Debye temperature.

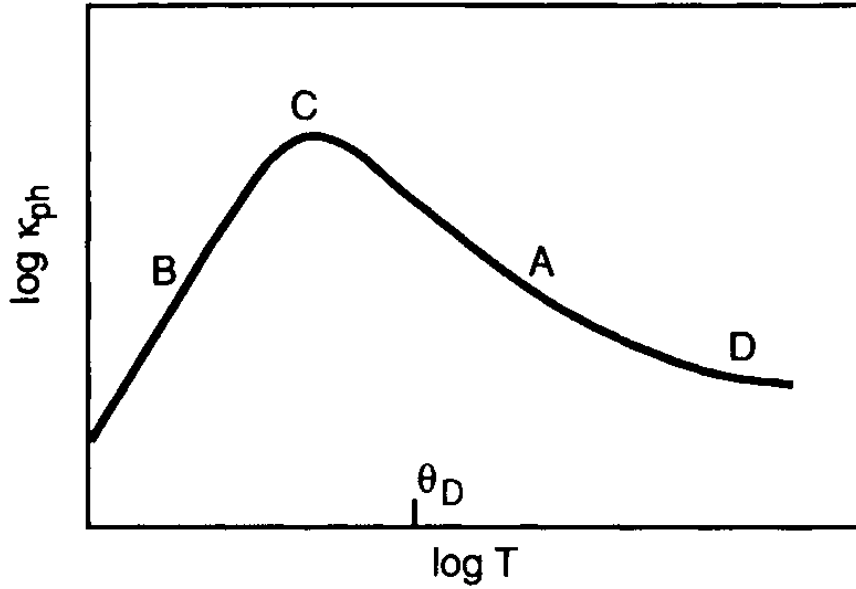


Figure 2.5: A schematic plot of $\log k_{ph}$ vs $\log T$ illustrating four regions of thermal conductivity with temperature [33].

In region B, thermal conductivity varies with temperature as $k_{ph} \sim T^n$, where typically $n \approx 3$. At low temperatures phonon-phonon collisions are rare since only a few phonons are excited, therefore the phonon mean free path is only limited by grain boundary and lattice defects. l is considered to be independent of temperature because the heat capacity of phonons varies as T^3 at low temperatures for crystalline solids hence $k \sim T^3$.

Region C is where the maximum thermal conductivity is obtained. The effect of phonon-phonon scattering on the phonon mean free path is comparable to effect due to phonon-defects scattering, i.e., $l_{ph-ph} \sim l_{ph-def}$. The l_{ph-def} is dependent on the number of defects on the material, so the temperature in this region is dependent on specimen.

In region A, thermal conductivity decreases as temperature increases. According to Bose-Einstein statistical factor the number of phonons in thermal equilibrium is given as

$$n = \frac{1}{\exp[\hbar\omega/k_B T] - 1} \approx \frac{k_B T}{\hbar\omega}. \quad (22)$$

Where n is number of phonons, $\hbar$ is the reduced Planck's constant, and ω is the phonon frequency. When $T > \theta_D$, the leading high temperature term is considered. At high temperatures $n \sim T$ and thermal conductivity is limited by a three-phonon process whereby two phonons collide and combine to form one new phonon or two phonons are formed from annihilating one phonon. The three-phonon process leads to phonon mean free path being inversely proportional to temperature hence thermal conductivity varies with temperature as $1/T$.

At very high temperatures, thermal conductivity decreases less rapidly and tends to be constant as seen in region D. The phonon mean free path decreases when temperature is increased but it cannot be less than the distance between two neighbouring atoms. This means that phonon mean free path in this region reaches its minimum value [33].

Callaway and Baeyer [34] assumed that all the phonon scattering processes can be represented by relaxation times τ that depend on phonon frequency ω . The expressions for relaxation time for phonon-defects scattering, phonon-phonon scattering, and boundary scattering are respectively given as

$$\tau_{D^{-1}} = A\omega^4 \quad (23)$$

$$\tau_{P^{-1}} = S(T)\omega^2 \quad (24)$$

$$\tau_{B^{-1}} = v_s/L. \quad (25)$$

Where A is independent of temperature, and $S(T)$ is proportional to temperature at high temperatures. v_s is the speed of sound and L is the characteristic length. The combined relaxation time is given as

$$\tau_{C^{-1}} = \tau_{D^{-1}} + \tau_{P^{-1}} + \tau_{B^{-1}}, \quad (26)$$

then thermal conductivity according to Callaway and Baeyer model can be expressed as

$$k = \frac{k_B}{2\pi^2 v_s} \left(\frac{k_B T}{\hbar} \right)^3 \int_0^{\theta_D/T} \tau_c(x) \frac{x^4 e^x}{(e^x - 1)^2} dx. \quad (27)$$

Where $x = \hbar\omega/k_B T$ [34].

2.4.6 Minimizing lattice thermal conductivity (k_l)

For a material to have a high value of ZT , it must have a larger value of Seebeck coefficient and electrical conductivity and have a lower value of thermal conductivity. Carrier concentration is directly proportional to electrical conductivity and inversely proportional to the Seebeck coefficient hence increasing one will decrease the other one. Thermal conductivity being composed of two components; electronic component k_e , which is also directly proportional to the carrier concentration, and lattice component k_l , which does not depend on carrier charge or carrier concentration but depend on phonon mean free path. The main objective of this work was then to lower the lattice thermal conductivity.

To keep the value of ZT at maximum, the idea of phonon glass electron crystal was proposed, which expresses that phonon transport ought to be restrained, as in glasses, and electrical conductivity ought to be kept up as in a crystal. The phonon mean free path l , is the maximum distance phonons can travel, and it can be disturbed by different scattering occasions. Some of the ideas developed in thermoelectric field on how to keep the values of k_l and l at lowest possible value are discussed below [35].

2.4.6.1 Rearranging of unit cells

Disordering or rearranging of unit cells can be done by introducing point defects like substitution atoms, vacancies, or interstitials. Bringing a foreign atom with similar valence as the compound being rearranged, does not scatter free carrier charges but instead scatter phonons. Therefore, the lattice thermal conductivity can be reduced without interfering with electrical transport. This was observed in an experiment carried by

Samunin et. al. [16] where they observed an increase in the figure of merit when Si was substituted with Sn in a compound of $Mg_2Si_{1-x}Sn_x$.

To maximize phonon scattering by point defects, the difference between the mass and size of substituted atom and original atom should be large [35].

2.4.6.2 Resonant scattering by localized rattling atoms

Localized rattling atoms are found in cubic compounds of formula RM_4Sb_{12} , where R is a rare earth element and M is a transition metal. A large atomic cage is formed by other atoms over the weakly bound rare earth ion. The ion gets localized and phonons get scattered [35], [36].

2.4.6.3 Complex crystal structure

Lattice thermal conductivity can be reduced by adopting materials with complex crystal structures. These structures are commonly found in zintl compounds, which exhibits low thermal conductivity. These compounds contain elements with greatly different electronegativity and between the elements exists ionic bonds and covalent bonds. The cations bonds to anions by electrostatic forces, and on the other hand covalent bonds are formed between the anions to keep the charge of the compounds neutral. The mixed bonding in these materials give rise to a complex crystal structure with a large number of atoms in a primitive unit cell. Some of the zintl compounds with such complex crystal structures are Sr_3GaSb_3 , $Ca_5M_2Sb_6$ where $M = Al, Ga, I$, and Yb_4MnSb_{11} [37].

2.4.6.4 Low-Dimensional Materials

Numerous studies have shown a significant improvement in thermoelectric properties of various nanostructured systems like nanowires, superlattices, etc., when compared to their bulk counterparts. Rama Venkatasubramanian et. al [38]. reported a decrease in lattice thermal conductivity of $Bi_{2-x}Sb_xTe_3$ ($0.49 \text{ Wm}^{-1}\text{K}^{-1}$) when they made a superlattice of Bi_2Te_3/Sb_2Te_3 ($0.22 \text{ Wm}^{-1}\text{K}^{-1}$). This decrease resulted in enhancement of $ZT(2.4)$ of a *p*-type Bi_2Te_3/Sb_2Te_3 superlattice device. Thermal conductivity was also

reduced through nanostructuring of ZnO in a study by Jood *et. al* [39]. It is reported that thermal conductivity reduced from $\approx 40 \text{ Wm}^{-1}\text{K}^{-1}$ of bulk ZnO to $\approx 1.5 \text{ Wm}^{-1}\text{K}^{-1}$ of ZnO nanocomposite.

2.4.6.5 Organic/Inorganic hybrids

Another method that can be used to enhance thermoelectric properties of materials is using organic thermoelectric materials, e.g., polyaniline (PANI) and poly (3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT: PSS), which have conjugated bonds to transport charge carriers. However, these materials have low Seebeck coefficient and low power factor therefore they are doped and made organic/inorganic hybrids to improve their power factors. Studies have shown that polarons are charge carriers in PANI and they can hop along the conjugated chains of the polymer and their contribution to thermal conduction is weak compared to phonons, and as a result PANI has more effect on electrical conduction than in thermal conduction [37].

2.5 BRIEF OVERVIEW ON CURRENT THERMOELECTRIC MATERIALS

A lot of experimental research in the past decades has been done on developing thermoelectric materials using different experimental techniques. The figure of merit of thermoelectric materials has shown a great improvement over the years. The ZT of different n -type and p -type bulk thermoelectric materials as a function of temperature is shown in Figure 2.6. For p -type materials, $MgAgSb$ shows high performance in a low range temperature (between room temperature and 550 K). In upper mid-range temperature of between 550 K and 900 K, thermoelectric materials with a high performance are $PbTe$ and $PbTe - SrTe$. For high temperature range of between 900 K and 1200 K, Cu_2Se and Zintl compound are thermoelectric materials that show a better performance. For n -type materials, in low range temperature between room temperature and 550 K, high performing thermoelectric material is Se -doped Bi_2Te_3 alloy. Skutterudite compounds are best performing thermoelectric materials at a temperature

between 550 K and 900 K. Thermoelectric materials with a high performance at temperatures above 900 K are $Si_{0.78}Ge_{0.22}$ and La_3Te_4 [40].

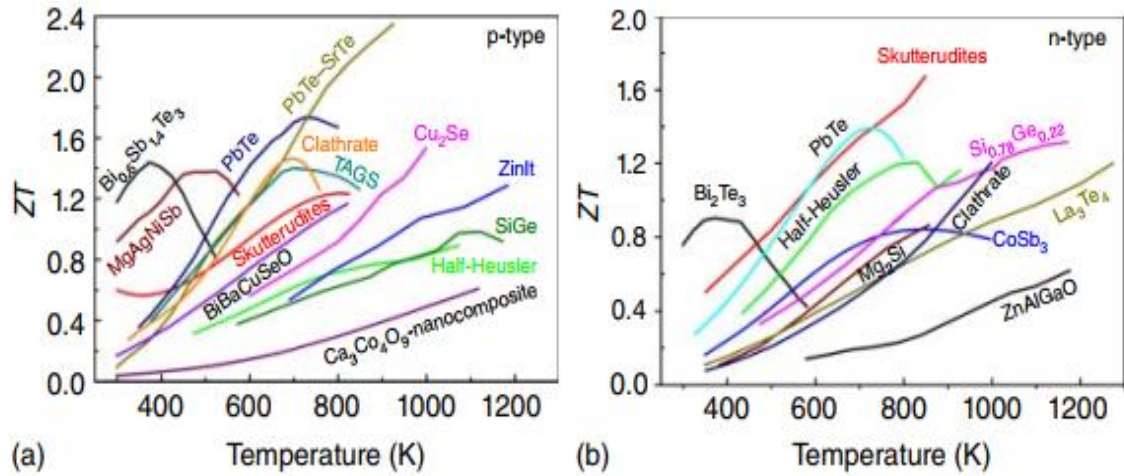


Figure 2.6 ZT of bulk thermoelectric materials as a function of temperature: (a) for p-type materials and (b) for n-type materials [41].

Developing of thermoelectric materials with enhanced thermoelectric properties has shown great progress over the years as the figure of merit for those materials was increasing. Such materials include Half-Heusler alloys [41], Skutterudites, Clathrates, metal oxide materials, complex Chalcogenides [36], and Bi_2Te_3 -Based nanocomposites [10]. $Fe_2V_{0.8}W_{0.2}Al$ based thin-film Heusler alloy prepared by magnetron sputtering is a thermoelectric material which is recently reported with a high figure of merit ZT of approximately 5 at a temperature between 350 K and 400 K [13]. The challenge with this material is its limitations for use in the industry since it is composed of some elements that are highly expensive and not environmentally friendly. Thermoelectric metal oxides are favorable materials as they are readily available and also friendly to the environment.

2.5.1 Thermoelectric oxides materials

Some of the best performing thermoelectric materials have a disadvantage of toxicity and high production costs, as a results metal oxide based thermoelectric materials have

gained interest for use as thermoelectric materials [12], [36], one such thermoelectric oxide material is NaCo_2O_4 prepared by sintering. The first reported figure of merit ZT for this material is 5×10^{-4} in a temperature range 373 – 673 K. Further research has been carried out on the material to improve its thermoelectric properties and electrical conductivity and Seebeck coefficient was increased when the material was prepared by double-sintering. This material reached ZT value of 0.78 at 1053 K. $\text{Ca}_3\text{Co}_4\text{O}_9$ is another p -type oxide material with similar values as NaCo_2O_4 . An interesting n -type oxide material is SrTiO_3 which reached a ZT value of 0.9 at 1000 K. An oxide material with ZT value greater than 1 is BiCuSeO [41]. In general oxide-based materials still have low figure of merit, highlighting the importance of this study.

2.6 Theory of Material processing - Spark plasma sintering

In this project Spark plasma sintering was used to prepare CuO pellets to make thermoelectric devices. For this reason, a brief discussion on the theory of Spark plasma sintering is presented. Sintering is the process of compacting powder particles under heat into a solid at temperatures below their melting point. It is done to produce bulk samples from different kinds of powders. There are various sintering techniques such as conventional sintering, hot pressing, hot isostatic press and spark plasma sintering (SPS) [42]. Using conventional sintering methods (i.e., hot pressing, high temperature extrusion, and hot isostatic pressing) to sinter the materials give rise to grain growth and this affect the properties of sintered materials [43]. They are also time consuming and limit control in structure and properties of a material [44]. Spark plasma sintering has an advantage over conventional sintering methods as it provides localized heat input and short sintering time, as result the grain growth is reduced. Therefore, it is most suited to sinter nanostructured powders since they are very sensitive to temperature [45].

2.6.1 Comparison of Spark Plasma Sintering and hot pressing

Spark plasma sintering also known as Field Assisted Sintering Technology (FAST), is almost similar to hot pressing, the difference between them comes from the type of heating, see

Figure 2.7 [43]. In hot pressing an external heat source is used while SPS uses a pulsed DC current which is passed through a graphite die. The die then acts as a heating source and the sample is now heated from both outside and inside.

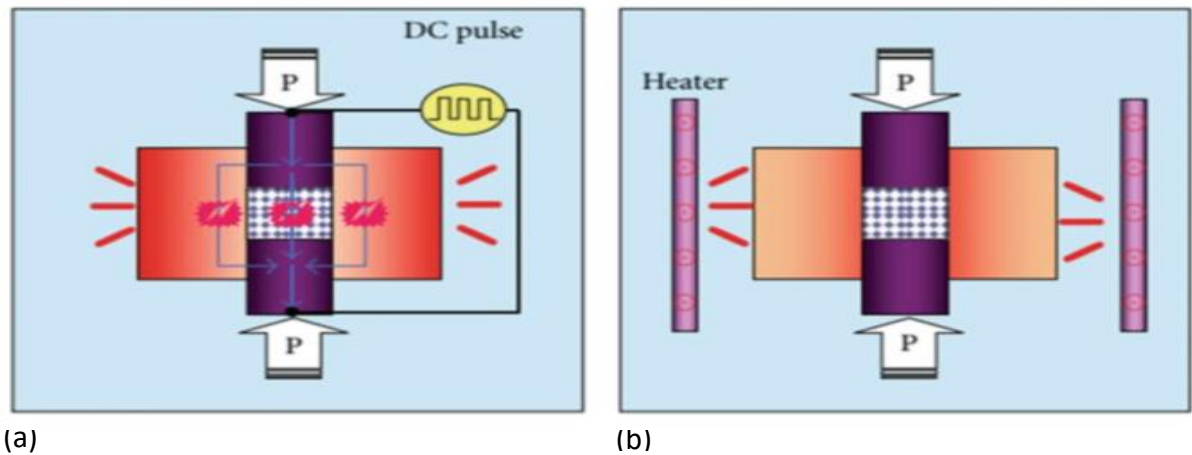


Figure 2.7: (a) *Spark Plasma Sintering (SPS)* and (b) *Hot Pressing*.

Chapter 3

EXPERIMENTAL TECHNIQUES

3.0 Overview

Materials and methods that were used in this research are discussed in this chapter. The technique which was used to synthesize pure CuO powders is discussed, followed by consolidation of the powder using spark plasma technique. A discussion on the characterization processes is also presented, which culminates on how the measurements of thermoelectric properties were performed.

3.1 Synthesis of pure copper oxide (CuO)

Copper oxide nanoparticles have shown unique physical and chemical properties from the bulk material [46], and it has many applications in various fields such as in catalysis, gas sensing, solar energy conversion, batteries, and magnetic storage media [47]. Different synthesis methods have been developed to prepare copper oxide nanoparticles of controlled size and morphology to suit their desired application. Some of these methods include the sol-gel method, electrochemical method, laser ablation, sonochemical method, chemical precipitation, and hydrothermal method [48]. For this study, the hydrothermal method is used as it is safe and environmentally friendly. It also allows the control of particle morphology [47]. A number of research works, J. G. Thangamani et. al. [49] and, M. Outokesh et. al. [50], have produced pure copper oxide nanoparticles using the hydrothermal route and below is a figure that shows how CuO was prepared step by step using this route.

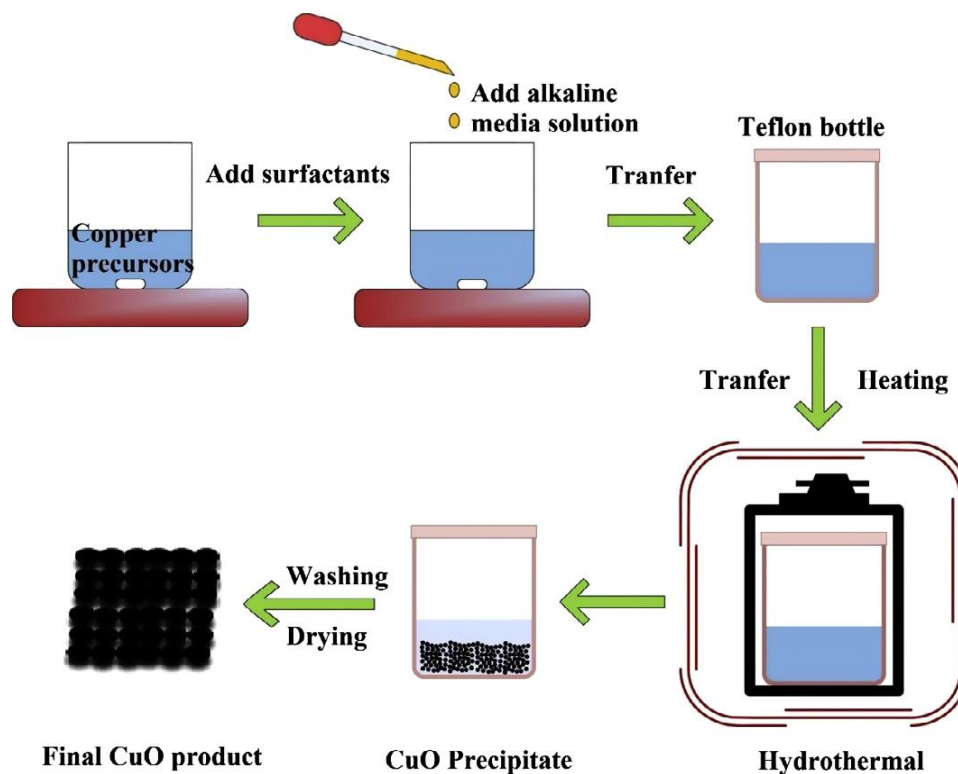


Figure 3.1: Schematic diagram of hydrothermal synthesis of CuO nanoparticles [46].

To prepare CuO nanoparticles by solution methods, a solution of alkaline hydroxide is added to a solution of copper salt to form copper hydroxide and a salt of alkaline metal, copper hydroxide formed is then heated to produce copper oxide. The concentration of solvent and a solute used to form a solution have effects on size and morphology of the final product. According to most reports, water is the mostly used solvent, however it is used with additives or surfactants. Few reports where water was used without surfactants led to a larger and nonuniform size and shape because crystals were agglomerated. Therefore, water was mostly used with surfactants since they restrain crystals from self-aggregating to produce particles with uniform size and shape. Alcohols and other solvents such as dimethylformamide and dimethyl sulfoxide were used in few reports but their effect on the size and shape of the crystals was not well discussed. The alkaline hydroxide also influences the growth of crystals, Figure 3.2, and the commonly used ones are sodium

hydroxide and potassium hydroxide since they give almost same effect because they have similar properties. Ammonia has also been used in few reports [48].

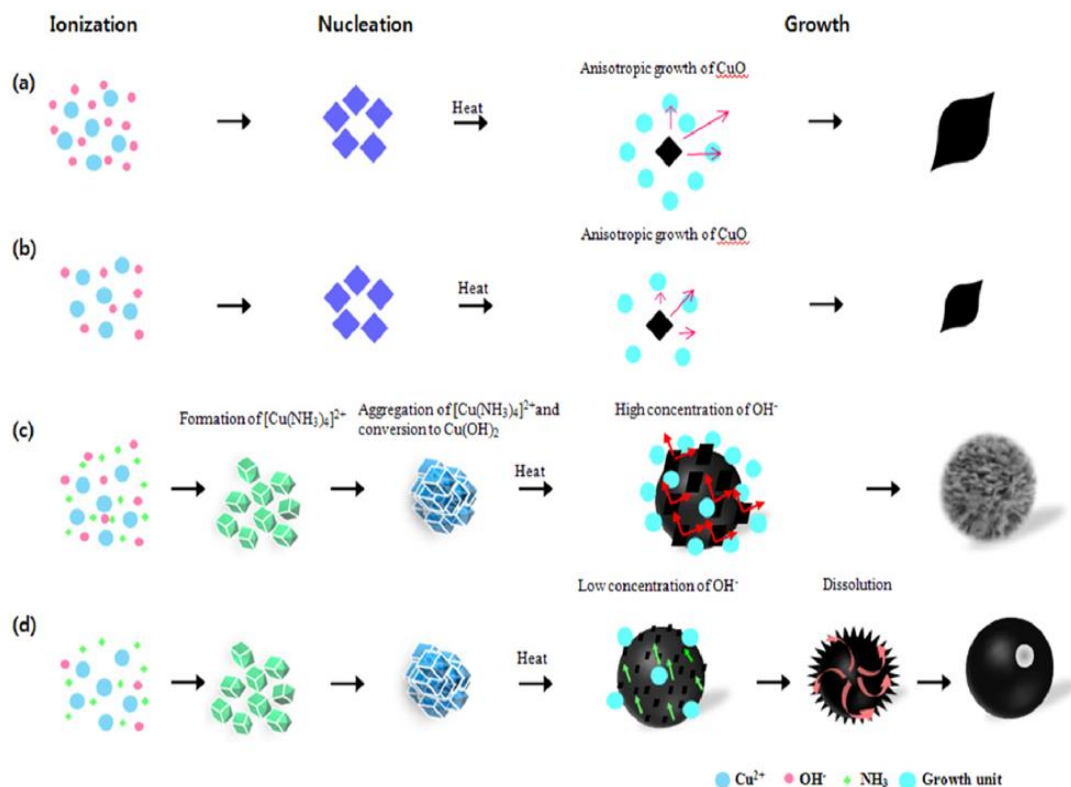


Figure 3.2: Schematic diagram showing effects of alkaline salt on the CuO structures: (a) leaf-like CuO structure synthesized in the presence of NaOH, (b) smaller leaf-like CuO structure synthesized in the presence of HMT, (c) spherical dandelion CuO structure synthesized in the presence of ammonia and, (d) hollow sphere CuO structure synthesized in the presence of urea [51].

In this project pure CuO powder was prepared using copper (II) nitrate trihydrate and sodium hydroxide as precursors. Copper (II) nitrate trihydrate was dissolved in distilled water in a conical flask using a magnetic stirrer. A solution of sodium hydroxide was also prepared the same way as a solution of copper (II) nitrate trihydrate. Sodium hydroxide solution was added under constant stirring to the solution of copper (II) nitrate trihydrate solution. A blue precipitate (copper hydroxide) was formed and was washed several times using distilled water. The washed precipitate was heated in an autoclave machine at

temperatures above 80 °C. After heating a black precipitate was formed and was dried in an oven at 100 °C for 12 hours. In order to do further analysis, the product was crushed into fine powder. The synthesis process is shown in Figure 3.3.

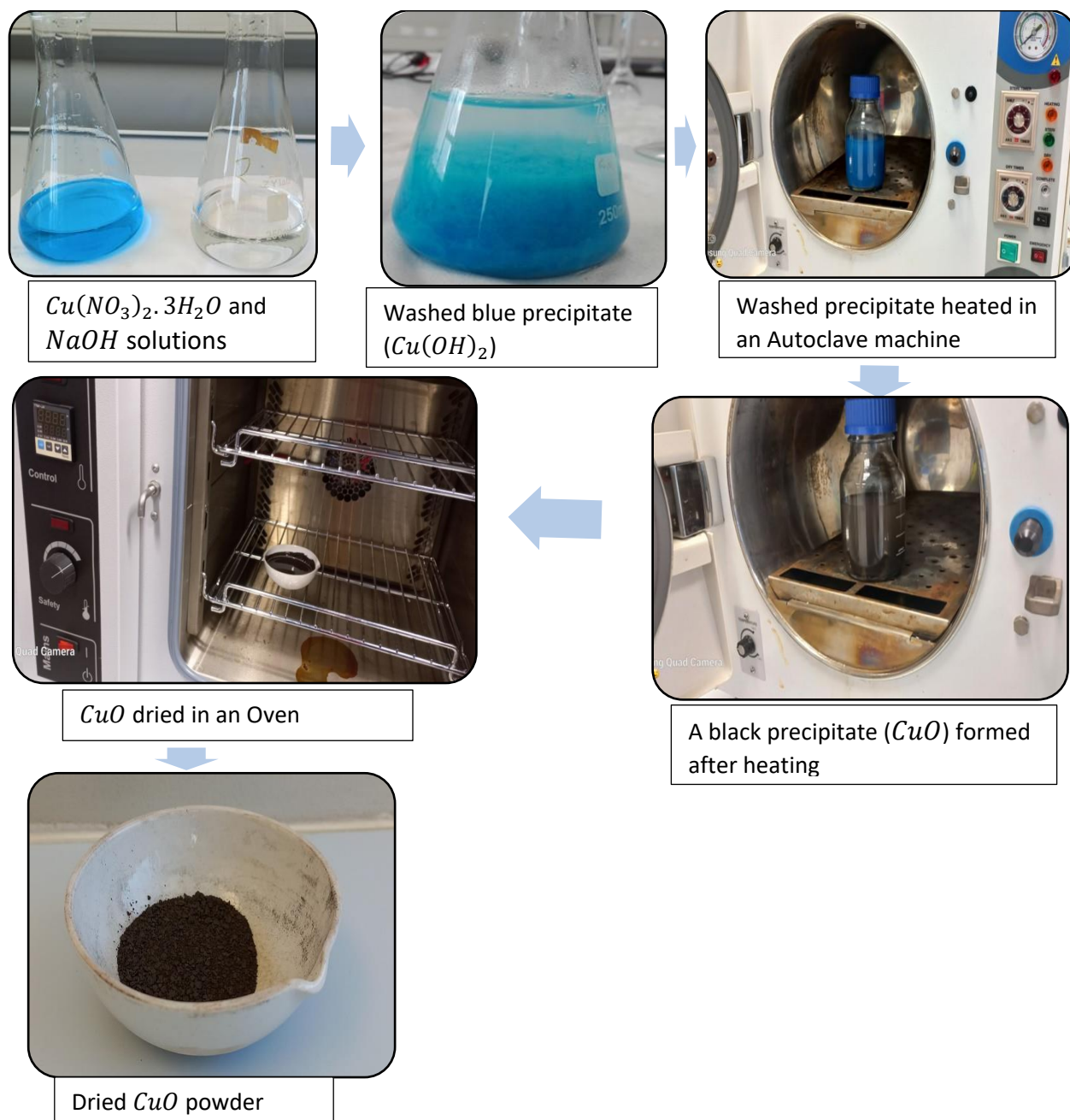
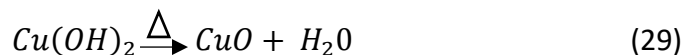
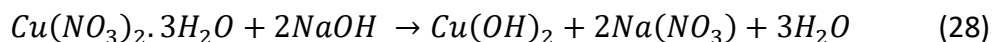


Figure 3.3: Pictures showing the synthesis process used for CuO powder production.

The chemical reaction of this process can be summarized in the following chemical equations,



To tune or alter the morphology of CuO, synthetic conditions were varied. The conditions varied were concentration of the active precursor ($Cu(NO_3)_2 \cdot 3H_2O$) and decomposition temperature. When varying decomposition temperature, the concentration of precursors was kept constant at 1:1 M for temperature of 85 °C, 95 °C, 100 °C, 120 °C, and 135 °C. When varying concentration of $Cu(NO_3)_2 \cdot 3H_2O$, decomposition temperature was kept at 135 °C and concentration of sodium hydroxide also remained constant at 1 M. Concentration of copper (II) nitrate trihydrate was varied at 0.2 M, 0.4 M, 0.6 M, 0.8 M, and 1.0 M.

The hydrothermal process produces pure powdered black copper oxide and therefore to produce solid pellets of the oxide, Spark plasma sintering was used.

3.2 Sintering of material

Sintering process was carried out using a spark plasma sintering (SPS) machine at Tshwane University of Technology in South Africa. The SPS equipment used is shown in Figure 3.4a and a schematic diagram of the equipment is shown in Figure 3.5. It is a fully automated instrument with computer used to monitor, control and record sintering processes. The temperature, pressure, gas flow and intensity controllers can all be adjusted from the control panel. The equipment has a furnace pressing chamber (see Figure 3.4b), where the sintering process takes place. The chamber is built to withstand sintering temperatures as high as 2200 °C and a vacuum pressure of at least 1×10^{-4} mbar under

cold conditions. It's size is made large enough to suit any mould without causing any obstructions. It also has a pressing system. To compact the powder inside the mould at a set pressure, a controlled pressing system (hydraulic pressing) was applied. The pressure is applied at the cylinders used as electrodes. The electrodes charge current through the sample and the die and apply axial pressure; on the other hand, graphite spacers connect the sample to the electrodes through a die. Other components of SPS equipment include Furnace power supply, Vacuum pumping system, Water circulating system, Gas inlet system, control and instrumentation, and temperature measurement tools [42].



Figure 3.4a: *Spark Plasma Sintering Machine*



Figure 3.4b: *SPS Chamber*

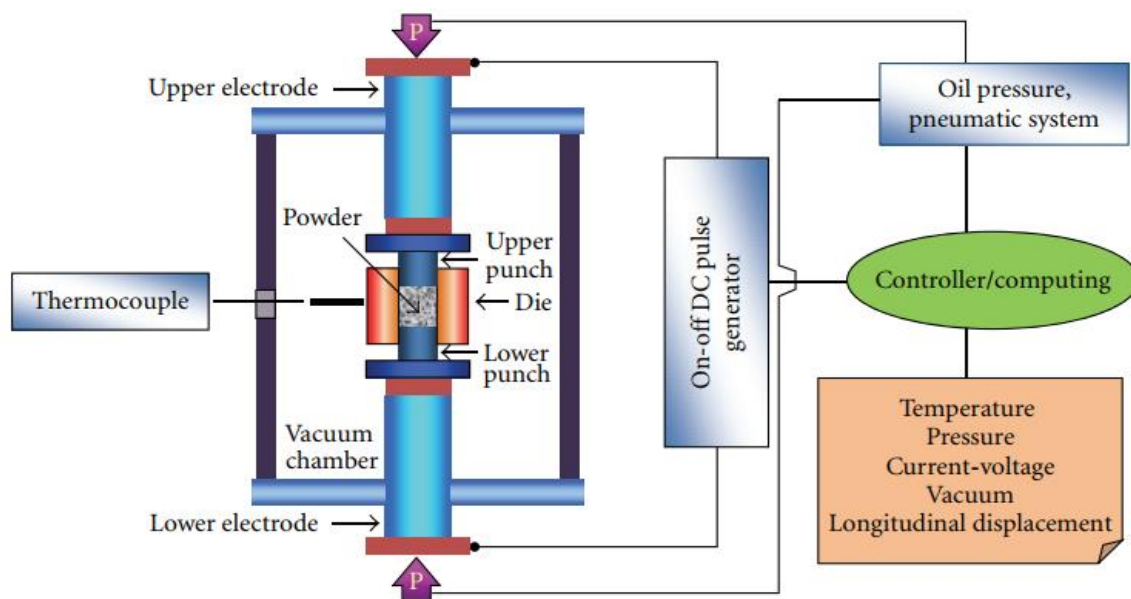


Figure 3.5: Schematic diagram of Spark plasma sintering machine [42] .

In this work samples of pure copper oxide with different morphology and samples of copper oxide/polyaniline composite in layers and copper oxide/polyaniline mixed powders were sintered. The sintering conditions of the samples are given in table 3.1.

Table 3.2: Sintering conditions for different samples of CuO and CuO-Polyaniline composite.

Sample	Temperature (°C)	Pressure (MPa)	Holding time (min)	Density (%)
CuO @100 °C	450	50	10	95.9
CuO @120 °C	450	50	10	79.7
CuO @135 °C	450	50	10	97.7
CuO@PANI (Mixed)	400	50	5	99.4
CuO@PANI (layers)	400	50	5	97.2

The sintering temperature was initially set to 800 °C with pressure of 50 MPa and holding time of 1 minute, for pure CuO a firm and more compact pellet was produced however for CuO@PANI the polymer melted and spilled over the mould. The temperature was then lowered to 400 °C where it did not spill anymore and holding time was increased to 5 min to improve its compactness. Pure CuO sintered at 450 °C with pressure of 50 MPa and holding time of 10 minutes showed similar compactness as the sample with initial settings. Some of pure CuO pellet and CuO mixed with PANI pellet produced from the SPS machine are shown on Figure 3.6.



Pure CuO pellet



CuO mixed with PANI pellet

Figure 3.6: *Images of pellets produced from SPS machine.*

To confirm the compactness of the sample, their density was measured using a laboratory balance and density kit as illustrated in Figure 3.7.

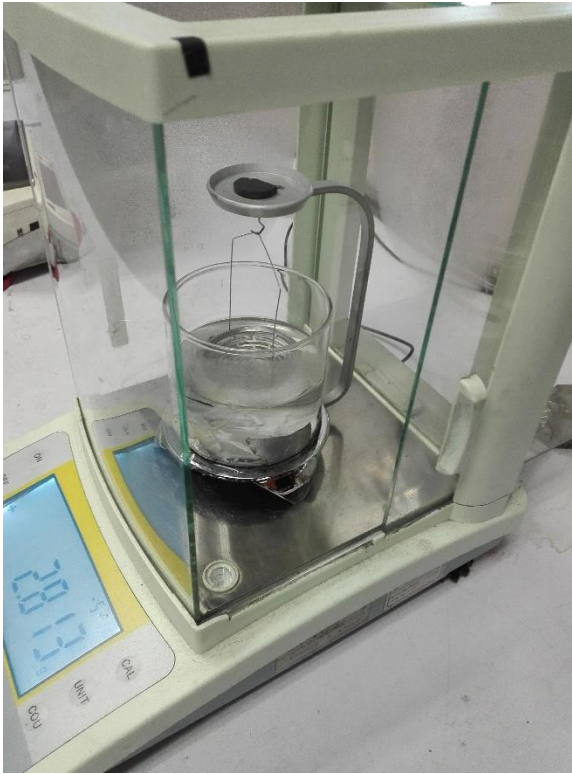


Figure 3.7a: *Weighing density of a pellet in air.*



Figure 3.7b: *Weighing density of a pellet in water.*

The method used is known as Buoyancy method governed by Archimedes' principle which states that a body immersed in a liquid experience a force acting upwards on it (Buoyancy force) is equal to the weight of the liquid it displaces. The density of the sample was determined by weighing the pellet in air and then again in water, the sample density was calculated as follows;

$$\rho = \frac{A}{A - B}(\rho_w - \rho_a) + \rho_a \quad (31)$$

where ρ is the density of the sample, A is weight of the sample in air, B is weight of the sample in water, ρ_w is density of water, and ρ_a is density of air.

The samples were sintered in a 20 mm diameter graphite die and their thickness was 2 mm, but the shape and dimensions of the samples were too large for thermoelectric measurements, hence they were cut using a saw to $10 \times 2 \times 2$ mm for electrical resistivity and Seebeck coefficient measurements and $6 \times 6 \times 1$ mm for thermal diffusivity measurements.

3.3 Characterization techniques

3.3.1 Structural characterization by X-Ray diffraction

X-ray diffraction is a characterization technique primarily used to identify the phase of crystalline material. The X-ray diffractometer consists of an X-ray generator, a sample holder, and an X-ray detector. The X-rays are generated from X-ray tubes by bombarding a metal target with high energetic electrons and the target emits an X-ray photon. The most commonly used metal target is Cu since it has strong $K\alpha$ at 1.5418 Å. The emitted X-rays strike the sample and are diffracted to the X-ray detector but before reaching the detector, other X-rays that might interfere with the X-ray spectrum are suppressed using crystal monochromators. When the sample and detector are rotated, or X-ray tube and detector rotates around the sample the intensity of diffracted X-rays is recorded. The X-ray detector receives and processes the X-ray signal then converts them to a count rate which is displayed on a computer monitor. Constructive interference and a peak in intensity occurs when the geometry of the incident X-rays striking the sample satisfies the Bragg's law illustrated in Figure 3.8. Bragg's law states that constructive interference only occurs when the angle θ of diffracted X-rays from a particular crystal plane is equal to the angle of incident X-rays from the same crystal plane.

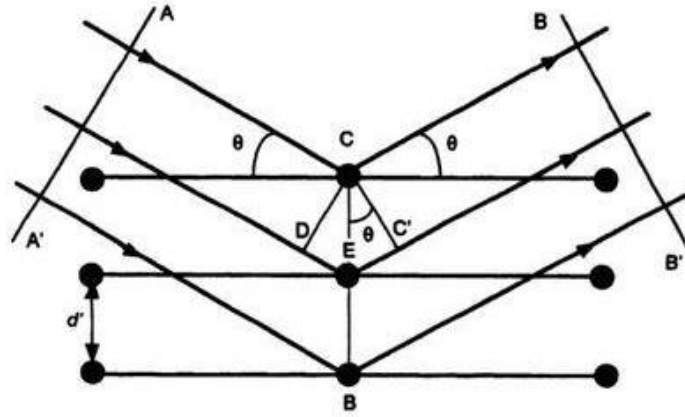


Figure 3.8: Bragg's principle of X-ray diffraction [52].

Bragg's law can be expressed in equation 32 as;

$$n\lambda = 2d \sin\theta \quad (32)$$

where n is an integer, λ is the wavelength of the radiation, d is the spacing between surfaces and θ is the angle between the X-ray beam and the crystal plane.

In this work the crystal structure of the prepared CuO powder was studied using Bruker D8 advance X-ray diffractometer (XRD) shown in Figure 3.9. The XRD uses copper cathode as a radiation source (CuK_{α} wavelength = 1.5418 Å) at 40 kV and 40 mA. The diffraction patterns were recorded in the 2θ range of 10 to 80°. EVA software installed with crystallographic database was used to identify available phases by matching. Peak positions and intensities were observed from the diffraction pattern. Crystallite sizes (in nanometers) were estimated using the Scherrer equation given as

$$d_{XRD} = \frac{K\lambda}{\beta \cdot \cos\theta} \quad (33)$$

Where K is dimensionless shape factor (0.9), λ is wavelength ((nm), β is full width at half maximum (FWHM in rads) [53].



Figure 3.9: *D8 Advance X-ray diffractometer.*

3.3.2 Scanning electron microscopy

A scanning electron microscopy (SEM) is primarily used to enlarge small feature or materials that cannot be seen by human eye just like any other microscopes. The advantages of an SEM is that it uses electron beam to obtain image resolution of 10 nm while optical light microscopes uses light to obtain image resolution of 2 μm . The specimen in a SEM is shot with high energy electrons which are then scattered by the specimen and the scattered electrons are analysed to give information about the morphology of a material. SEM equipment is shown in Figure 3.10 showing the three major sections of the equipment which are the electron column, Specimen Chamber, and computer control system. Electron column located above the specimen chamber consist of electron gun, condenser and objective lens, and scanning coils as seen in Figure 3.11. The specimen chamber has important components including specimen stage, specimen

holder, infrared camera, and Energy Dispersive Spectroscopy (EDS) and secondary electron detectors. The control system is equipped with a computer for control of the SEM, imaging, analysis and storing of data.

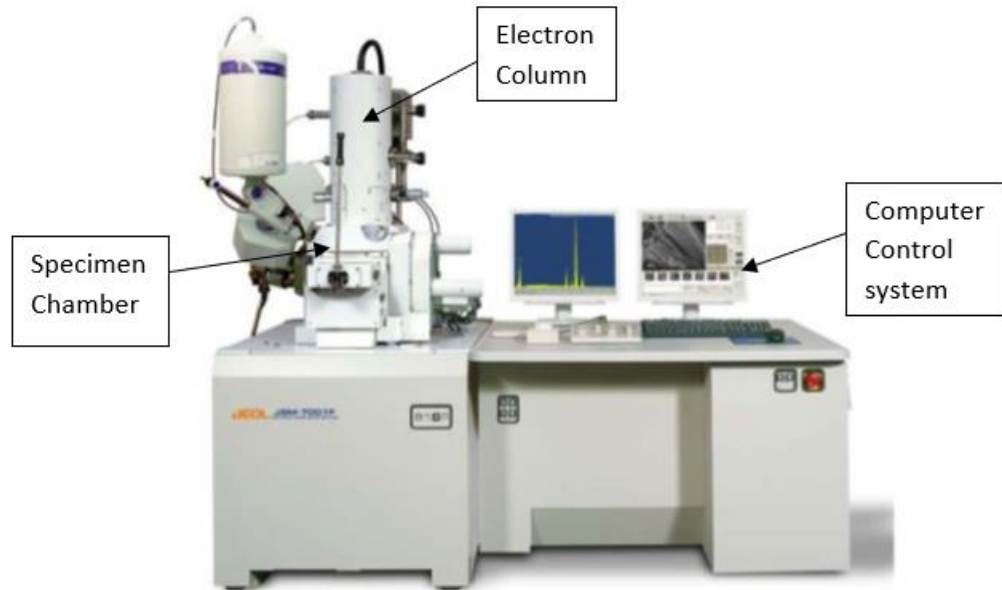


Figure 3.10: A picture of JEOL SEM used to examine surface morphology of CuO nanoparticles showing three major sections.

The electron gun produces electrons by field emission which are accelerated by a high voltage of 30 - 40 kV to the surface of the sample with high energies in the range of 1-30 keV. The accelerated high energy electrons are focused on the sample surface by condenser lens and objective lens. Once the beam of this electrons hits the sample surface, they interact with the sample and as a results electrons and X-rays are ejected from the sample. A vacuum is generated in a specimen chamber to avoid the interaction between electrons and atoms in the air as this may impair signals or image resolution. The scattered electrons and X-rays are collected by detectors which then converts them to a signal to give information about morphology of the material on computer monitor [54], [55].

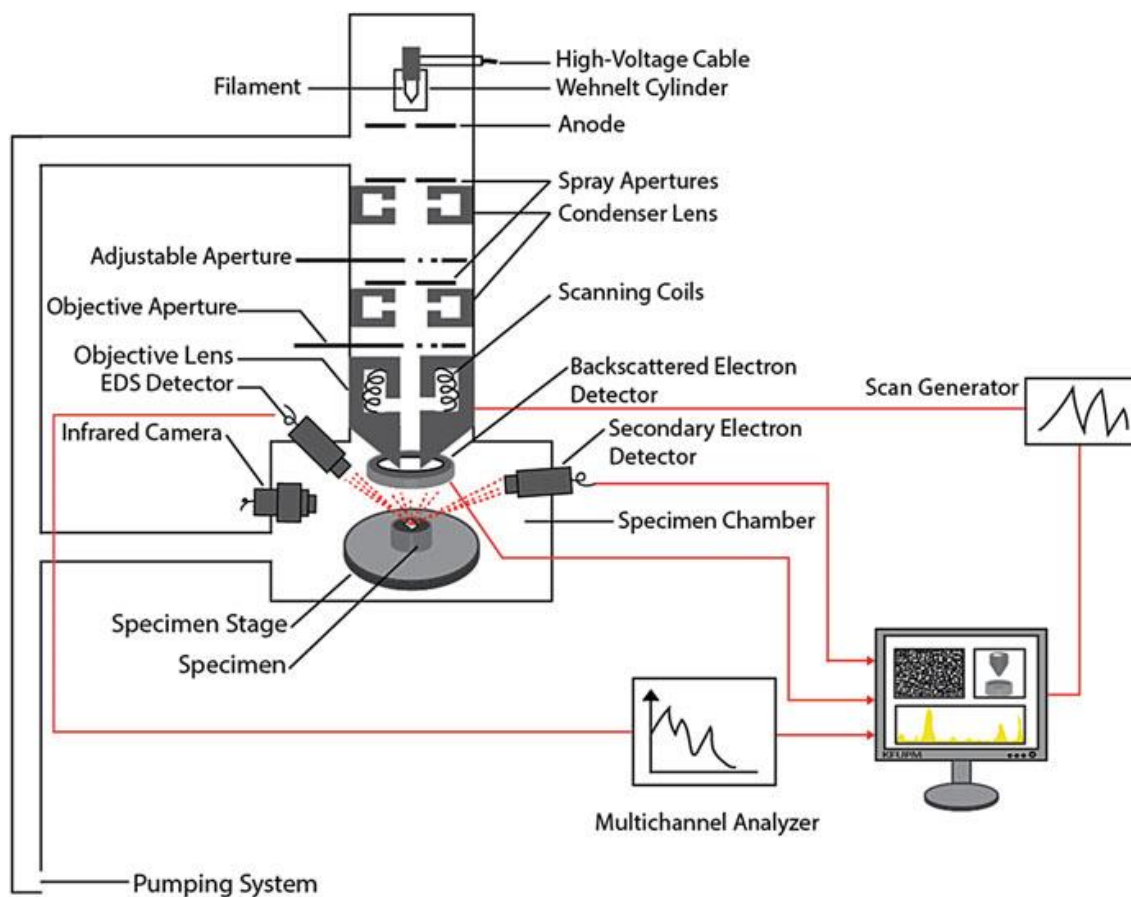


Figure 3.11: Illustration of various components of SEM in electron column and specimen chamber [55].

In this study, the surface morphology of CuO powder was studied using JEOL SEM (Model JSM-7100F) shown in Figure 3.10.

3.4 Theory of Thermoelectric Measurements

As mentioned before, the efficiency of thermoelectric power generation depends on the figure of merit ZT of a thermoelectric material. To precisely determine the value of ZT , high accuracy measuring techniques should be used to measure electrical conductivity, Seebeck coefficient, and thermal conductivity [56].

3.4.1 Measurement techniques for determining electrical resistivity

The electrical resistivity of a material describes the ability of the material to resist the flow of electricity. The material has high resistivity if electricity does not easily flow through the material, and it has low resistivity when electricity can easily flow through the material. It is measured in units of ohm meter. The inverse of electrical conductivity (σ) is electrical resistivity (ρ):

$$\sigma = \frac{1}{\rho}. \quad (34)$$

Two point and four-point techniques are mostly used to measure the electrical resistance of materials.

3.4.1.1 Two probes Technique

It is the simplest method of measuring resistivity and is shown in Figure 3.12. The resistivity of a material is obtained by measuring the resistance and physical dimensions of the material. The material is cut into a rectangular shape of length l , height h , and width w . Each end of the bar is attached to a copper wire hence the name two probes because wires are attached to the material at two probes. A voltage V across the bar and the amount of current I that flows through the bar is measured by voltmeter and ammeter respectively. The physical dimensions are measured with a suitable instrument, then two-point resistivity of the material is given by:

$$\rho = \frac{V A}{I l} \quad (35)$$

where $A = h \times w$ is the cross sectional area of the bar.

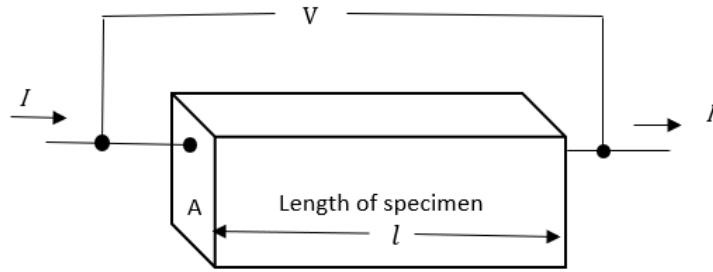


Figure 3.12: *Two probes technique for measuring electrical resistivity.*

3.4.1.2 Four probes technique

Four probes technique is the most widely used for measuring resistivity on materials with low resistivity. The voltage drop V_D is measured across two probes that are a distance D between each other. Figure 3.13 shows a schematic diagram of this technique. In this case ρ is given by

$$\rho = \frac{V_D A}{D I} \quad (36)$$

This method can be used to measure the resistance of the single crystal and a bulk material. Current flows through the outer contacts that are close to the edges of the sample, and voltage is measured across the inner contacts. Four probe method is most suitable for low and accurate resistance measurements since it can eliminate the effect of contact resistance between the sample and electrical contacts [57], [58].

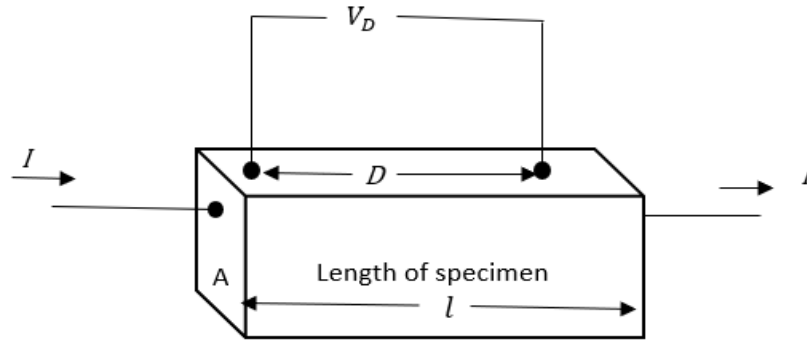


Figure 3.13: *Electrical resistivity measurement by four probes technique.*

3.4.2 Measurements of Seebeck coefficient

The Seebeck coefficient is a useful parameter to determine the figure of merit ZT of a thermoelectric material. It is usually measured using a commercial or a home-made equipment depending on different methods [59]. A thermal gradient must be created along a sample then thermoelectric voltage and temperature difference can both be measured between two points along the length of the sample [60]. Temperature gradient can be inaccurate because of different temperature offsets in the measurement, and this makes a Seebeck coefficient to have a large uncertainty. To rectify the error from temperature gradient, analysis of errors has been carried out on commercial systems.

One of the commercial system equipment that have been used to measure the Seebeck coefficient is shown in Figure 3.14. Linseis LSR-3 system equipped with an infrared furnace has Seebeck coefficient measurement uncertainty of $\pm 5\%$ at room temperature.

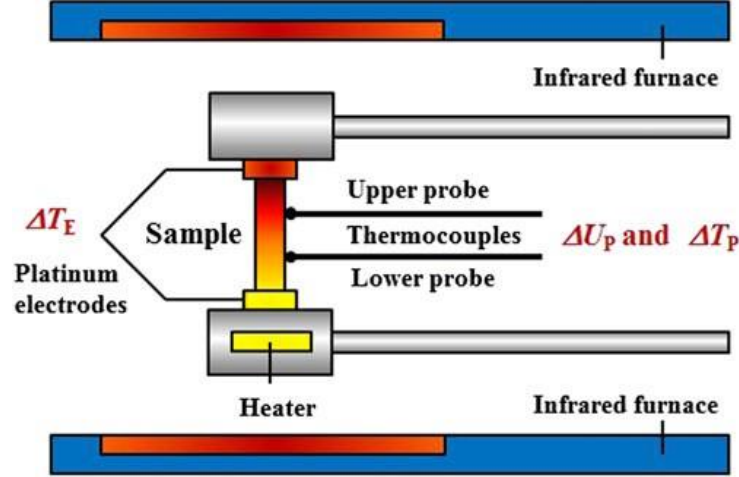


Figure 3.14: Schematic diagram of commercial Seebeck coefficient measurement system.

The sample is cut into a bar of known physical dimensions and is mounted between two platinum electrodes and held in place with pressure. A thin graphite foil is placed between the sample and each electrode to improve thermal and electrical contact. The foil can also prevent any chemical reactions between the sample and the electrodes. Temperature difference and voltage are measured by two pairs of Pt-Pt + 10% Rh standard thermocouples. The thermocouple is covered by a twin bore alumina sheathing to prevent it from contaminations and to avoid strain. Probe spacing on the sample should be chosen appropriately such that there will be uniform electrical conduction profile within the sample. Normal sample temperature is monitored by infrared furnace. After the furnace has completely settled, an extra power is provided from the lower electrodes to acquire a temperature difference between the upper and lower electrodes, ΔT_E . The corresponding electric voltage ΔU_P and temperature gradient ΔT_P between two probe thermocouples can be measured consecutively in seconds. The Seebeck coefficient of the sample is then given by,

$$\alpha_A = \frac{\Delta U_P}{\Delta T_P} - \alpha_{Pt} , \quad (37)$$

where α_A is the sample's Seebeck coefficient, α_{Pt} is tabulated Seebeck coefficient of Pt wires [59].

3.4.3 Measurements of thermal conductivity

Thermal conductivity can be measured in several ways. Each of them is suitable for a certain type of materials, depending on the thermal properties and the medium temperature. The two basic techniques for measuring thermal conductivity are:

- The **steady state** technique which is used to obtain a measurement when a measured material is in equilibrium or when the temperature of the material does not vary with time. The process of analyzing signals becomes easy with this method. The disadvantage is that it is time consuming to reach the equilibrium.
- The **non-steady state**, a measurement is obtained while heating up and the process is much quicker than the steady state [61], [62].

The instruments that are mainly used to measure thermal conductivity are, a guarded hot plate, a hot wire, a modified hot wire, and a laser flash diffusivity.

Guarded hot plate. A solid sample is sandwiched between hot and cold plate. Temperature of the plates is then monitored until they are in equilibrium. The steady state temperatures, thickness of the sample and the input heat on the hot plate are used to calculate thermal conductivity. Schematic diagram of guarded hot plate is shown in Figure 3.15.

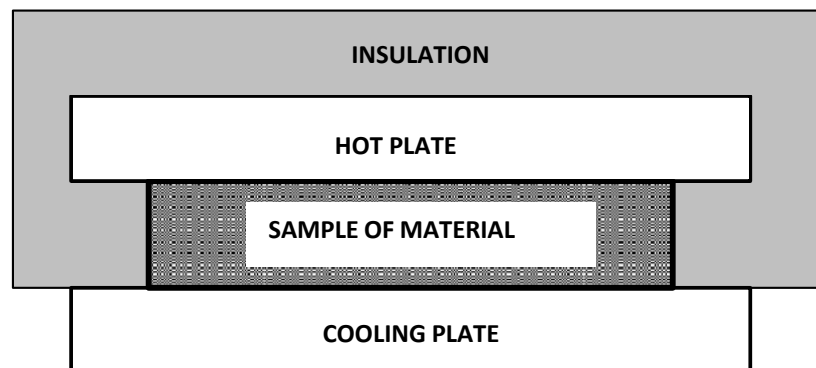


Figure 3.15: Scheme of guarded hot plate

Hot wire. A hot wire is inserted into the sample, then heat is transferred from the wire into the sample, Figure 3.16. Change in temperature of the wire is recorded. To calculate thermal conductivity, temperature of the wire is plotted against the logarithm of time if density and capacity are known. The instrument can be used to measure foams, liquids and melted plastic materials. It is not used to measure solid samples.

Modified hot wire. The wire is modified such that it can perform measurements of solid samples. A support on backing is added to the hot wire so that it does not go through the sample.

Laser flash diffusivity. A short pulse of heat is induced to the front of the sample by a laser flash, then temperature change as a function of time is observed in an infrared scanner [61].

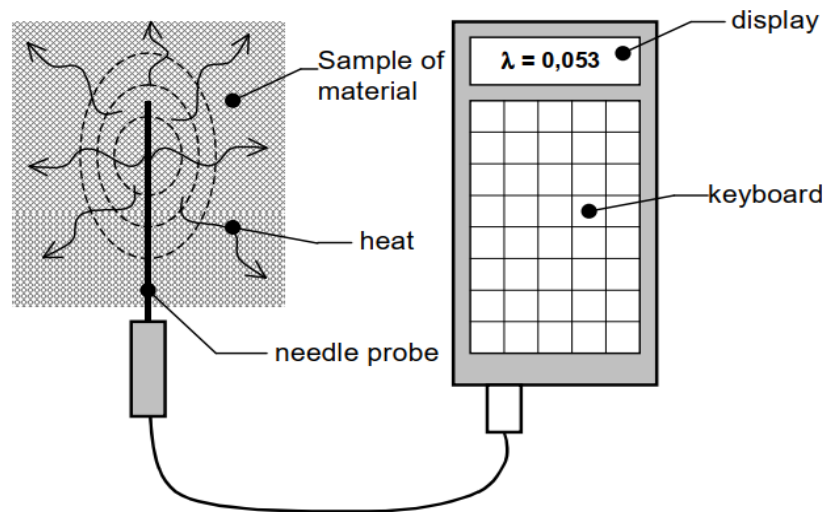


Figure 3.16: *Illustration of hot wire instrument.*

3.5 Thermoelectric measurements

3.5.1 Electrical Resistivity and Seebeck Coefficient measurement

The obtained CuO pellets and CuO/PANI pellets were cut into bars with dimensions $10 \times 2 \times 2$ mm which were used for the measurement of electrical resistivity and Seebeck coefficient using an Ulvac Riko ZEM-3 instrument under a low-pressure

atmosphere at a temperature range of 50 °C and 200 °C. The ZEM-3 equipment is shown in Figure 3.17.



Figure 3.17: A picture of ZEM-3 (Ulvac-Riko) instrument [63].

The pellet samples were coated with a thin layer of gold to ensure that there is electric ohmic contact and were placed in a vertical position between the upper block and lower block in a heating furnace as illustrated in Figure 3.18. The sample is heated and held at a specified temperature, to create a temperature difference it is then heated by the heater in the lower block. Seebeck coefficient was measured by taking the upper and lower temperatures T_1 and T_2 using a thermocouple in contact with the other side of the sample and the change in voltage was measured between the same wires on one side of the thermocouple. Seebeck coefficient was determined by equation 2 ($\Delta T = S\Delta V$) discussed in Chapter 2 section 2.2.1. Electrical resistivity measurements were taken following four-point method whereby a constant current I was applied at both ends of the sample to measure voltage drop at T_1 and T_2 by eliminating thermos electromotive force.

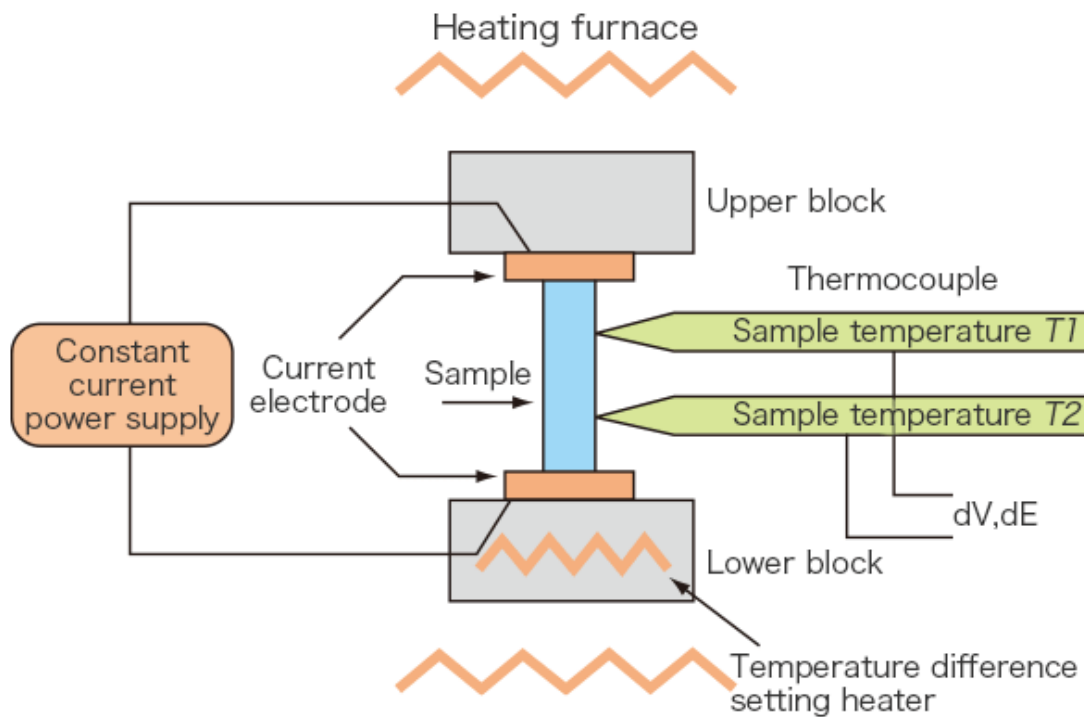


Figure 3.18: Illustration of Seebeck coefficient and electrical resistivity measurement [63].

3.5.2 Thermal conductivity measurement

Thermal conductivity was determined from measuring thermal diffusivity of the pellets based on the following equation.

$$k = \alpha(T)C_p(T)\rho(T) \quad (38)$$

Where k is thermal conductivity, α is the thermal diffusivity, C_p is heat capacity, and ρ is the density of the material.

Thermal diffusivity was measured using laser flash method and the schematic diagram of the laser flash instrument is shown in Figure 3.19. The instrument is equipped with a pulsed laser, a sample holder, a furnace capable of maintaining and recording the sample reference temperature, power supply for the furnace, a system that measures and records the rear-face transient temperature, and a computer control system for controlling the experiment, data processing and analysis.

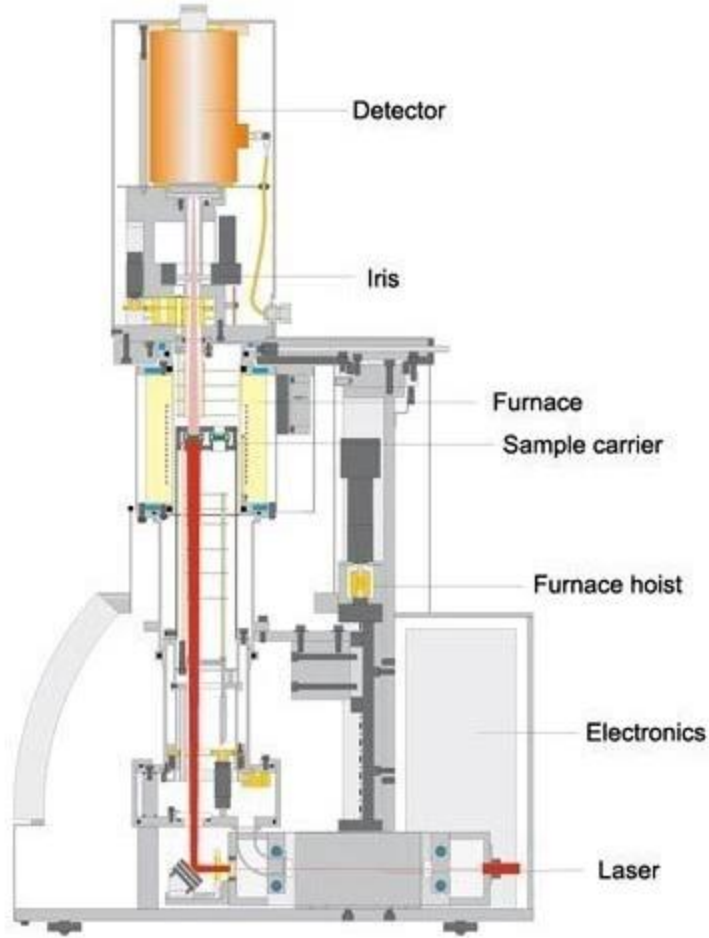


Figure 3.19: A schematic diagram of laser flash instrument [64]

The samples were cut into a bar with dimensions $6 \times 6 \times 1$ mm and placed in a sample carrier. Short energy laser pulse was used to heat the lower surface of the sample and as a result caused a rise in temperature at the upper surface of the sample. The temperature rise at upper surface of the sample was measured by the detector and temperature rise versus time data were recorded to compute thermal diffusivity values using the following equation:

$$\alpha = 0.1388 \frac{L^2}{t_{0.5}} \quad (39)$$

Where L is the sample thickness, and $t_{0.5}$ is half time measurement [65].

CHAPTER 4

4.0 Results and Discussion

4.1 Structural and Morphological Characterization

4.1.1 X-ray Diffraction spectroscopy of powdered samples

X-ray Diffraction (XRD) measurements of the synthesized powdered samples (synthesized at different conditions and varying concentrations) were carried out to identify crystal phase, measure micro size and determine purity of the copper oxide powders. Figure 4.2 shows the XRD spectra of the as-prepared CuO samples. The XRD spectra shows peaks corresponding to (110), (-111), (111), (-112), (-202), (020), (202), (-113), (022), (-311), (113), (220), (311), (004), (-222) planes which are well indexed to a monoclinic structure of CuO of space group C2/c in accordance with crystallography open database (COD) of ID number 9016105, see Figure 4.1 below.

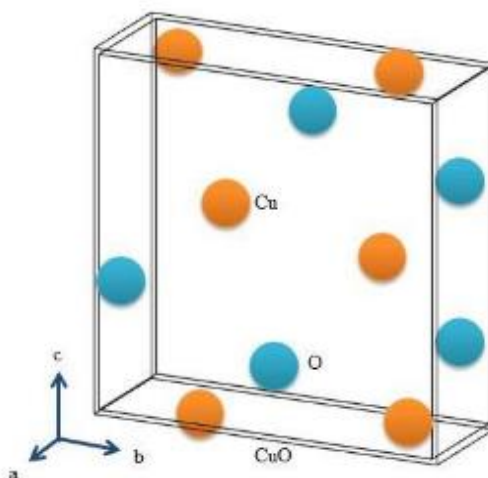


Figure 4.1: Crystal structure of CuO showing a copper atom surrounded by 4 atoms of oxygen in approximately square planar configuration.

This observation agrees with previously reported findings by Qiaobao Zhang *et. al.* [46], and N Calos *et. al.* [46], [66]. Diffraction peaks corresponding to expected impurities such as $\text{Cu}(\text{OH})_2$, $\text{Na}(\text{NO}_3)$ or Cu_2O were not observed, indicating that the prepared CuO powders were pure crystalline phase. This is a conformation of the efficiency of the purification process that was used in the experiments. Using the full width at half maximum (FWHM) of the peaks (which shall be illustrated later) the crystallite sizes was estimated.

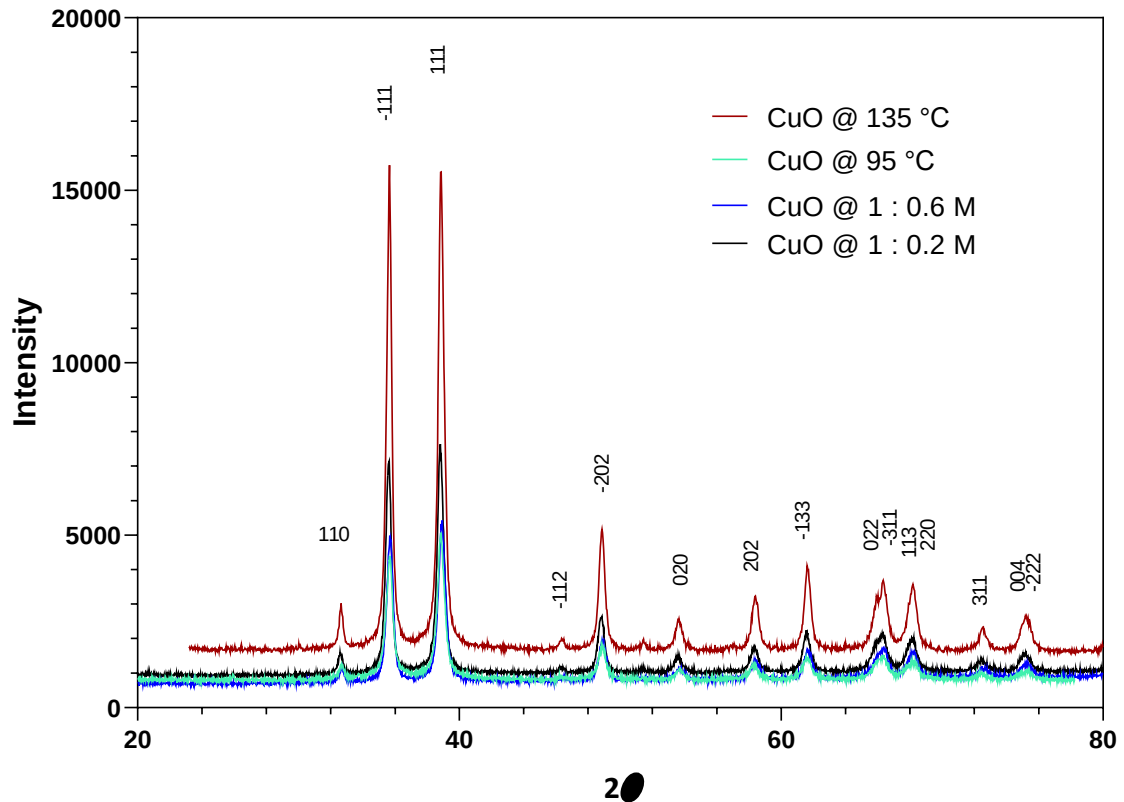


Figure 4.2: XRD Spectra of several samples CuO powder.

After determining the purity and crystal phase of the samples, the next objective of the research was to attempt to manipulate the morphology of the CuO nanoparticles. This was done because it is understood that this has a significant effect on thermal transport of the material, as alluded to earlier in Chapter 2. To achieve this, the morphology was controlled by varying the decomposition temperature of samples and concentration of

the active precursor. From this investigation it was observed that, the XRD peaks were broadening as the decomposition temperature was decreasing and when the concentration of the active precursor was increased. Figure 4.3 shows the broadening of peaks when copper oxide nanoparticles were prepared at different decomposition temperature, 95 °C, 100 °C, 120 °C, and 135 °C, and different concentrations of the active precursor solution, 1: 0.2, 1: 0.4, 1: 0.6, and 1: 0.8 indicating a decrease in the crystallite size. The peak intensities of CuO samples are largely reduced with broadening of the peaks as their crystallite size decreases. The crystallite size of the most intense peak at ($2\theta \cong 38^\circ$) for the samples was calculated using the Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (40)$$

Where D is the crystallite size, $K = 0.9$ is the Scherrer's constant, λ is the X-ray wavelength (1.54060 Å for Cu K_α radiation), β is the FWHM of the diffraction peak and θ is the Bragg diffraction angle. β and 2θ and their standard errors were determined using Origin data analysis software where the peaks were fitted to a nonlinear curve fit (Gauss). The standard errors for 2θ and β ranged between 0.00914° and 0.01260° and between 0.02175 and 0.03000 respectively for different samples.

The calculated crystallite size using the Scherrer equation of samples prepared through varying decomposition temperature and concentration of the active precursor solution are shown in Table 4.1 and Table 4.2.

Table 4.1: Crystallite sizes of CuO samples prepared at various decomposition temperature.

Sample	Crystallite size (nm)
CuO @ 95 °C	14.2
CuO @ 100 °C	15.1
CuO @ 120 °C	16.3
CuO @ 135 °C	18.6

Table 4.2: Crystallite size of CuO samples prepared at various concentration.

Sample	Crystallite size (nm)
CuO @ 0.2	20.1
CuO @ 0.4	19.3
CuO @ 0.6	18.2
CuO @ 0.8	17.9

The graph, in Figure 4.3a, shows that increasing decomposition temperature increases the crystallite size of CuO. The graph shows a broadening of the peaks with a decrease in the decomposition temperature from 135 °C to 95 °C. This could be due to the fact that an increase in temperature increases the rate of reaction, and when this occurs, a nucleus with a large size is formed in short period. This observation agrees with the work of Anayara Begum *et. al.* [67], Sattar A. Abass *et. al.* [68] and Habiba Elhendawi *et. al.* [69]. Slight shifts in peak positions (2θ) were also observed in peaks of CuO samples indicating that the lattice parameters of the CuO are slightly changed for the different CuO samples prepared under decomposition temperatures.

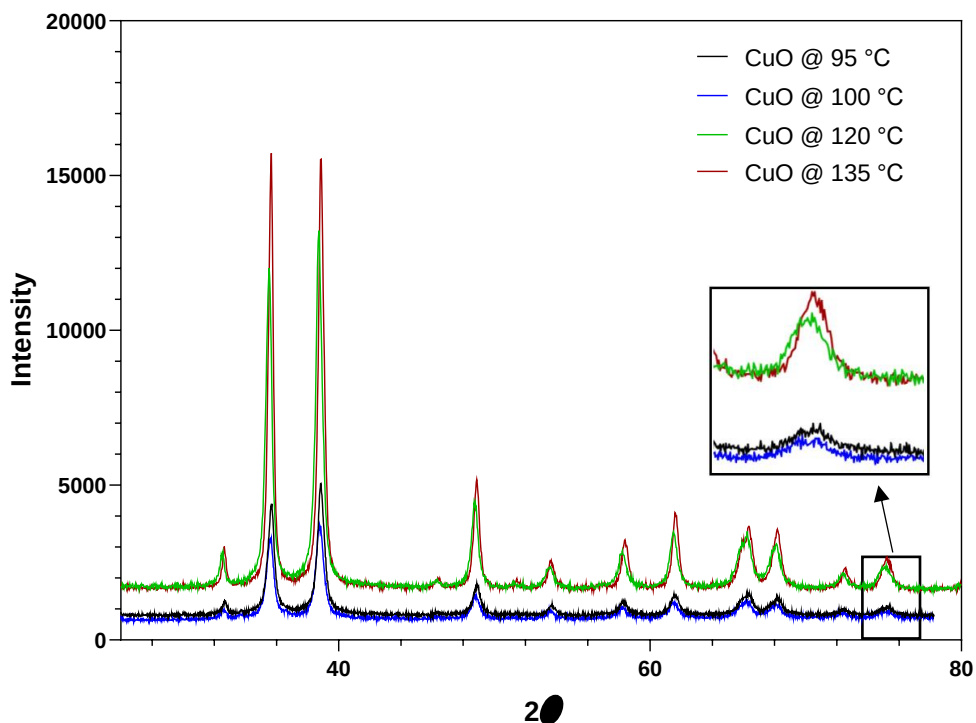


Figure 4.3a: XRD patterns of CuO nanoparticles prepared at different decomposition temperatures.

A similar observation was made in Figure 4.3b, which shows that the peaks get broader when concentration is increased from 0.2 M to 0.8 M and it can be concluded that an increase in concentration of the active precursor solution decreases the crystallite size of CuO. As concentration increases, the surface area for chemical reactions is reduced hence the crystallite size decreases. This observation agrees with the findings of N. Ahmad *et. al.* [70] and Hamed S. Dehsari *et. al.* [71].

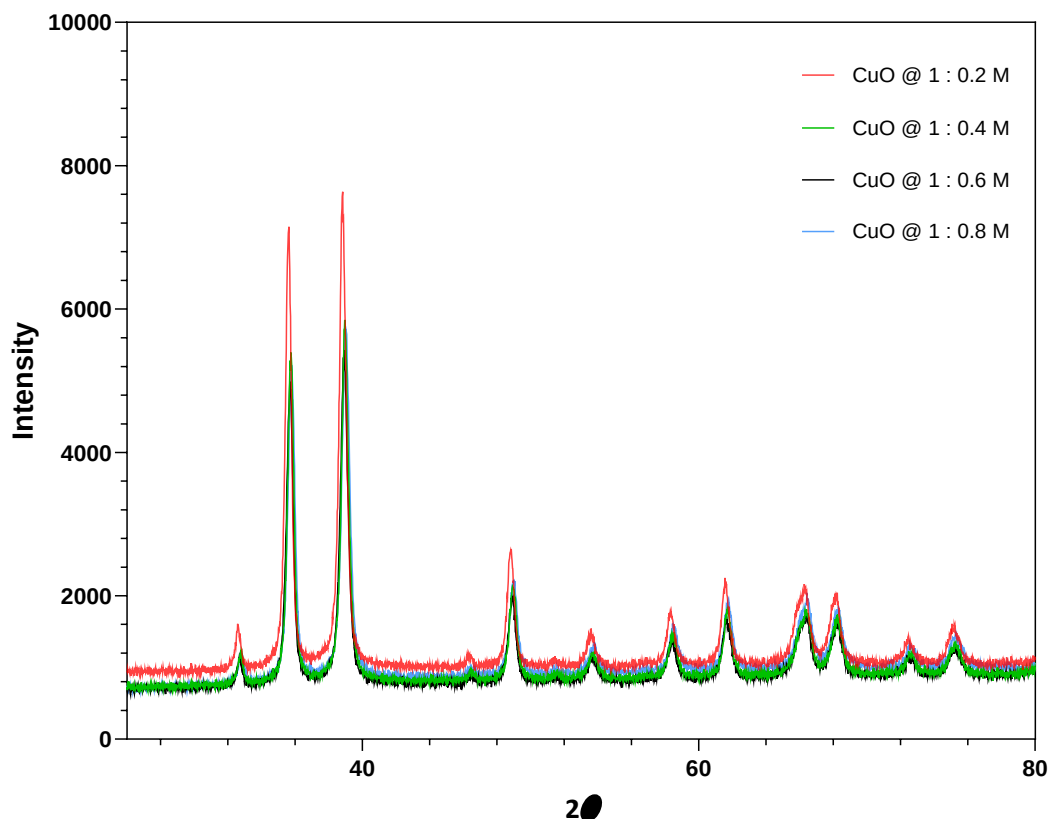


Figure 4.3b: *XRD patterns of CuO nanoparticles prepared at different concentrations.*

4.1.2 Scanning Electron Microscopy analysis

The surface morphology of the synthesized powders was examined by scanning electron microscope. The SEM images of CuO nanoparticles prepared at different decomposition temperatures are shown in Figure 4.4. It was observed that for most samples the sizes of particles were in the nano range, and hence it was concluded that the samples constitute mainly of nanoparticles of CuO. These micrographs show a structural evolution in crystal shape with increasing decomposition temperature. Figure 4.4a and 4.4b consists of ellipsoidal like morphology, the ellipsoidal width decreases with increasing decomposition temperature to 120 °C, as shown in Figure 4.4c. Further increase in temperature to 135 °C, result in both ellipsoidal and rod-like morphologies being present as depicted in Figure 4.3d. In essence higher temperature promotes the rod-like morphology.

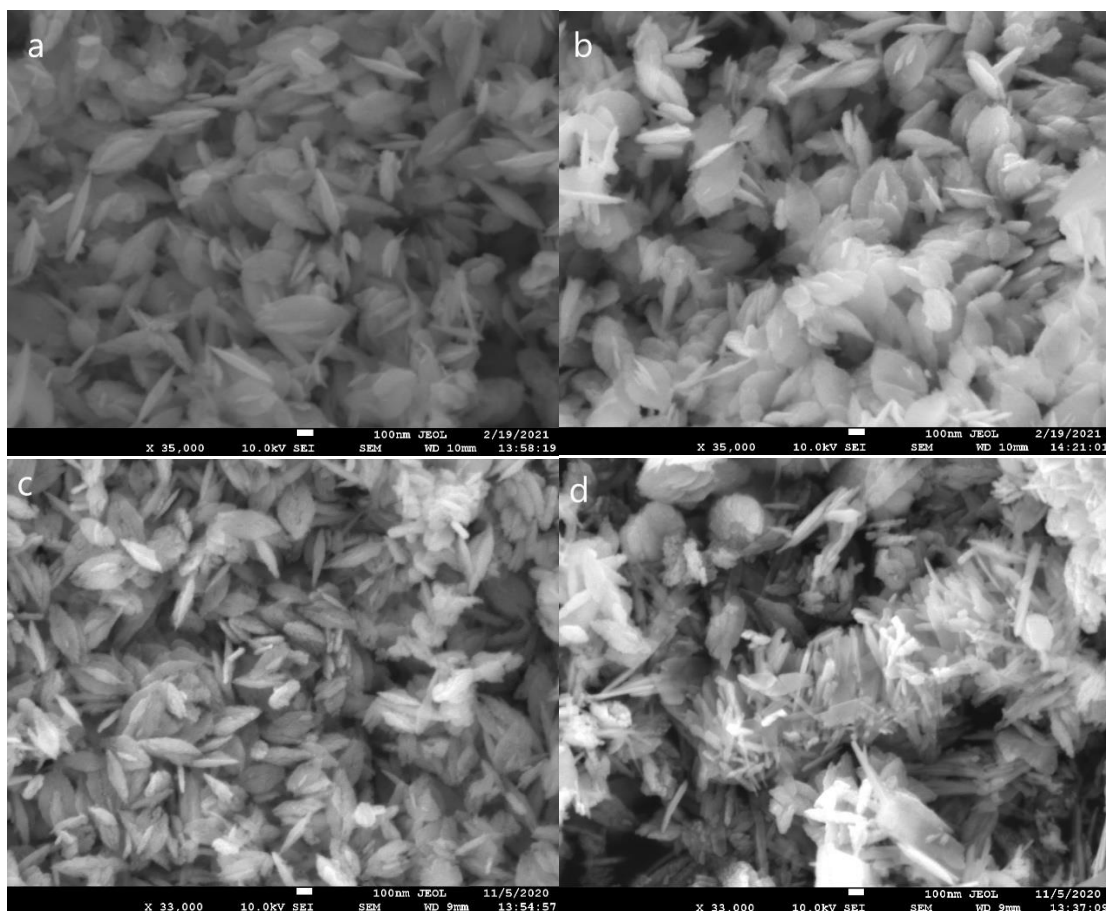


Figure 4.4: Typical SEM images of CuO nanoparticles prepared at decomposition temperature of (a) 95 °C, (b) 100 °C, (c) 120 °C, and (d) 135 °C.

Another parameter of interest on the morphology manipulation which was considered is the concentration of the active precursor solutions. Figure 4.5 shows SEM images of CuO nanoparticles prepared at different concentration of the active precursor solution. Varying concentration has no effect on shape of CuO nanoparticles as they all consist of ellipsoidal like morphology at different concentrations, however the concentration appears to affect the agglomeration of the particles. In Figure 4.5d there is significant agglomeration, and this is even more in Figure 4.5c.

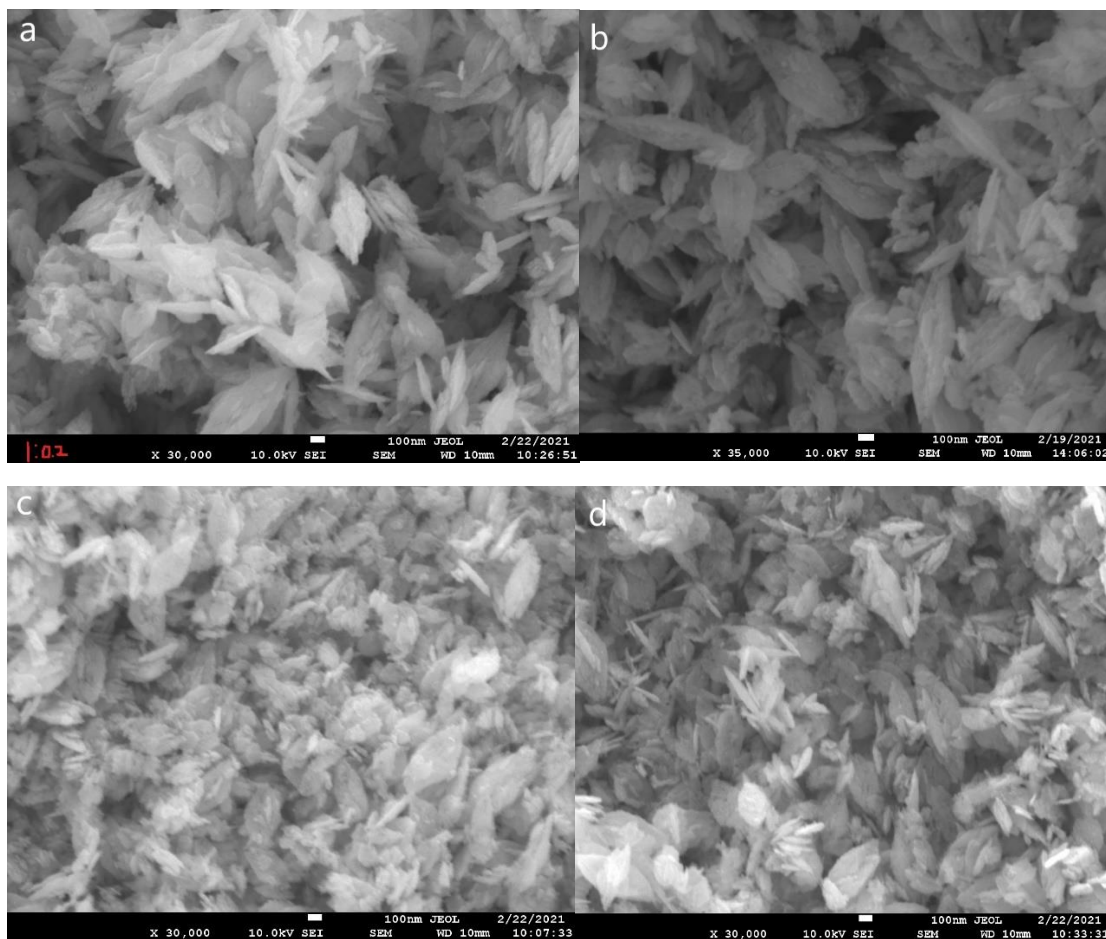


Figure 4.5: SEM images of CuO nanoparticles prepared with concentrations of precursors at (a) 0.2 M, (b) 0.4 M, (c) 0.6 M, (d) 0.8 M.

From the structural and morphological characterization, the structure of CuO nanoparticles was identified as a monoclinic structure from Crystallography Open database (COD) and had different surface morphologies as the decomposition temperature was varied. The significance of investigating the structure and morphology of the materials is that they affect the electron and phonon transport. To observe how the structure and morphology affected these parameters, the thermoelectric parameter measurements were investigated.

4.2 Thermoelectric Measurements

4.2.1 Electrical conductivity Analysis

After structural and morphology analysis, the CuO was made into pellets using Spark plasma sintering as described in Chapter 3. Electrical conductivity of CuO pellets prepared at different decomposition temperatures were measured in the temperature range from 50 °C to 200 °C by four-point probe method. The electrical conductivity of CuO nanoparticles was observed to increase with temperature as shown in Figure 4.6. This is a typical semiconducting behaviour in the electrical transport mechanism and can be explained as thermal excitation of charge carriers from valence band to conduction band. As the temperature is increased more carriers are given enough energy to move into the conduction band.

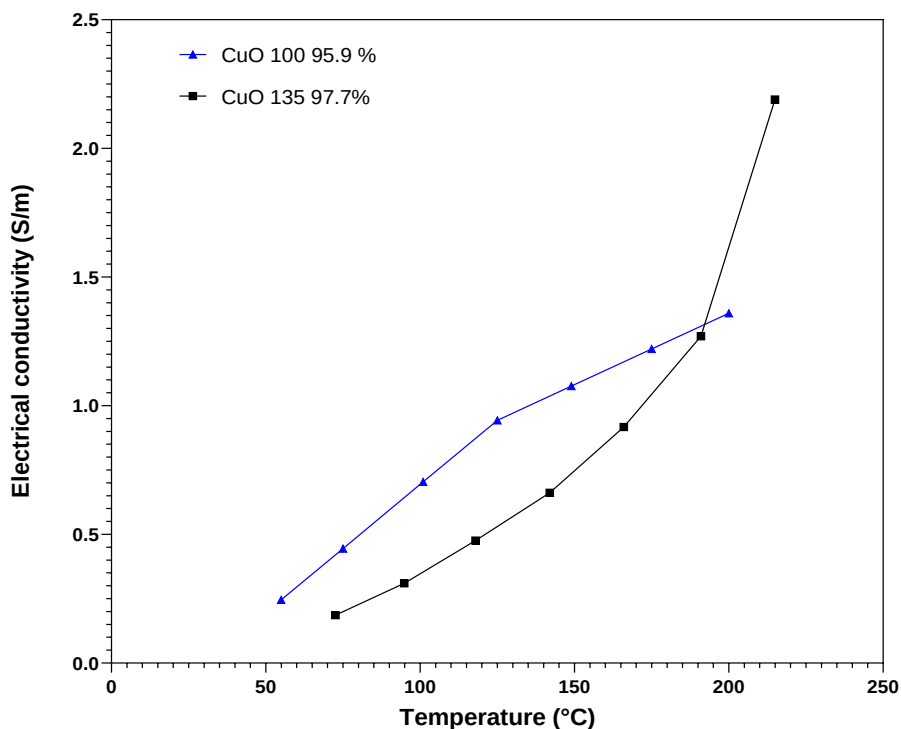


Figure 4.6: *Electrical conductivity of CuO nanoparticles prepared at decomposition temperature of 100 °C and 135 °C.*

It was also observed that the crystallite size and density of CuO pellets has an influence on the electrical conductivity. For example, results for samples, CuO @100, and CuO @135 with crystal sizes, 15.10 nm and 18.60 nm respectively show that electrical conductivity is high for CuO with small crystallite size which results in higher dense pellets. It is important to point out that the sintering was done at the same conditions and the samples had different densities, which was due to different crystal sizes. This observation is in agreement with the findings reported by O. Belahssen *et. al.*, when investigating effects of crystallite size in electrical conductivity of ZnO thin films [72]. We can also conclude that electrical conductivity is affected by the crystal size of the nanoparticles.

One of the objectives of this project was to investigate the effect of introducing a conducting polymer in CuO nanoparticles on the thermal conductivity. It is well known that electrical and thermal conductivity are interdependent because free charge carriers which transport electricity also carry heat energy and as a result introducing conducting polymer will also affect electrical conductivity. Figure 4.7 shows how the introduction of polyaniline (PANI) affect electrical conductivity.

Figure 4.7 shows electrical conductivity of pure copper oxide nanoparticles (Pure CuO) and the electrical conductivity when mixed with conductive polyaniline (CuO@PANI).

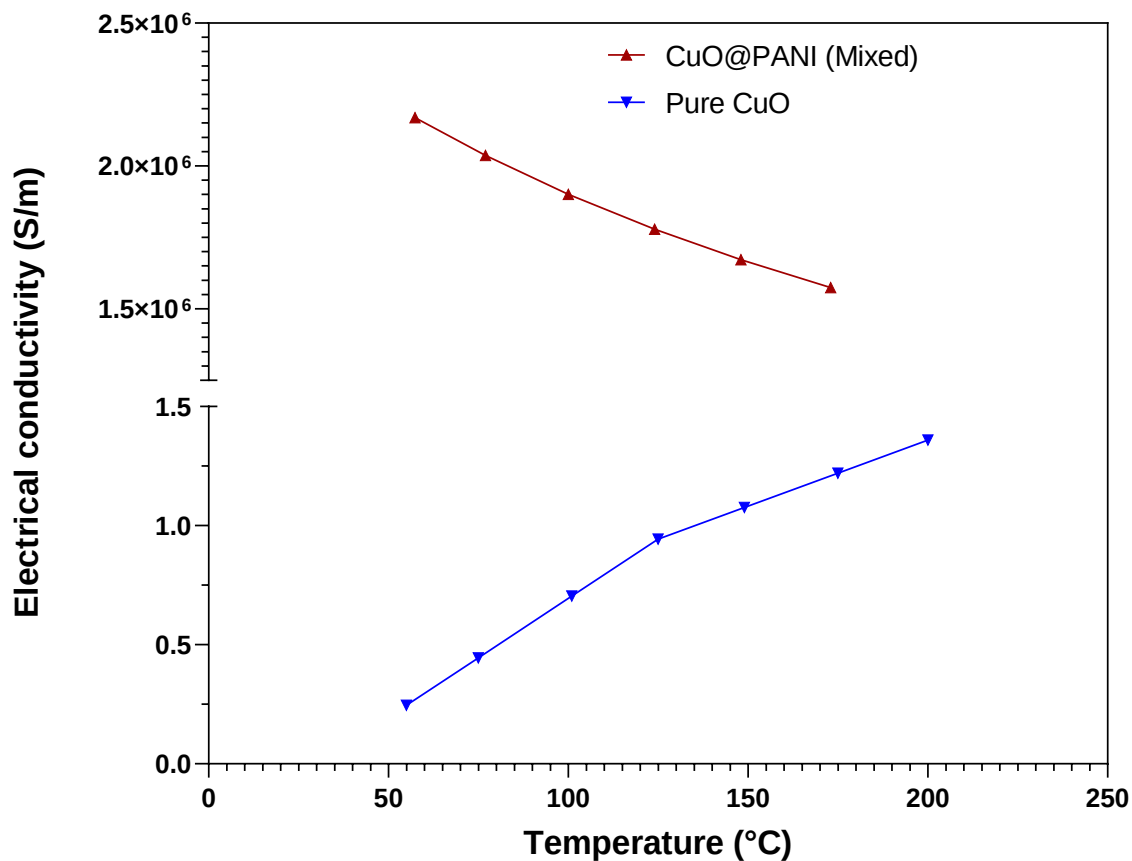


Figure 4.7: *Electrical conductivity data showing the effect of polyaniline on electrical conductivity of CuO.*

It was observed that introducing polyaniline to CuO nanoparticles increased electrical conductivity by a factor of 10^6 , and this could be explained as due to the increase of free or delocalised electrons in the composite coming from PANI since it is well-known conducting polymer. Furthermore, it was also observed that the electrical conductivity behaviour changes from semiconducting behaviour to metallic conduction when polyaniline is introduced. The transition in the behaviour of conduction suggests an overlap between the valence and conduction bands due to the introduction of PANI and hence a transition from semiconducting to metallic conduction behaviour. The electrical conductivity of CuO@PANI exhibiting metallic conduction behaviour is expressed by Drude model as;

$$\sigma = n \frac{e^2 \tau}{m^*}, \quad (43)$$

where symbols have their usual meaning. The average time between collisions τ , is a parameter that is dependent on temperature, and it decreases when temperature is increased. Charge carriers gain more kinetic energy as temperature is increased and begin to move faster and collide rapidly with other carriers/atoms in the material. The rapid collisions decrease the parameter τ , since $\sigma \propto \tau$ the electrical conductivity decreases as temperature increases.

The conducting polymer (PANI) was added to the oxide in two ways, first it was added in layers to make a superlattice-like structure of copper oxide polymer composite because in the proposed hypothesis, phonon scattering would occur at the layer boundaries of the superlattice structure, and this would lower thermal conductivity of the composite material. However due to technical constrains in measuring electrical conductivity of the superlattice-like structure, the instrument could not measure perpendicular to the layers. As a result, the final measurement data show electrical conductivity values of CuO mixed with PANI in layers similar with electrical conductivity values of pure CuO see Figure 4.7 and Figure 4.8. This is because conductivity was measured parallel to the layers and not perpendicular or across the material, and this means the results of conductivity obtained are for a dominant material in the superlattice which in this case is CuO nanoparticles.

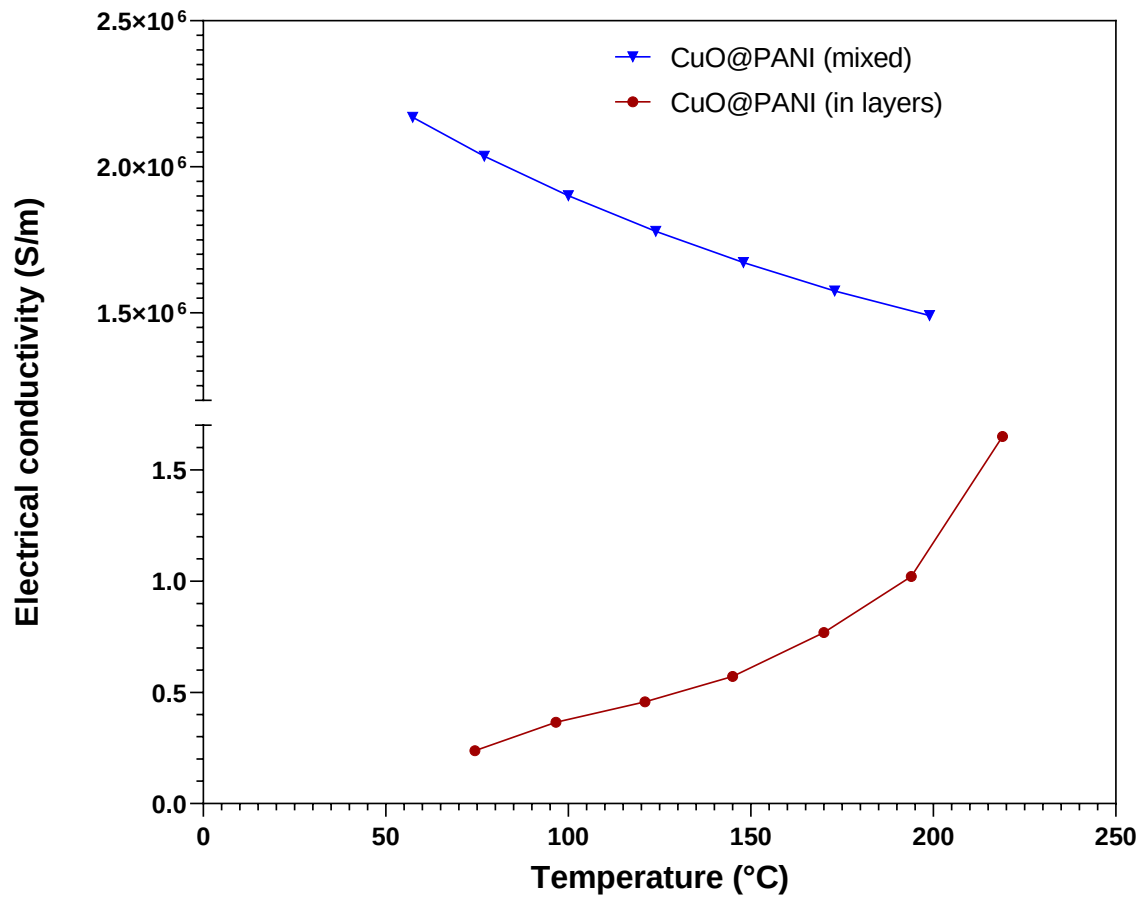


Figure 4.8: *Electrical conductivity of CuO polymer composite in a mixed form and in layers.*

4.2.2 Seebeck Coefficient Analysis

Another thermoelectric property which was measured is the Seebeck coefficient which is a parameter that is desirable to be high in the figure of merit, ZT . Figure 4.9 shows the Seebeck coefficient results of CuO nanoparticles with different morphologies.

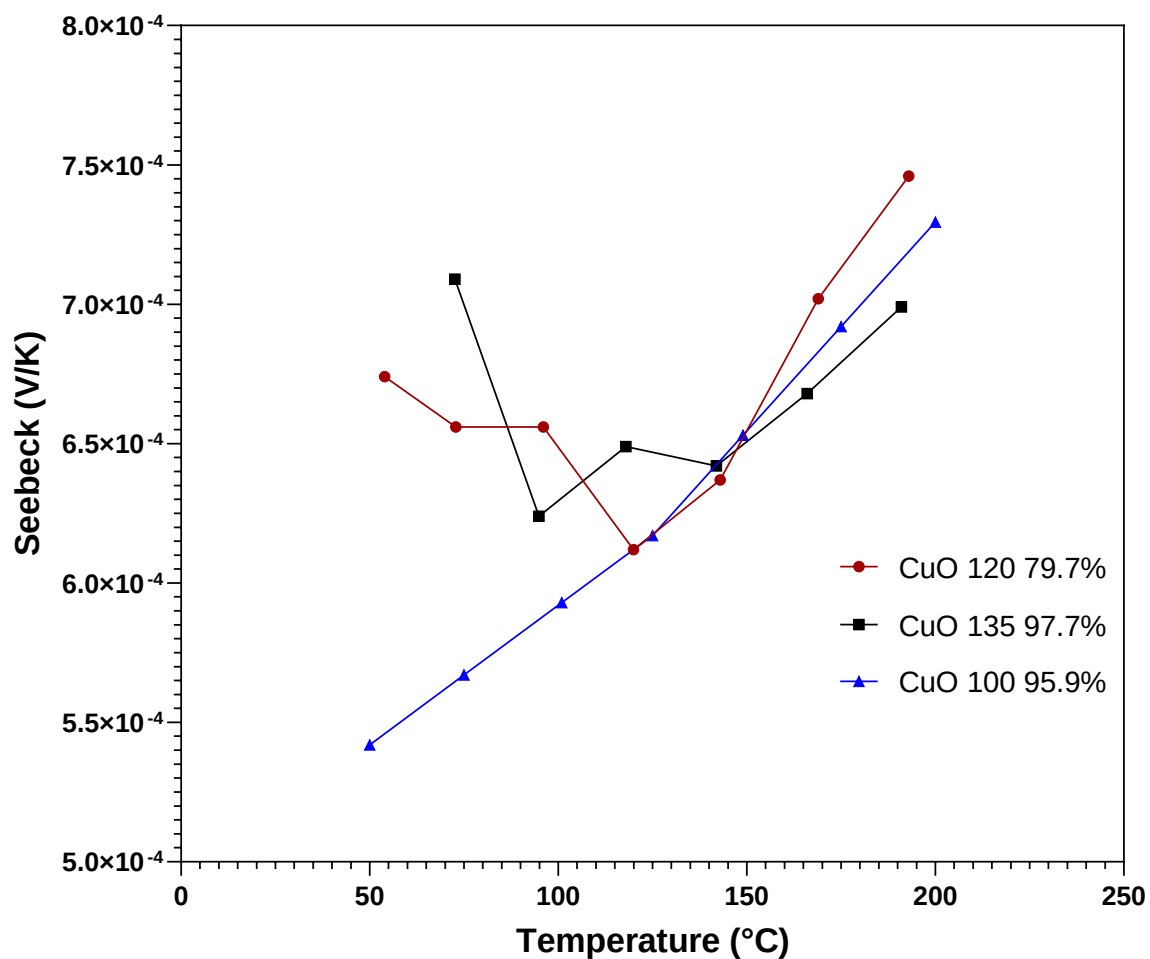


Figure 4.9: Seebeck coefficient of CuO pellets with different morphologies.

The Seebeck coefficient of all the samples fluctuates around $6 \times 10^{-4} \text{ V/K}$ in the temperature range of 50 °C to 250 °C and these results are similar to those obtained by J. Linnerra *et. al.* [73] and N. Salah *et. al.* [74]. From the results obtained, it is evident that difference in morphology does not have any significant change in Seebeck coefficient, indicating that morphology alone does not affect the Seebeck coefficient. But when polyaniline was introduced to CuO nanoparticles the Seebeck changed in magnitude significantly indicating that introduction of polyaniline has an effect on the Seebeck coefficient see Figure 4.10.

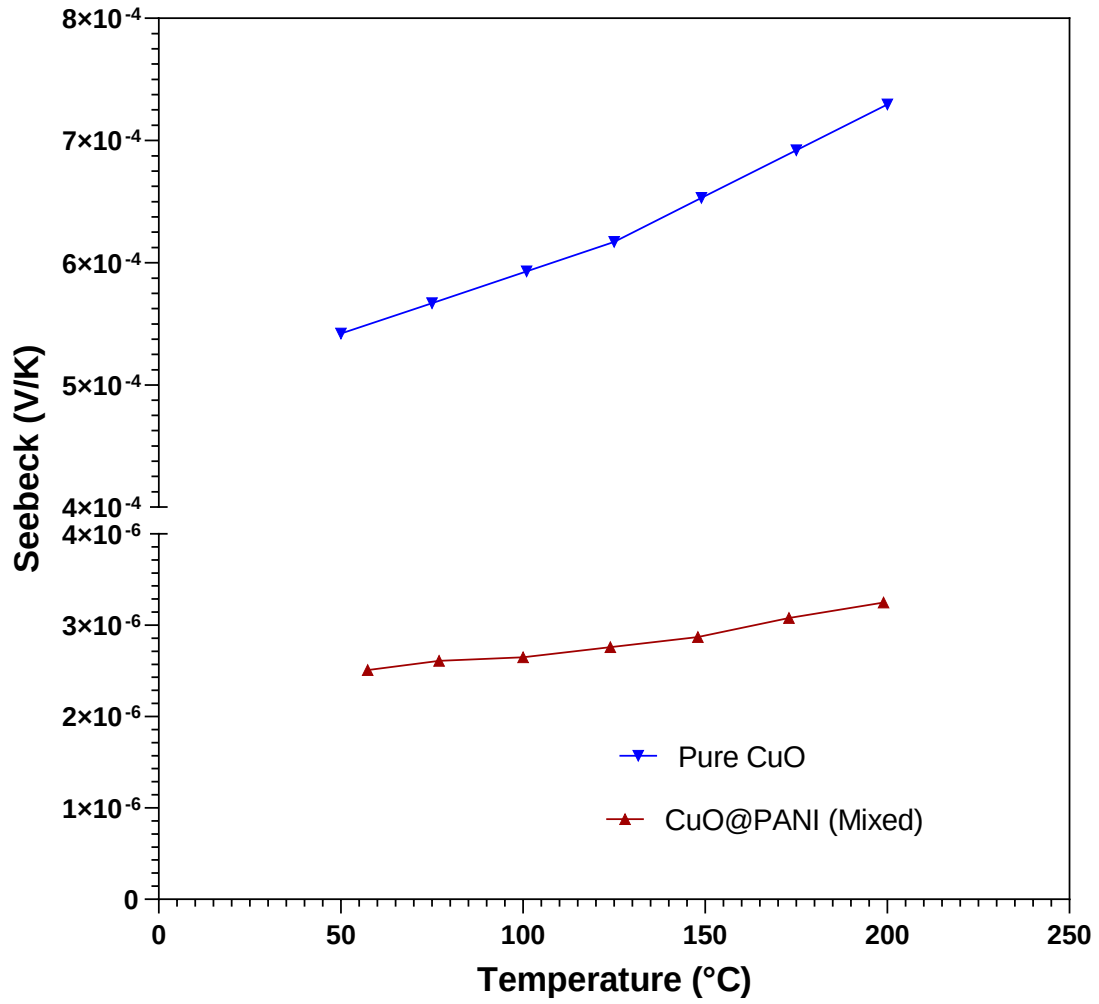


Figure 4.10: Seebeck coefficient of pure CuO and CuO@PANI pellets with polyaniline.

Figure 4.10 shows how the Seebeck coefficient of CuO nanoparticles dropped significantly by a factor of 10^2 when polyaniline was mixed with CuO nanoparticles. If equations 44 and 45 are considered, it is clear as to why the Seebeck coefficient dropped when PANI was introduced into the oxide. The conductive polymer increases the number of charge carriers as mentioned earlier which leads to a decrease in the Seebeck coefficient, the Seebeck coefficient will decrease because the two are inversely proportional.

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{\frac{2}{3}} \quad (44)$$

and

$$S \propto \frac{m^*}{n^{\frac{2}{3}}}. \quad (45)$$

The Seebeck coefficient of CuO nanoparticles with polyaniline in layers was measured and compared it to the Seebeck coefficient of CuO nanoparticles mixed with polyaniline see Figure 4.11. It was observed that there is no significant effect on addition of polyaniline in layers since the magnitude of Seebeck coefficient is close to that for CuO without polyaniline. This aspect raises good prospects for the layered structure to produce materials with higher ZT , if a configuration to measure the thermoelectric parameters perpendicular to the layers can be made which should be an objective for future work.

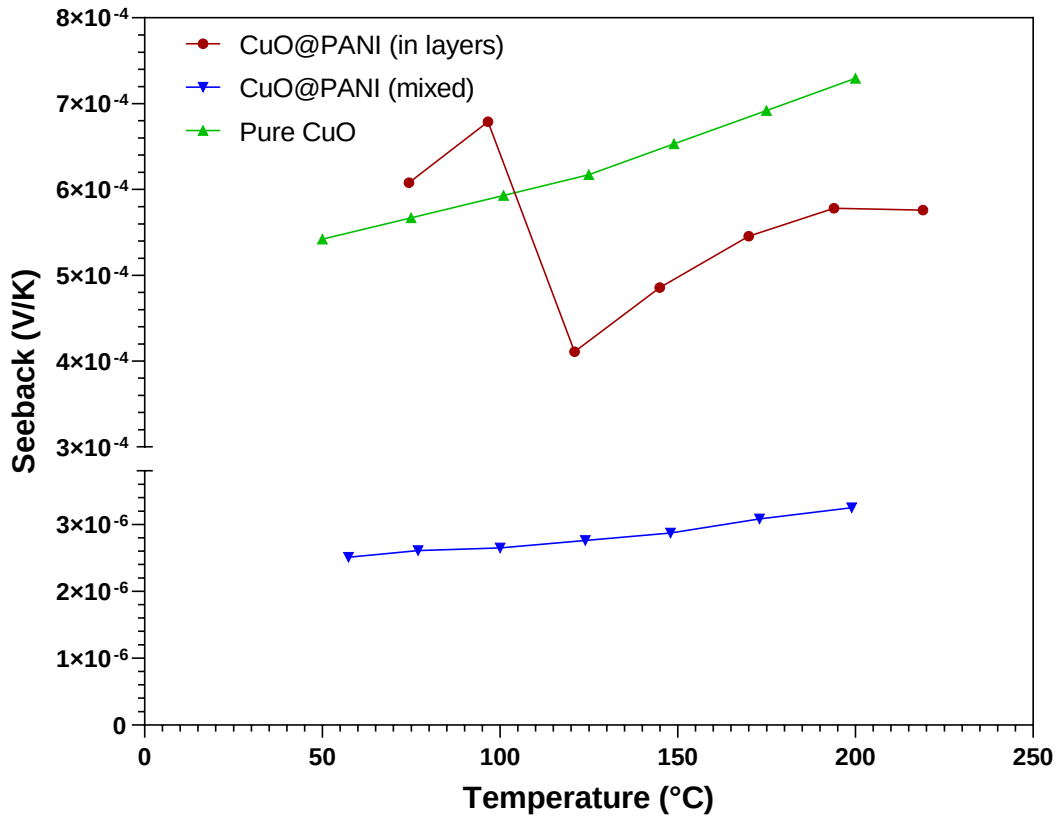


Figure 4.11: Seebeck coefficient of CuO polymer composite in layers and in mixed form.

This far, the electrical conductivity and Seebeck coefficient have been considered, which together they give the power factor which is a parameter that should be high to have a high value of figure of merit. In this project it was observed that introducing PANI results in an increase in electrical conductivity by 10^6 times and yet reduced Seebeck coefficient by a factor of 10^2 , effectively the power factor expressed as $P_F = S^2\sigma$, has been increased by a factor of 10^2 by introducing PANI into the CuO. Thermal conductivity is a denominator in the equation of figure of merit, so it must be lower to have a high value of figure of merit.

4.2.3 Thermal Conductivity Analysis

Thermal conductivity measurements were performed on samples of pure CuO pellets with different crystal sizes, to investigate how morphology affects thermal conductivity. Figure 4.12 shows a general decrease in thermal conductivity as temperature increases for all samples prepared at different decomposition temperature. This is expected because at temperatures above Debye temperature of the material (approximately 560 K [75] for CuO), thermal conductivity is dominated by the vibrations of the lattice and it decreases as temperature increases. This is because a rise in temperature increases lattice vibrations and as a result phonon mean free path is reduced due to phonon scattering.

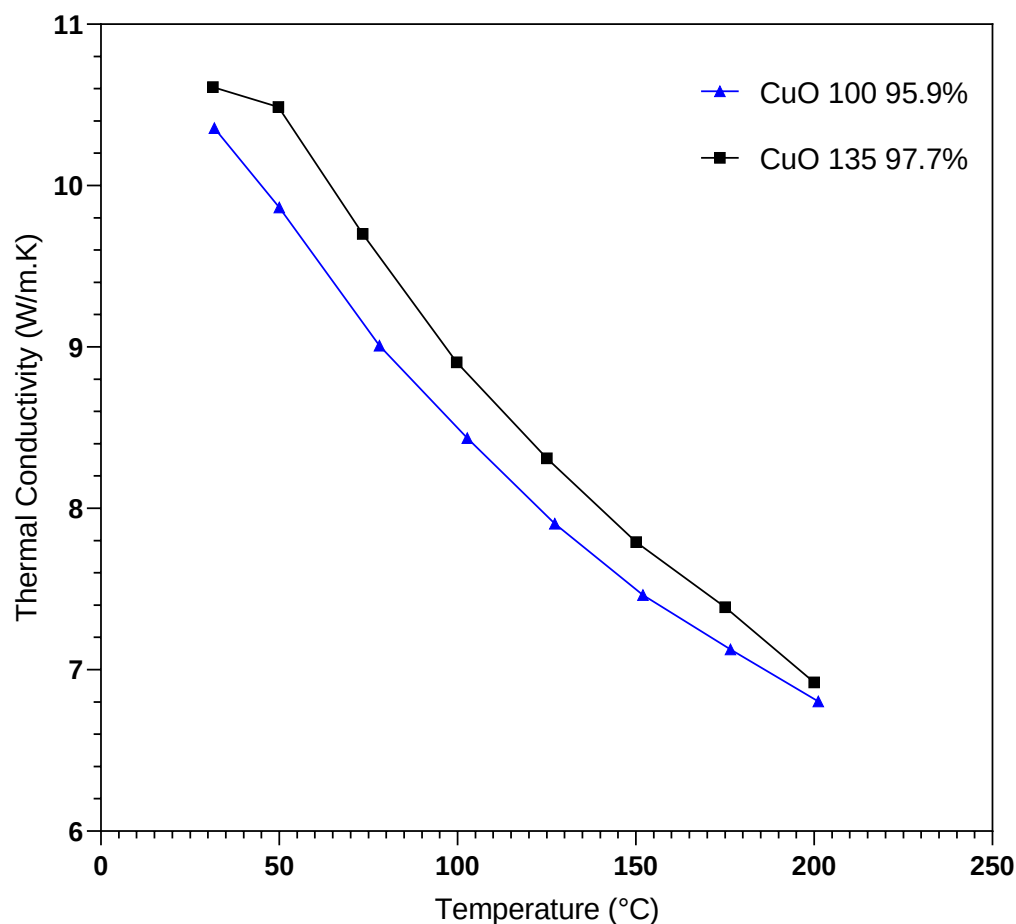


Figure 4.12: Thermal conductivity of CuO pellets with different morphologies and density.

It was also observed that there is a difference in the value of thermal conductivity of CuO nanoparticles with different surface morphologies and densities and this indicates that morphology and density have an effect on thermal conductivity of CuO nanoparticles. Samples of CuO 100 95.9 % with ellipsoidal morphology have low value of thermal conductivity as compared to CuO 135 97.7 % with surface morphology (mixed ellipsoidal and nanorods) and this could be so because there are more phonons scattering at the surface boundary due to the non-uniformity of the nano particle sizes. The cross-sectional area of ellipsoidal morphology is larger than of nanorods morphology hence there is higher phonon scattering at the interface of the two. See Schematic diagram below.

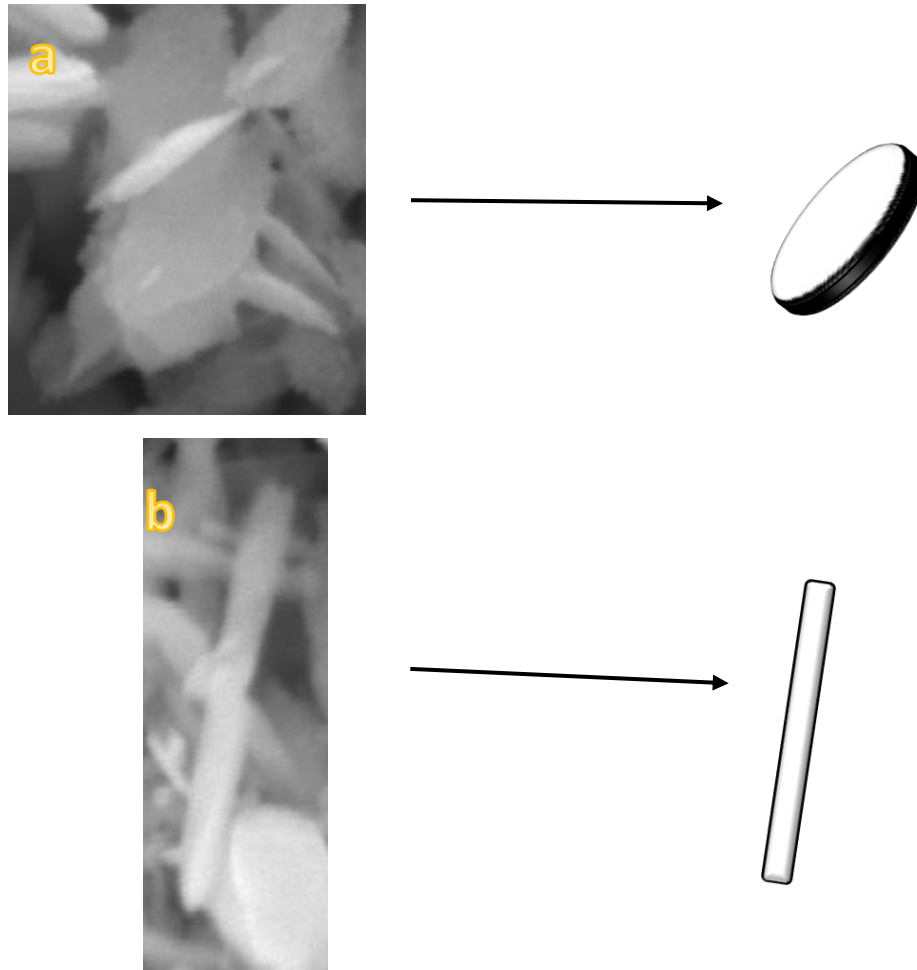


Figure 4.13: A schematic diagram showing the surface area of a) ellipsoidal morphology, and (b) nanorods morphology.

Thermal conductivity of these samples is also affected by their densities. Samples of CuO 135 97.7 % are more compact because of 97.7 % theoretical density as compared to samples of CuO 100 95.9 % with 95.9 % theoretical density. From Figure 4.12 it is observed that samples that are more compact have high thermal conductivity than samples that are less compact and this is expected as it is known that $k = \alpha \rho C_p$, where α is thermal diffusivity, ρ is the density, and C_p is the specific heat capacity, so from this it can be noted that thermal conductivity is proportional to the density of the material ($k \propto \rho$) because the phonon mean free path is greater in denser materials.

From literature review it was noted that phonon scattering is not only affected by morphology but also by point defects from foreign materials, which is why the effect of adding polyaniline to CuO nanoparticles on thermal conductivity was then investigated.

From figure 4.14 it was observed that adding polyaniline to CuO nanoparticles reduces thermal conductivity of the material.

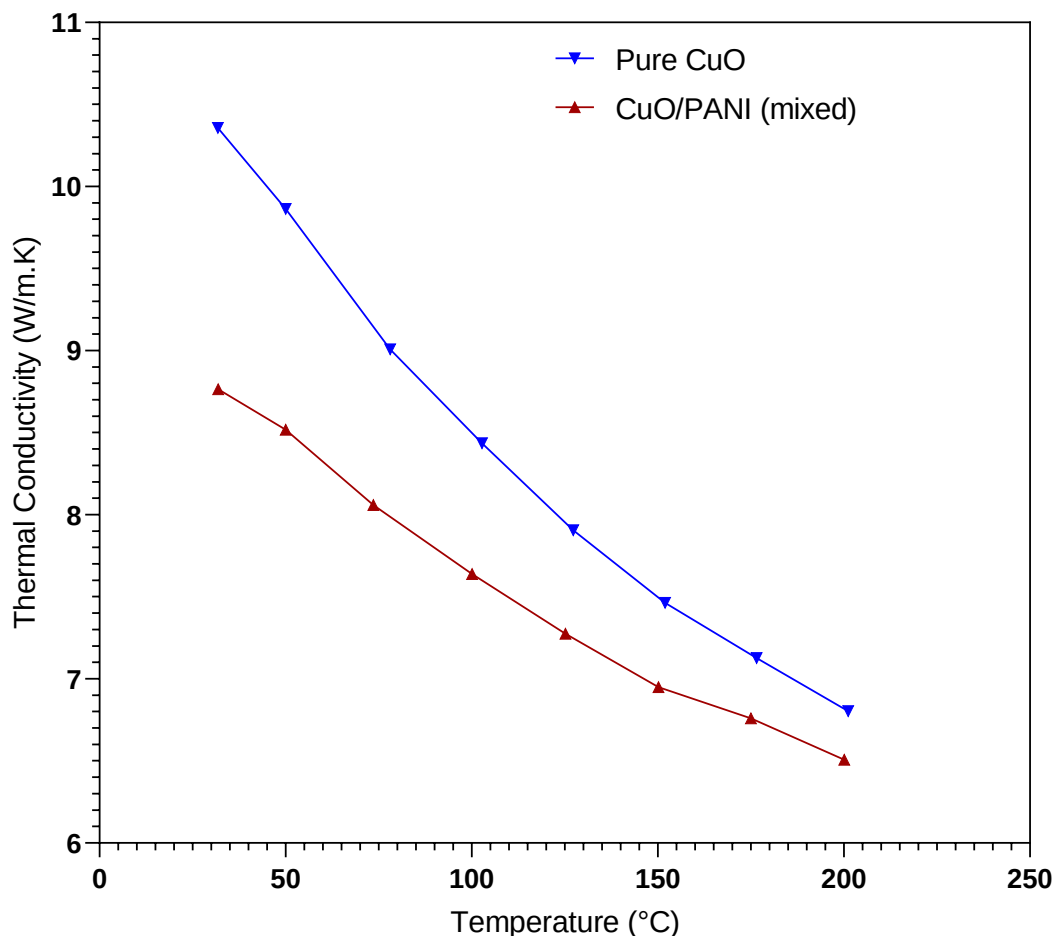


Figure 4.14: *Thermal conductivity of CuO nanoparticles with and without polyaniline.*

When polyaniline was mixed with CuO nanoparticles, there is a significant decrease in the value of thermal conductivity and this is because, point defects were created through addition of the polymer and this led to phonon scattering in the material. For the pure CuO pellets in the temperature range of 25 °C to 200 °C, thermal transport is dominated

by three phonon process where two phonons collide to form one new phonon or where a phonon is utterly destroyed to form two new phonons. In this region the phonon mean free path is limited by these phonon interactions called phonon-phonon scattering. It is also noted that in this region $k \propto T^{-1}$ and this is also because at thermal equilibrium according to Bose-Einstein statistical factor the number of phonons is given by

$$n \approx \frac{k_B T}{\hbar \omega}, \quad (46)$$

Where symbols have their usual meanings. An increase in temperature increases number of phonons and therefore there will be an increase in phono-phonon scattering hence a decrease in thermal conductivity as temperature increases was as observed. After adding PANI to CuO which introduced point defects in the material, now the phonon mean free path is limited by both phonon-phonon scattering and phonon-defects scattering, the total phonon mean free path can be written as

$$\frac{1}{l_{tot}} = \frac{1}{l_{ph-ph}} + \sum \frac{1}{l_{ph-def}}. \quad (47)$$

The total mean free path in the material is now reduced due to phonon-defects scattering hence a decrease in lattice thermal conductivity after adding PANI. It was also observed that the thermal conduction mechanism in the pellets is in accordance with Callaway and Von Baeyer model [34], which expresses thermal conductivity as

$$k = \frac{k_B}{2\pi^2 v_s} \left(\frac{k_B T}{\hbar} \right)^3 \int_0^{\theta_D/T} \tau_c(x) \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (48)$$

where $x = \hbar \omega / k_B T$ and θ_D is Debye temperature. The model predicts that in a perfect crystal or when there is small defect scattering, thermal conductivity decreases with temperature as $\propto T^{-1}$, and when there are large defect scattering at high temperatures thermal conductivity decreases with temperature as $T^{-1/2}$. To confirm this model, the

experimental data were plotted with $T^{-1/2}$ and the graph showed a linear trend indicating that it fits well with the model. See Figure 4.15.

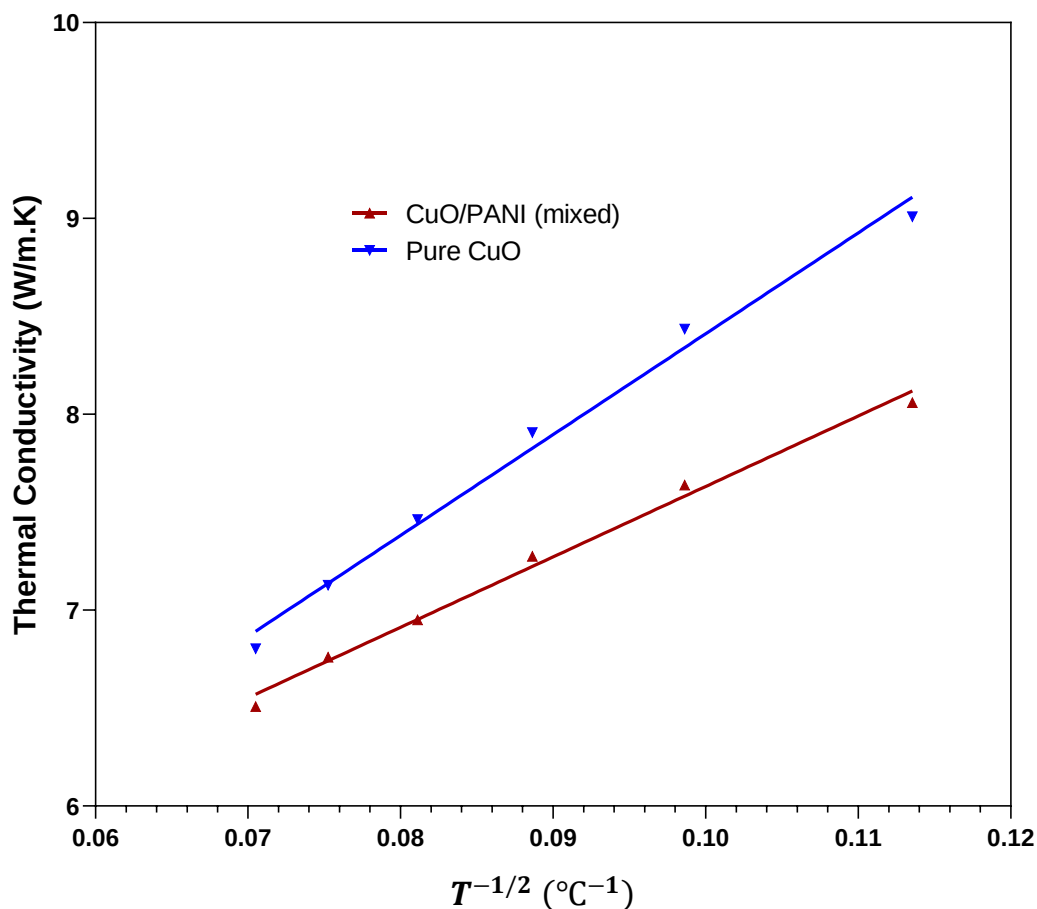


Figure 4.15: A plot of thermal conductivity (k) vs $T^{-1/2}$ for pure CuO and CuO/PANI nanocomposite (mixed).

Since there are two ways in which polyaniline was incorporated into CuO nanoparticles, the thermal conductivity of CuO polymer composite in layers was measured and compared to the thermal conductivity of CuO polymer composite (mixed) as shown in Figure 4.16. Samples of CuO polymer composite in layers shows lower values of thermal conductivity as compared to a sample of CuO polymer composite in a mixed form. At the

grain boundary between the layers of CuO nanoparticles and polymer phonons are scattered hence there is lower thermal conductivity for CuO polymer composite in layers than CuO polymer composite in a mixed form.

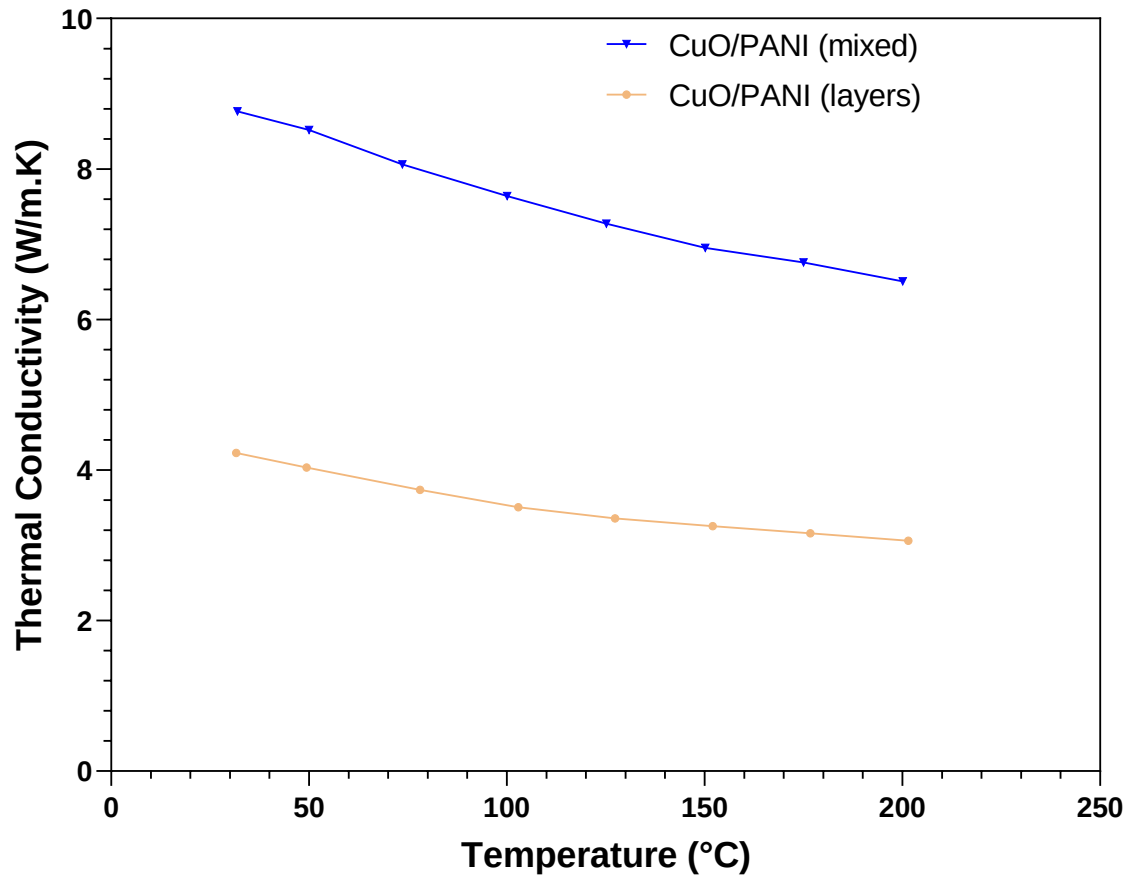


Figure 4.16: Thermal conductivity of CuO polymer composite in layers and in a mixed form.

The main objective of this project was to increase thermoelectric figure of merit of CuO nanoparticles by adding polymer to the material. The proposed hypothesis was that adding polyaniline will reduce thermal conductivity; the result above clearly show that this was successful. However, it is known that the introduction of PANI would lower power factor. From figure 4.17 it was observed that introduction of polymer affected all the parameters of the figure merit hence there is a difference in the values of ZT for pure

CuO nanoparticles and CuO nanoparticles mixed with polyaniline. Electrical conductivity increased by a factor of 10^6 but the Seebeck decreased a factor of 10^{-2} and this means there is an overall increase in power factor. Thermal conductivity on the other hand was lowered and as a result the value of ZT increased by 10^2 . R. Mulla and M. Rabinal have reported on their work a ZT value of 3.2×10^{-8} for pure CuO with a spherical-like morphology and particle size that ranged from $5 - 10 \mu\text{m}$ [76]. Their ZT value is lower than the ZT value ($\approx 3 \times 10^{-7}$) of pure CuO prepared in this work. The morphology of CuO particle could be the reason for a low value of ZT compared to the results of this project as it has been shown in this study how the size of the crystal and surface morphology affect thermoelectric properties.

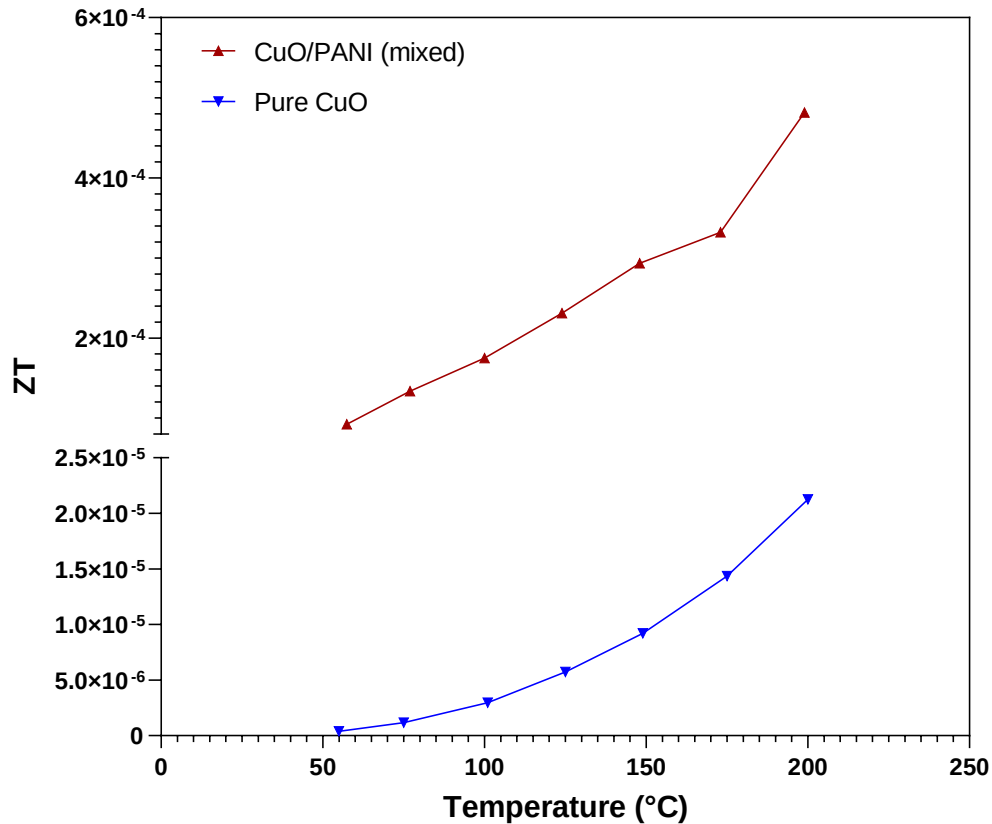


Figure 4.17: Thermoelectric properties of pure CuO nanoparticles and CuO nanoparticles mixed with polyaniline.

CHAPTER 5

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This study has demonstrated a simple solution-based method to synthesize CuO nanoparticles using Copper (II) nitrate trihydrate and Sodium hydroxide as precursors. CuO nanoparticles with different morphologies were successfully prepared through varying concentrations of $Cu(NO_3)_2 \cdot 3H_2O$ and decomposition temperature using hydrothermal synthesis technique. XRD and SEM were used to confirm the structure and morphology of the nanoparticles, and analysis shows that all the samples are of monoclinic structure of CuO and there was no phase transition when synthesis conditions were varied. The crystallite sizes were deduced from the XRD data and the surface morphology was determined using the SEM. It was found that the crystallite sizes increased with the increase in concentration of Copper (II) nitrate trihydrate and also when the decomposition temperature was increased. The surface morphology also changed from being dominant ellipsoidal morphology to dominantly nanorods-like morphology when decomposition temperature was increased.

The prepared CuO powders and CuO/PANI nanocomposites, mixed and superlattice-like, were successfully sintered into pellets using Spark plasma sintering and their compactness or density was confirmed using a laboratory balance.

Thermoelectric properties of pure CuO and CuO/PANI nanocomposites were measured and figure of merit ZT was determined. Electrical conductivity of CuO pellets with different morphology were measured and it was found that electrical conductivity was higher in CuO pellets with small crystallite sizes. The conductivity of pure CuO ranges from approximately 0.2 to 1.4 S/m between 50 °C and 200 °C, and dramatically increased by a

factor of 10^6 to σ in the range of 1.5×10^6 to 2.2×10^6 S/m in the same temperature range, when mixed with PANI. Meanwhile the Seebeck coefficient dropped significantly from $\approx 6 \times 10^{-4}$ V/K to $\approx 3 \times 10^{-6}$ V/K when mixed with PANI. It can be concluded that the power factor was improved by a factor of 10^2 from introducing PANI into CuO. Thermal conductivity of CuO/PANI nanocomposites and pure CuO with different surface morphology was successfully measured. CuO pellets of surface morphology with large surface area has low thermal conductivity, so lattice thermal conductivity can be lowered through manipulating surface morphology of nanoparticles. Thermal conductivity of pure CuO pellets ranges from ≈ 10.5 W/mK to ≈ 6.8 W/mK between 30 °C and 200 °C and dropped to a range of ≈ 8.8 W/mK and ≈ 6.5 W/mK in the same temperature range when CuO was mixed with PANI. It dropped further to a range of ≈ 4.2 W/mK and ≈ 2.8 W/mK when PANI was added in layers. Figure of merit ZT for pure CuO pellet and CuO/PANI mixed nanocomposite was successfully determined from thermoelectric measurement. It was found that the ZT value of the materials increases with temperature, hence our materials perform better at high temperatures. ZT values of pure CuO ranges from $\approx 3 \times 10^{-7}$ to $\approx 2 \times 10^{-5}$ and improved by a factor of 10^1 when CuO was mixed with PANI. This study shows that all the three thermoelectric properties of CuO (summarised in figure 5.1) are affected by addition of the polymer, with the power factor being improved and thermal conductivity being lowered. Figure of merit ZT was enhanced by mixing CuO with PANI and that shows that CuO/PANI nanocomposite is a potential candidate to be used as a cheap and environmentally friendly thermoelectric material.

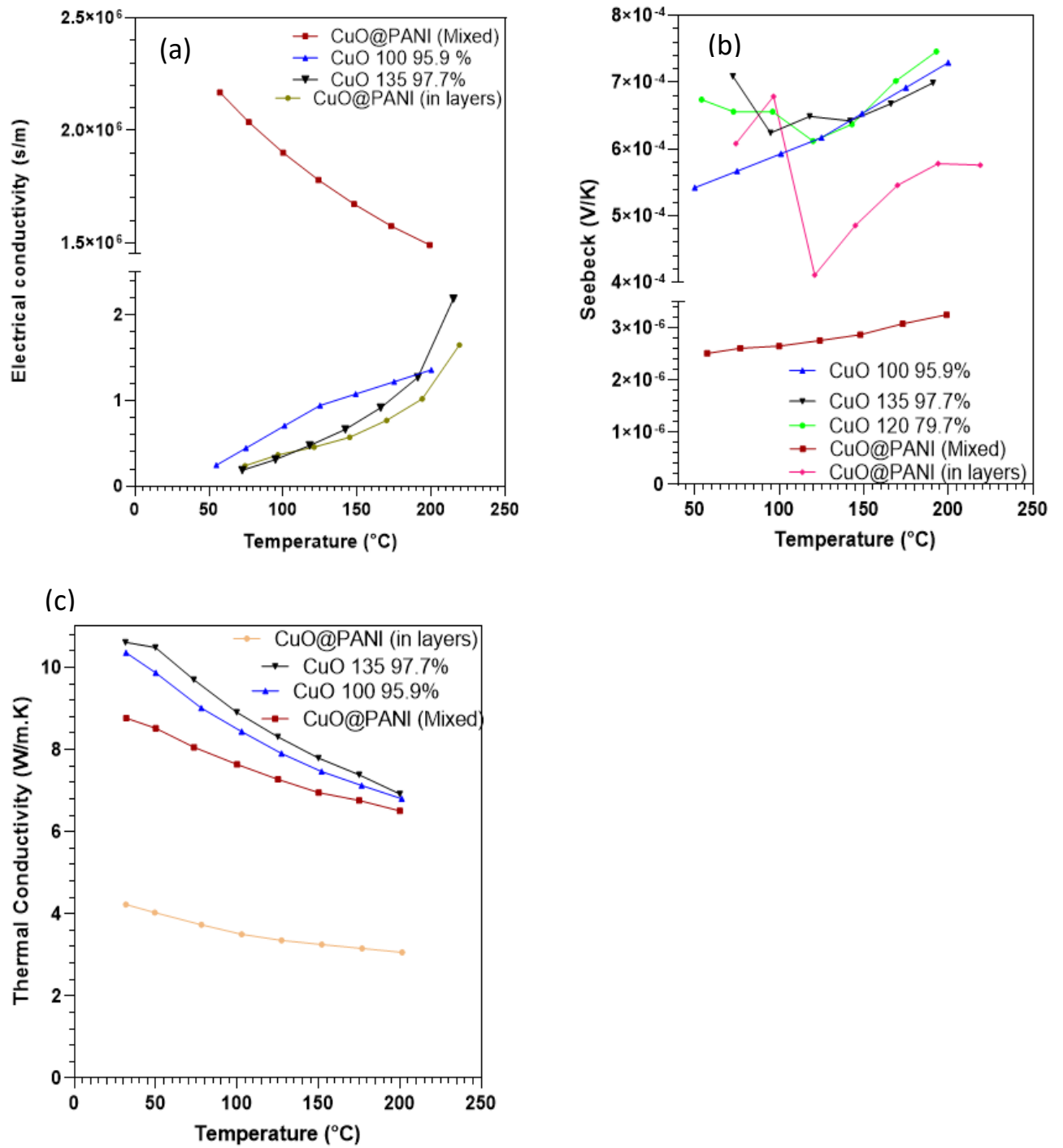


Figure 5.2: Temperature dependence of thermoelectric properties for CuO sample with and without PANI. (a) Electrical conductivity, (b) the Seebeck coefficient, and (c) thermal conductivity.

5.2 Recommendations for Future Work

The aim of this work was to enhance the ZT value of CuO by using a superlattice-like structure of CuO/PANI nanocomposite and this was achieved. There are few suggestions that will be recommended for future work.

- 1) PANI layers in a superlattice should be placed in a way that allows electrical conductivity and Seebeck coefficient to be measured perpendicular to the layers of the polymer.
- 2) Varying the number of polymer layers in a superlattice should be considered in studying the effect of superlattice period on lattice thermal conductivity.
- 3) Varying the concentration of $NaOH$ with $Cu(NO_3)_2 \cdot 3H_2O$ to determine the optimum concentration.

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