# THERMOELECTRIC PROPERTIES OF LaCo<sub>4</sub>Sb<sub>12</sub> SKUTTERUDITE MATERIALS BY ADDITION OF AI, In, Ni & Te

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# FACULTY OF ENGINEERING UNIVERSITY OF MALAYA KUALA LUMPUR

2017

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### THESIS SUBMITTED IN FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

## FACULTY OF ENGINEERING UNIVERSITY OF MALAYA KUALA LUMPUR

2017

# UNIVERSITY OF MALAYA ORIGINAL LITERARY WORK DECLARATION

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Registration/Matric No: X51677983/KHA120090

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# Thermoelectric Properties of LaCo<sub>4</sub>Sb<sub>12</sub> Skutterudite Materials by Addition of Al, In, Ni & Te

Field of Study: Energy

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#### ABSTRACT

Skutterudite is a superior material used in thermoelectric application. In this work, the crystal structure and morphology of the ternary skutterudite (La/Yb)<sub>x</sub>Co<sub>4</sub>Sb<sub>12</sub> were modified by incorporating of various addition such as Al, In, Ni and Te. This process was conducted via two step method namely mechanical alloying and spark plasma sintering technique. Specifically, the phase structure and morphology of the bulk samples were examined by X-ray diffraction (XRD) and scanning electron microscopy integrated energy-dispersive X-ray spectroscopy analysis (SEM-EDS), respectively. The thermoelectric properties of the bulk samples were measured in a temperature range of 300 K to 800 K. Furthermore, the oxidation and thermal properties of the samples were studied using a thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) that measured from 25 °C to 1000 °C. Evidently, it is proved that all of the samples demonstrated a dominant phase of polycrystalline CoSb<sub>3</sub> skutterudite. Among the sample, Al<sub>0.05</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> exhibited an excellent electrical properties, as manifested by its optimum carrier concentration and lowest electrical resistivity of 7.6μΩm at 314 K. In terms of the Seebeck coefficient, La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>11.7</sub>Te<sub>0.3</sub> recorded a highest value of 300 µV/K at 404 K. In the thermal conductivity behaviors, Al<sub>0.3</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample showed the lowest thermal conductivity and lattice thermal conductivity values of 1.1 W/mK (314 K) and 0.64 W/mK (595 K), respectively. This occurrence can be related to the enhancement in phonon scattering by rattling Al atom into the lattice cages. Al<sub>0.05</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> also presented a highest dimensionless figure of merit (ZT) which is 1.36 at 789 K, validating the substantial mitigation in electrical resistivity and lattice thermal conductivity. In conclusion, it has been proven that the modified materials possess notable oxidation and thermal stability in high temperature regime up to 800 °C.

#### ABSTRAK

Skutterudite merupakan bahan terunggul yang digunakan dalam aplikasi termoelektrik. Dalam kajian ini, struktur kristal dan morfologi skutterudite dari tiga bahagian bahan iaitu (Yb/La)<sub>v</sub>Co<sub>4</sub>Sb<sub>12</sub> telah diubahsuai melalui penggabungan dengan penambahan seperti (Al, In, Ni dan Te). Proses ini telah dijalankan melalui dua langkah yang dinamakan kaedah pengaloian mekanikal dan teknik-teknik persinteran percikan bunga api plasma (SPS). Secara khususnya, Struktur fasa dan morfologi bagi setiap sampel di analisis dengan menggunakan XRD dan SEM-EDS. Sifat-sifat termoelektrik setiap sampel di sukat pada suhu 300 ke 800K. Tambahan pula, analisis termogravimetri (TGA) dan pembezaan imbasan kalorimeter (DSC) digunakan untuk mengkaji pengoksidaan dan sifat-sifat haba yang diukur dari suhu 25°C hingga 1000°C. Jelas membuktikan bahawa semua sampel menunjukkan fasa dominan polihabluran CoSb3 skutterudite. Antara kebanyakkan sampel, Al<sub>0.05</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> mempamerkan sifat elektrik yang sangat baik dengan kepekatan pembawa optimum dan kekonduksian elektrik terendah iaitu 7.6  $\mu\Omega$ m pada suhu 314 K. Dari segi pekali Seebeck, nilai tertinggi yang diperolehi adalah 300 µV/K dicatatkan oleh sampel La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>11.7</sub>Te<sub>0.3</sub> pada suhu 404 K. Di dalam tingkahlaku kekonduksian terma, sampel Al<sub>0.3</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> menunjukkan kekonduksian terma dan kekonduksian terma kekisi yang rendah iaitu masing-masing 1.1 W/mK (314 K) dan 0.64 W/mK (595 K). Hal ini boleh dikaitkan dengan peningkatan dalam fonon berselerak melalui atom Al berdetar-detar ke dalam sangkar kekisi. Sampel Al<sub>0.05</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> mempamerkan nilai ZT tertinggi sebanyak 1.36 pada suhu 789K, yang mengesahkan pengurangan besar dalam kekonduksian elektrik dan kekonduksian terma kekisi. Kesimpulannya, ianya terbukti bahawa bahanbahan ini mempamerkan pengoksidaan terkemuka dan kestabilan terma pada suhu optimum iaitu 800 °C.

#### ACKNOWLEDGEMENTS

First and foremost, I would like to acknowledge my supervisors, namely Associate Professor Dr. Mohd Faizul Mohd Sabri and Associate Professor. Dr. Suhana Mohd Said. Dr Faizul has provided excellent supervision, consistent support, encouragement and insightful advice to me. His guidance has helped me in all the time of my research. I could not have imagined having a better supervisors and mentor for my study. On the other hand, Dr Suhana has dedicated so much time in giving me valuable suggestions, recommendations, motivation, enthusiasm, patience and immense knowledge.

Besides, I would like to dedicate my deepest gratitude to Professor Yuzuru Miyazaki for giving me the opportunity to join his laboratory at Tohoku University, Japan. His immense inspiration, invaluable help, contribution and permission to use the facilities in his lab to complete my research work would forever be appreciated. I would also like to express my appreciation to Dr. Dhafer and Dr. Mohamed Hamid for their great guidance and valuable scientific discussions during my study. Simultaneously, I wish to express gratitude to Dr. Abbas Saeed Hakeem from King Fahd University of Petroleum and Minerals (KFUPM) for their collaboration efforts in the synthesis of materials through SPS. I would also like to take the opportunity to thank Mr. Mohd Said Sakat for providing me lab facilities. I would also wish to thank all of my colleagues and friends who have directly or indirectly supported me throughout my study.

On top of all, I would like to thank my parents, i.e. Dr. Bashir and Mrs. Mariam. I have no idea how they did it, but I am forever indebted to them for all the things they have done for me since my birth. In particular, my father has always encouraged and given me the strongest support to lead me forward during my studies. Last but not least, my sincerest thanks go to my dear wife, Sara for all of her sacrifice, unflagging love, unconditional support, consistent caring and instilling confidence in me in the entire journey of my study.

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## LIST OF SYMBOLS AND ABBREVIATIONS

TE	:	Thermoelectric
Ζ	:	Thermoelectric figure of merit
ZT	:	Dimensionless thermoelectric figure of merit
α	:	Seebeck coefficient
σ	:	Electrical conductivity
Т	:	Temperature
k	:	Thermal conductivity
PF	:	Power factor
$\Delta V$	:	Voltage difference
$\Delta T$	:	Temperature difference
Ke	5	Electrons and holes transporting heat
κL	:	Phonons travelling through the lattice
L	:	Lorenz number
K <sub>B</sub>	:	Boltzmann constant
е	:	Electron charge
PGEC	:	phonon-glass electron-crystal
ρ	:	Electrical resistivity
Ec	:	Conduction band

$E_{v}$	:	Valence band
Ef	:	Fermi level
Eg	:	Band gap
n	:	Carrier density
h	:	Planck's constant
<i>m</i> *	:	Effective mass of the charge carrier
υ	:	Directional velocity component
j	:	Current density
Ε	:	Applied electric field
μ	:	Charge-carrier mobility
$l_e$	: X	Electron mean free path
$l_p$	5	Phonon mean free path
ρ <sub>m</sub>	:	Mass density
$v_s$	:	Velocity of sound in the crystal
с	:	Specific heat of the crystal
<i>M</i> <sub>e</sub>	:	Electron mass
SPS	:	Spark plasma sintering
RSPs	:	Rapid solidification processes
LAST	:	Lead-antimony-silver-tellurium

В	:	Bulk moduli
G	:	Shear moduli
Ε	:	Young's moduli
α	:	Thermal expansion coefficient
CTE	:	Coefficient of thermal expansion
$T_m$	:	Melting temperature
HPT	:	High pressure torsion
TEGs	:	Thermoelectric generators
TECs	:	Thermoelectric coolers
СОР	:	Coefficient of performance
MS	:	Melt spinning
TEACs	5	Thermoelectric air conditioners
η <sub>te</sub>	:	Energy-conversion efficiency
$T_h$	:	Hot-side temperature
Tc	:	Cold-side temperature
QW	:	Quantum-well
IR	:	Infrared
MHW	:	Multi-hundred watt
МА	:	Mechanically alloying

XRD	:	X-ray diffraction
SEM	:	Scanning electron microscope
EDS	:	Energy-dispersive X-ray spectroscopy
FIB	:	Focused ion beam
Ι	:	Current
D	:	Thermal diffusivity
$C_p$	:	Specific heat
$ ho_d$	:	Density
Т	:	Thickness
STA	:	Simultaneous thermal analysis
DSC	: X	Differential scanning calorimetry
TG	6	Thermogravimetry
μн	:	Hall mobility

#### **CHAPTER 1:INTRODUCTION**

#### 1.1 Background

Global energy consumption has increased exponentially in the last century, with the majority of the energy being supplied by fossil fuels (Martín-González et al., 2013; Sootsman et al., 2009) such as petroleum, natural gas and coal (Chen et al., 2010; Fthenakis et al., 2010). The burning of fossil fuels has led to the emission of greenhouse gases which directly imposes adverse impacts on the environment, such as global warming, climate change and pollution (Afshar et al., 2012; Chen et al., 2012b; Dmitriev et al., 2010; Hayakawa et al., 2011; Kalkan et al., 2012). In heat engines, only approximately 30 - 40% of the fossil fuels burnt are utilized as useful energy, while the rest is wasted heat in the form of exhaust gases and friction (Wang et al., 2011b). The International Energy Agency indicated that the electricity and heat production sectors produce about 32% of the global greenhouse gas emissions, which amounts to an equivalent to 49.5 gigatonnes of carbon dioxide in 2010. In the automobile sector, Alam and Ramakrishna reported that 191 million vehicles in the United States (US) have dissipated about 66% of energy as wasted heat, in which the total amount of the annual emissions to the environment is approximately 36 TWh (Alam et al., 2013). Therefore, the world is more focused on obtaining and implementing an alternate, environmentally friendly energy resource to recover the wasted heat. Moreover, thermoelectric (TE) devices are considered as a leading technology for harvesting the heat waste and cutting down the greenhouse gas emissions, which plays an important role as the alternative resources and waste heat recovery.

The introduction of TE aims to mitigate the effect of fuel consumption, and consequently, reduce the  $CO_2$  emissions. Thermoelectric generators (TEGs) have a potential of reducing about 40 million tons of  $CO_2$  emissions annually based on a 20% of TEG's efficiency (Kawamoto, 2009). Collectively, TEGs are thought to be applied in

harvesting the wasted heat from the industrial, transportation and domestic sectors (Akasaka *et al.*, 2008; Hmood *et al.*, 2013; Tomeš *et al.*, 2010). As an introduction, thermoelectric is an energy conversion technology which allows solid-state conversion of thermal energy directly into electrical energy and vice versa. TEG modules are scalable and thus applicable to the systems ranging from miniature milliwatt level (body heat and portable electronics devices) to large scale megawatt applications such as in the steelworks and cement industries (Itoh *et al.*, 2009; Keskar *et al.*, 2012; Kishi *et al.*, 1999). There is currently a concerted effort to reduce energy consumption and environmental emissions through TEG technology.

Recognizing the potential of TEGs as an energy harvesting technology, the nations and industrial sectors have recognized the value of TEG technology as a large-scale program. Its extensive implementation is crucial for energy planning and policies in term of cost savings, resource optimization, and environmental protection on a national and global scale (Ali *et al.*, 2013; Balandin, 2011; Cederkrantz *et al.*, 2012; Omer, 2008; Toberer *et al.*, 2010). For instance, the Japanese government has embarked on a 30-year thermoelectric roadmap (2010 – 2040). This roadmap starts from the synthesis of nanostructured thermoelectric materials to eventual implementation of TEGs in smart grid cogeneration systems and large scale centralized TEG systems, as shown in Figure 1.1 (Kajikawa, 2011). On a similar scale, Germany is targeting an era of renewable energies by 2050. A key component of this program is the driving of thermoelectric technologies through a "nanothermoelectrics" research program, (2011 – 2014) (Böttner, 2012).



Figure 1.1: The TEG systems applications development roadmap (Kajikawa, 2011).

In the industry, the Bayerische Motoren Werke (BMW) group, has embarked on a 20-year thermoelectric roadmap which is expected to result in an approximately 10% improvement in vehicle fuel economy through thermoelectric waste heat recovery (Liebl *et al.*, 2009), as shown in Figure 1.2. Similarly, the US Department of Energy has initiated a "FreedomCAR" program for trucks and vehicles which utilize the TEGs to convert the heat waste from automobile engines with the aim of improving fuel economy by 10% (Vining, 2009).



**Figure 1.2:** Thermoelectric generators roadmap of the BMW Group (Eder *et al.*, 2011).

The key to achieving highly efficient TEGs is through the development of highly efficient thermoelectric materials. However, other criteria such as cost, ease of fabrication, availability of raw resources, toxicity, environmental impact and end of life processing also play important roles in the selection of thermoelectric material for TEGs (Jund *et al.*, 2013; Szczech *et al.*, 2011). Currently, the high cost of the materials (\$7 - \$42 per watt) and the relatively low efficiency (6 – 8%) of the TEGs have hindered the development of TEG applications on a large scale (Elsheikh *et al.*, 2014; Savary *et al.*, 2012). However, TEGs do have the advantages of having a lack of moving parts or circulating liquid, solid state conversion, low weight, free maintenance, wide operating temperature range, flexible shape, silent and reliable with a long lifetime (typically more

than 100,000 hours) and in most cases, environmentally compatible. On the other hand, the main disadvantages are high cost and poor power efficiency. Furthermore, they are compact and scalable, and thus suitable for a wide range of applications.

Currently, there are widespread research activities in the field of thermoelectric focusing on the thermoelectric materials improvement in order to obtain cheaper and more efficient material. Moreover, the potential of improving the efficiency of thermoelectric materials is governed by key parameters including thermal conductivity, electrical conductivity and Seebeck coefficient. The selection of thermoelectric materials is dictated by the current structure of materials and the doping with heavy elements, which may enhance the performance of thermoelectric materials. Over the decades, some novel classes of thermoelectric materials such as skutterudites, clathrates, chalcogenides, and silicides have been developed. The skutterudites materials are great contenders for thermoelectric materials in the medium temperature range, given the advantages including the abundancy of raw resources, relatively high thermoelectric performance, and lower cost of production. For example, in the families of filledskutterudite thermoelectric materials, they have great advantages in term of abundance of starting materials, lower cost of production, high mechanical strength, good thermal stability, high oxidation resistance, chemical stability and possess a relatively high dimensionless figure of merit (> 1.6) at the mid-temperature range of 300 - 800 K (Truong et al., 2014). However, CoSb<sub>3</sub> binary skutterudite system could not be used in thermoelectric applications due to its low carrier concentration, whilst having a high electrical resistivity and thermal conductivity (II-Ho et al., 2010b).

The development of these materials through the use of heavy filler atoms and element doping approaches have been established via ball milling, annealing, and spark plasma sintering techniques, which serve to improve the thermoelectric dimensionless

figure of merit. Furthermore, the heavy filler atoms play an important role in decreasing the lattice thermal conductivity and improving the overall performance of the filledskutterudite system. However, the low efficiency of CoSb<sub>3</sub> binary skutterudite thermoelectric materials remains as the primary concern. Researchers have tried to improve the performance of thermoelectric materials but to no avail as the challenge is dependent of Seebeck (S), thermal conductivity (k) and electrical conductivity ( $\sigma$ ). Moreover, the filled skutterudite particularly CoSb<sub>3</sub> is considered a great candidate for thermoelectric materials owing to its many benefits such as the availability of raw resources, ease of fabrication and high stability. Nevertheless, the most important aspect is the high thermal conductivity of CoSb<sub>3</sub>, which has an adverse impact on the TE performance. Furthermore, the major challenge is to develop complex materials through the addition of Aluminium (Al) and Indium (In) fillers, in the aim to reduce the thermal conductivity of the material by increasing phonon scattering. In filler are expected to make a new phase such as InSb with free electrons, which will augment the electrical conductivity and enhance the overall dimensionless figure of merit (ZT). Additionally, Ni and Te doping may enhance the Seebeck coefficient, which leads to the improved performance of thermoelectric materials.

#### **1.2 Problem Statement**

- 1. The binary skutterudite  $CoSb_3$  TE material has a low figure of merit *ZT*, mainly due to its high electrical resistivity and thermal conductivity.
- 2. Effective fillers such as Ba and Ce elements are costly.
- 3. Furthermore, multiple techniques and long preparation process are required for a high-performance skutterudite thermoelectric material with dopant (for example; Rogl *et al.* (2014) studied (R<sub>0.33</sub>Ba<sub>0.33</sub>Yb<sub>0.33</sub>)<sub>0.35</sub>Co<sub>4</sub>Sb<sub>12.3</sub> compound synthesized via first reaction in evacuated silica tubes at 600°C for 7 days followed by arcmelted, ball milling, heating (550 to 950°C) for 1 h, annealing at 700°C for 4 days, manually ground, ball milling for 2 h and hot press at 650°C for 56 MPa (2 h) in order to achieve *ZT* =1.9 at a temperature of 835 K.
- 4. Therefore, the primary challenge is to synthesize TE materials with additional elements which is cost-friendly, easy to synthesize and most importantly, exhibit excellent TE performance.

### **1.3 Research objectives**

- 1. To formulate a new thermoelectric materials by incorporating Al, In and Te into  $La_xCo_4Sb_{12}$  (x = 0.25 and 0.5) and Ni into  $Yb_{0.25}Co_4Sb_{12}$  skutterudite thermoelectric materials.
- 2. To synthesize high-performance skutterudite thermoelectric materials through a simple and shorter synthesis process of mechanical alloying and spark plasma sintering.
- 3. To study the influence of various addition of elements (Al, In, Ni and Te) on the microstructural properties of the developed thermoelectric materials.
- 4. To investigate the thermoelectric properties such as the Seebeck coefficient, electrical resistivity, thermal conductivity, thermal stability and the oxidation behavior of the developed thermoelectric materials.

### **1.4** Organization of the dissertation

This dissertation is organized as follows. Chapter 1 presents the background knowledge of this study. In Chapter 2, the literature background and theory behind thermoelectric, including the fundamentals of thermoelectric materials, properties, devices, fabrication techniques and applications have been reviewed in-depth. Chapter 3 describes the details of methodology and experimental measurement steps. Chapter 4 represents the centre focus of this work, in which it presents and thoroughly discusses the microstructural properties, thermoelectric properties, oxidation behavior and thermal stability of the developed materials. Finally, the conclusions and possibilities for future work are presented in Chapter 5.

#### **CHAPTER 2: LITERATURE REVIEW**

In this chapter, the background, overview and properties of thermoelectric materials were described. Firstly, the theory and principle phenomenon that affect thermoelectric materials were discussed in detail. Secondly, the thermoelectric properties such as; electrical resistivity, Seebeck coefficient and thermal conductivity of TE materials were described. Thirdly, the fabrication methods along with the effect of filling and doping techniques were illustrated. Lastly, the application and the performance of thermoelectric generation were clarified.

### 2.1 Introduction to thermoelectricity

The discovery of thermoelectricity can be dated back to the beginning of the  $19^{\text{th}}$  century by Thomas Johann Seebeck, who found that when two dissimilar metals are joined together and the junctions maintained at two different temperatures will provide a potential for electric current flow. Thermoelectric is one of the technologies that exhibits immense potential to play an important role as alternative energy, which converts the thermal energy into electrical energy or vice versa. Thermoelectric devices offer a solution to the global energy problems especially to achieve a significant energy saving by using the application such as cooling, heating and power generations. However, the main disadvantages of the thermoelectric materials are the high production cost and low energy efficiency as compared to the conventional devices. In addition, the thermoelectric material performance is defined by their dimensionless figure of merit, *ZT* as shown in Equation (2.1) (Rowe, 2005).

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

where a high *ZT* would result from maximizing the Seebeck coefficient *S* and electrical conductivity  $\sigma$ , and minimizing the thermal conductivity *k*. Existing TEG systems rely

on materials generally with a *ZT* of 1.3 - 1.5 in the medium and wide temperature range applications, but the true commercial viability can only be achieved when *ZT* > 4 (Gao *et al.*, 2006).

Currently, in commercial applications, the leading materials used in TEGs are bismuth telluride and the members of the skutterudite family (Stranz et al., 2011; Yang, 2005). Moreover, filled-skutterudite materials are gaining interest as favorable candidates for thermoelectric materials given their advantages of relatively high figure of merit, high carrier mobility, low cost, high mechanical strength, high chemical strength and abundance of raw materials. Generally, the ZT of skutterudite materials is comparable to bismuth telluride, which is typically in the range of 1.0 - 1.6 (Ballikaya et al., 2014; Park et al., 2014b; Xu et al., 2014). However, the cost of skutterudite materials such as Ca<sub>0.18</sub>Co<sub>3.97</sub>Ni<sub>0.03</sub>Sb<sub>12.4</sub> (13\$ / Kg) and CeCo<sub>4</sub>Sb<sub>12</sub> (37\$ / Kg) are much lower as compared to the conventional thermoelectric materials particularly bismuth telluride Bi<sub>0.52</sub>Sb<sub>1.48</sub>Te<sub>3</sub> (125 \$ / Kg) and silicon germanium, SiGe (679\$ / Kg) (LeBlanc et al., 2014). According to a study by Sano et al. (2003), the selling prices of bismuth telluride thermoelectric modules are reported to be in the range of \$7 - \$42 per watt. Therefore, skutterudite material such as CoSb<sub>3</sub> is a better candidate than bismuth telluride pricewise. The figure of merit can also be evaluated through another material parameter, A', (where A'  $\alpha$  ZT) which can be described by the following equation (Gao *et al.*, 2011):

$$A' \approx \left(\frac{T}{300}\right) \cdot \left(\frac{m^*}{m}\right)^{\frac{2}{3}} \cdot \left(\frac{\mu}{k_L}\right)$$
(2-2)

where m\* represents the carrier effective mass,  $\mu$  is the mobility in cm<sup>2</sup>V/s and  $k_L$  is the lattice thermal conductivity in mW/cmK. High carrier mobility will directly contribute to the electrical conductivity. CoSb<sub>3</sub> has been shown to possess a significantly higher carrier mobility at room temperature, 6000 cm<sup>2</sup>/V.S for n-type (Kanatzidis *et al.*, 2003)

as compared to Mg<sub>2</sub>Si, which has a carrier mobility ranging from  $56 - 406 \text{ cm}^2/\text{V.S}$  (Chen, 2013), Ag<sub>x</sub>Sb<sub>2-x</sub>Te<sub>3-x</sub> which is in the range of  $14 - 144 \text{ cm}^2/\text{V.S}$  (Zhang *et al.*, 2010), Zn<sub>3</sub>P<sub>2</sub> (177 cm<sup>2</sup>/V.S), and MnSi<sub>1.73</sub> (130 - 200 cm<sup>2</sup>/V.S) (Itoh *et al.*, 2009). Moreover, the aforementioned equation (2-2) also indicates that CoSb<sub>3</sub> filled/doped-skutterudite is a viable candidate for commercial thermoelectric materials, particularly in the medium-high temperature range.

### **2.2** The principle of thermometric effects

### 2.2.1 Seebeck effect

Three fundamental thermoelectric effects were discovered in the nineteenth century. In 1821, Thomas J. Seebeck discovered the first phenomenon of thermoelectric effect, when two dissimilar materials (iron and copper) were connected together and the two junctions were held at different temperatures, the voltage potential generated was proportional to the temperature difference (Hummel, 2000). This phenomenon is known as the Seebeck effect as shown in Figure 2.1(a) (Nicolaou, 2009; Rowe, 2005). The factor of proportionality,  $S_{AB}$  is called the relative Seebeck coefficient or as known as thermoelectric power or thermopower of the couple. In general, this coefficient also varies with the level of temperature at which the temperature difference occurs.



Figure 2.1: Stoichiometric diagram of the thermoelectric effects (Nicolaou, 2009; Rowe, 2005)

$$S = \frac{\Delta V}{\Delta T} = \frac{V_{\rm h} - V_{\rm c}}{T_{\rm h} - T_{\rm c}}$$
(2-3)

where *S* is the Seebeck coefficient,  $\Delta V$  is the voltage produced and  $\Delta T$  is the temperature difference. The sign of Seebeck coefficient S can be positive or negative, which indicates the direction of potential voltage. *S* is positive when the direction of electric current or voltage is same as the direction of the thermal current. The Seebeck voltage appears due to the charge diffusion of particles from the hot end at temperature T +  $\Delta T$  to the cold end at temperature T.

### 2.2.2 Peltier effect

The second phenomenon of thermoelectric effect is Peltier effect which was discovered by Jean Charles Athanase Peltier in later of 1834. Peltier observed that when an electrical current is applied to the junctions of two dissimilar materials, heat is either absorbed or liberated by the electrons or holes at the junctions. Depending on the direction of the current, one junction become hot and the other become cold, as shown in Figure 2.1(b). The Peltier effect can be calculated via the formula below (Bux *et al.*, 2010):

$$\Pi = \frac{Q}{I} \tag{2-4}$$

where  $\Pi$  is the Peltier coefficient, Q is the amount of heat and I is the electrical current. The Peltier coefficient and the Seebeck coefficient can be expressed in the Kelvin relations by the formula (Alam *et al.*, 2013):

$$\Pi = S.T \tag{2-5}$$

A research study conducted by Nolas *et al.* (1999) has found that the relation between the Seebeck voltage and the temperature is linear only when there are small changes in temperature. However, for high temperature ranges, the relationship becomes non-linear. Hence, it is important to state the temperature at which the Seebeck coefficient is being specified. Nevertheless, Tritt *et al.* (2006) suggested that a thermopower > 225 is required to achieve ZT > 2.

### 2.2.3 Thomson effect

In 1855, William Thomson (later Lord Kelvin) discovered the third thermoelectric effect. He observed the relationship between the Seebeck and Peltier effects, which is a significant contribution to the understanding of thermoelectric phenomena. Thomson described that when an electric current flows through a segment of the conductor, the potential heat expelled or absorbed in the presence of a temperature gradient  $\Delta T$ . This phenomenon is known as Thomson effect or Kelvin heat (Lee, 2013; Tritt, 2000), as seen in Figure 2.1(c). Furthermore, the Peltier and Seebeck coefficients can be computed from the Thomson coefficient. In the principle of Thomson effect, it allows all three thermoelectric coefficients to be found without involving a second material (Dommelen, 2011). The relationship of Thomson effect or Kelvin heat can be expressed as follows (Goldsmid, 2009):

$$\frac{\mathrm{dq}}{\mathrm{dt}} = -\tau J \Delta T \tag{2-6}$$

where dq/dt is the rate of heating, *J* is the current density and  $\tau$  is Thomson's coefficient. The three coefficients can be related by Thomson relations (Kelvin relations) below:

$$\Pi_{AB} = T.S = q.J \tag{2-7}$$

where  $\Pi_{AB}$  is Peltier coefficient, and

$$\tau = T \frac{dS}{dT}$$
(2-8)

#### 2.3 Thermoelectric properties

#### 2.3.1 Thermal conductivity

The thermal conductivity k is related to the transfer of heat through the materials, either by charge carriers (electrons or holes), lattice waves (phonons), electromagnetic waves, spin waves, or other excitations. Normally, the total thermal conductivity k can be expressed by the Fourier Law, 1822 (Hummel, 2000):

$$q = -k.\left(\frac{dT}{dx}\right) \tag{2-9}$$

where q is the heat current density flowing through the material, dT/dx is the temperature gradient in the material and the negative sign indicates that the heat flows from the hot to the cold end. A reduction of thermal conductivity *k* is desirable to increase the *ZT* and may be achieved by phonon scattering. Phonons are an important source of scattering in heat transfer and its scattering in bulk matrix is defined by the local changes in density associated with the different atoms (Joshi, 2010). The total thermal conductivity through a crystalline lattice can be described in terms of its lattice vibration and electron contributions as follows (Kang *et al.*, 2013):

$$k_{tot} = k_L + k_e \tag{2-10}$$

where  $k_{\rm L}$  and  $k_{\rm e}$  represent the lattice vibration and electron thermal conductivity, respectively. The lattice thermal conductivity component can be expressed as follows (Zheng *et al.*, 2005):

$$k_{\text{Lattice}} = \frac{1}{3} \left( C_v \, V_s \, \lambda_{\text{ph}} \right) \tag{2-11}$$

where  $C_v$  is the heat capacity (specific heat of the lattice),  $V_s$  is the velocity of sound, and  $\lambda_{ph}$  is the phonon mean free path (mfp). In metals, electron carriers are mainly responsible for heat transfer, carrying the majority of the heat. While in insulators, lattice waves dominate the heat transfer mechanism. However, in semiconductor materials, heat conduction is attributed to both electron carriers and lattice waves (Pulikkotil *et al.*, 2010).

A very low thermal conductivity is required to improve the performance of the thermoelectric materials. In thermoelectric materials, there are several ways to reduce the *k* without affecting the *S* and  $\sigma$  of materials, such as; (a) the use of complex structures with heavy atomic weight to enhance the phonon scattering, (b) reduce the frequency of vibration, (c) and formation of a polycrystalline nanostructure (Majumdar, 2004). Low thermal conductivity materials which have the complex structures such as skutterudites, clathrates, half-heusler alloys, chalcogenides and novel oxides are the main focus for high efficiency thermoelectric materials (Tritt, 2004). For example, skutterudites have two voids which can be filled with heavy atoms acting as "rattlers" to reduce the thermal conductivity as well as to maintain high electrical conductivity; and consequently improve its thermoelectric properties (Elsheikh *et al.*, 2014; Koza *et al.*, 2008).

Apart from the modification on the molecular level as described above, low thermal conductivity may also be achieved through process such as mechanical alloying to produce nanocomposites. This idea was first proposed in the late 1950s, where mechanical alloying or high energy ball milling is an established process to achieve the synthesis of nanocrystalline thermoelectric materials (Bux *et al.*, 2010; Thiagarajan *et al.*, 2010) through the reduction of grain size of powder particles. The enhancement in thermoelectric properties of these nanocrystalline materials arises mainly from the reduction of the lattice thermal conductivity, with its  $k_L$  being less than half as compared to the bulk material at room temperature (Medlin *et al.*, 2009). The reduced lattice thermal conductivity coupled with slight reduce in carrier mobility can yield an increase in overall *ZT* of these nanocrystalline materials (Bux *et al.*, 2010). For CoSb<sub>3</sub> binary

skutterudites thermoelectric materials, their high atomic weight, high electrical conductivity and high carrier concentration had resulted in a relatively high thermal conductivity, owing to the strong covalent bonding between pnicogen atoms (Ballikaya *et al.*, 2012). Generally, the thermal conductivity of the unfilled CoSb<sub>3</sub> thermoelectric materials lies in the range of 10 - 15 W/mK at room temperature (Li *et al.*, 2014). However, several studies have proved that doping and/or filling are the effective approaches to reduce the thermal conductivity of skutterudites materials and directly enhance their thermoelectric performance (Deng *et al.*, 2009). Moreover, CoSb<sub>3</sub> with filler atoms such as Ce and Yb have been proven to be a useful in increasing the phonon scattering and reducing the thermal conductivity. In addition, double and triple filling skutterudites are also the promising and effective approach in reducing the lattice thermal conductivity as compared to single filling (Yang *et al.*, 2009b).

Jung *et al.* (2008) examined In-filled and Te-doped CoSb<sub>3</sub> skutterudites synthesized by encapsulated induction melting. The result showed that the thermal conductivity of In<sub>0.25</sub>Co<sub>4</sub>Sb<sub>11.9</sub>Te<sub>0.1</sub> was significantly reduced by In filling and Te doping to the range of 2.5 – 3 W/mK at all temperatures with the maximum value for the dimensionless figure of merit of 0.56. In 2011, Deng *et al.* (2011a) studied the Pb<sub>x</sub>Ba<sub>y</sub>Co<sub>4</sub>Sb<sub>11.5</sub>Te<sub>0.5</sub> prepared via high pressure and high temperature (HPHT) technique. In their study, Pb<sub>0.05</sub>Ba<sub>0.25</sub>Co<sub>4</sub>Sb<sub>11.5</sub>Te<sub>0.5</sub> shows the lowest thermal conductivity of 2.73W/mK at 663 K, with the maximum value of *ZT* 0.63 at 673 K. Another study had also been carried out by Alleno *et al.* (2013) on n-type CeO<sub>2</sub>/Co<sub>0.97</sub>Pd<sub>0.03</sub>Sb<sub>3</sub> prepared via spark plasma sintering. The results showed that the lattice thermal conductivity in nano-Co<sub>0.97</sub>Pd<sub>0.03</sub>Sb<sub>3</sub> is significantly decreased (– 40% at 300 K). However, there was an enhancement in *ZT* value (+32%) of nano-Co<sub>0.97</sub>Pd<sub>0.02</sub>Sb<sub>3</sub> sample. Most of the recent investigations focused on CoSb<sub>3</sub>-binary skutterudites thermoelectric materials with the
objective of simultaneously increasing the electrical conductivity whilst decreasing the thermal conductivity. The thermal conductivity and the electrical conductivity are coupled based on the Wiedemann–Franz law where the electronic thermal conductivity,  $k_e$  can be estimated by the following equation (Chen *et al.*, 2012a):

$$k_e = L_0 \sigma T \tag{2-12}$$

where  $L_0$  is the Lorenz number,  $\sigma$  is the electrical conductivity and T is the absolute temperature. The  $L_0$  can be expressed as follows (Kumar *et al.*, 1993):

$$L_o = L = (\pi K_B)^2 / (3 e^2) = 2.44 \times 10^{-8} (V^2 K^{-2})$$
(2-13)

where  $K_B$  is the Boltzmann's constant, *e* is the electron charge and L is the Sommerfeld value. The Lorenz number for the filled skutterudites CoSb<sub>3</sub> has been found to be 2.0 × 10<sup>-8</sup> V<sup>2</sup>K<sup>-2</sup> for the carrier concentration of 10<sup>20</sup> cm<sup>-3</sup> (Qiu *et al.*, 2011). Therefore, the Lorenz number depends on the majority and minority carrier concentrations, as well as temperature (Gao *et al.*, 2011). It was found that Yb-filled skutterudites compounds show a high figure of merit for n-type materials doped with GaSb (Xiong *et al.*, 2010). Figure 2.2 shows the plots of the *ZT* region of materials parameters of lattice thermal conductivity and weight mobility. To achieve *ZT* = 3, the lowest lattice thermal conductivity (*k*<sub>Lattice</sub>) and highest weight mobility must approach 0.4 W/mK and 0.2 m<sup>2</sup>/v.S, respectively (Sharp, 1997).



**Figure 2.2:** Plots of constant *ZT* showing the region of materials parameters space that can lead to ZT > 1. The lines are for the extrinsic and optimally doped semiconductor at room temperature with carriers scattered by acoustic phonons (Sharp, 1997).

This discussion indicates that a good thermoelectric material must have high carrier mobility, high effective mass, and low lattice thermal conductivity. Moreover, materials with complex crystalline structure and high atomic weight such as skutterudites, clathrates and chalcogenides are preferable candidate for thermoelectric materials due to their ability to enhance phonon scattering. This is in good agreement with the study conducted by Harnwunggmoung *et al.* (2011) on CoSb<sub>3</sub> filled by Tl and substitution of Rh for Co, where their results concluded that the lattice thermal conductivity was strongly minimized due to the rattling and alloy scattering effects, resulting in a lattice thermal conductivity of 1.54W/mK at 550K for Tl<sub>0.2</sub>(Co<sub>0.8</sub>Rh<sub>0.2</sub>)<sub>4</sub>Sb<sub>12</sub>. The maximum *ZT* value reached 0.58 at around 600 K. Interestingly, these results indicate that CoSb<sub>3</sub>-filled skutterudite materials have the potential to reduce the lattice thermal conductivity via enhanced phonon scattering through the filler atoms. In addition, a fundamental understanding of the physical explanation behind the reduction of lattice thermal conductivity of CoSb<sub>3</sub> thermoelectric material is much needed, which may contribute towards improvement of the material properties and scattering of phonons.

## 2.3.2 Seebeck coefficient

The Seebeck coefficient, *S* or also known as thermoelectric power, is an intrinsic property of the material which is closely related to the electronic structure of materials (Tritt, 1997). The voltage difference is called Seebeck voltage, which is relative to the temperature difference between the two junctions. The Seebeck coefficient can be expressed by the following equation (Bux *et al.*, 2010).

$$S = \frac{V}{(T_h - T_c)}$$
 (2-14)

where *S* is the Seebeck coefficient (V/K or  $\mu$ V/K), V is the voltage, whereas T<sub>h</sub> and T<sub>c</sub> are the temperature of the hot side and cold side, respectively. For p-type semiconductors, the sign of the Seebeck coefficient is positive when electricity is carried by holes. Inversely, for n-type semiconductors, the sign of the Seebeck coefficient is negative when electricity is carried by electrons (Li, 2006). Moreover, the improvement of Seebeck coefficient can be accomplished by increasing the density of states near the Fermi level via doping and increasing the energy dependence of mobility using energy filtering (Liu *et al.*, 2012). The value of Seebeck coefficient is very small for metals (~ 0 – 3  $\mu$ V/K) but much larger for semiconductors (~ 200 – 300  $\mu$ V/K) (Auparay, 2013; Elsheikh *et al.*, 2014).

For example, n-type CoSb<sub>3</sub> skutterudite obtained a large Seebeck coefficient of – 200  $\mu$ V/K at room temperature (Kanatzidis *et al.*, 2003). The absolute Seebeck coefficient value improved through addition of dopant and/or filling skutterudite materials to ~ 225  $\mu$ V/K for Co<sub>4</sub>Sb<sub>11.5</sub>Te<sub>0.5</sub> compound at ~ 750 K (Qin *et al.*, 2013) and to ~ 255  $\mu$ V/K for In<sub>0.113</sub>Co<sub>4</sub>Sb<sub>12</sub> compound at ~ 300°C (Visnow *et al.*, 2015). A further study has been conducted by Park *et al.* (2014b) on Yb<sub>z</sub>Co<sub>4</sub>Sb<sub>12</sub> filled skutterudites synthesized via encapsulated melting followed by hot pressing. The results show that the maximum absolute value of the Seebeck coefficient is 231  $\mu$ V/K and it increased with increasing

temperature. After Yb filling, the the increase of carrier concentration has resulted in the higher electrical conductivity of the sample. However, the thermal conductivity was reduced significantly after Yb filling, hence, the Yb<sub>0.2</sub>Co<sub>4</sub>Sb<sub>12</sub> sample exhibited the highest figure of merit of 1.0 at 823 K.

## 2.3.3 The power factor

The power factor is defined as the ability of a material to produce useful electrical power. Power facor contains both of the Seebeck coefficient *S* and the electrical conductivity  $\sigma$  and it can be conveniently served as an indication of the power produced by the thermoelectric material. The classical approach to achieve a high value of the power factor is by maximizing the Seebeck coefficient *S* and conversely, minimizing the electrical resistivity  $\rho$  or (1/ $\sigma$ ), as presented in the equation below (Medlin *et al.*, 2009):

$$PF = \frac{S^2}{\rho}$$
(2-15)

The optimization of the thermoelectric material properties by the enhancement of the power factor (high electrical conductivity) and reduction of the thermal conductivity  $K_{ph}$  was conceived by Slack, through the introduction of the concept of Phonon–Glass– Electron–Crystal (PGEC) materials (Gao *et al.*, 2006). The PGEC describes that an ideal thermoelectric material should have a low lattice thermal conductivity as in a glass or an amorphous material, and a high electrical conductivity as in a crystal such as skutterudites (CoSb<sub>3</sub>), clathrates (Ba<sub>8</sub>Ga<sub>16</sub>Ge<sub>30</sub>) and Zintl phases (Zhu *et al.*, 2009). Slack estimated that an optimized PGEC materials would have a value of ZT = 4 at a temperature range of 77 – 300 K (Fedorov *et al.*, 2011). The PGEC approach is a superior strategy which can reduce the thermal conductivity without affecting the electronic properties, which subsequently enhances the *ZT* of the thermoelectric material. In recent years, PGEC materials have contributed significantly in improving the field of thermoelectric primarily through the reduction of lattice thermal conductivity (Beekman *et al.*, 2015; Biswas, 2015).

The carrier concentration that yields the maximum power factor of a given material usually has the highest figure of merit (Goldsmid, 2009). Generally, the range of electrical conductivity for semiconductor materials is lying between  $10^3$  to  $10^{-8}$  S/cm (Shaheen et al., 2011). Typically, the electrical resistivity for skutterudites CoSb<sub>3</sub> materials in the range of  $33 - 100 \text{ m}\Omega \text{cm}$  (Kanatzidis *et al.*, 2003). However, the power factor of CoSb<sub>3</sub> could be improved by filler and/or doping. Simultaneously, noticeable enhancement on the dimensionless thermoelectric figure of merit value may be achieved. In relation to this, Deng et al. (2009) studied the Co<sub>4</sub>Sb<sub>12-x</sub>Te<sub>x</sub> skutterudite and found out that the presence of Te substantially decreased the electrical resistivity of the Seebeck coefficients without any detrimental effect, thereby improving the power factor of Co<sub>4</sub>Sb<sub>11.5</sub>Te<sub>0.5</sub> to 35.3  $\mu$ w/cmK<sup>2</sup> along with the figure of merit ZT to 0.67 at 710 K. Similarly, a study conducted by Jiang et al. (2010) on n-type Co<sub>4</sub>Sb<sub>12</sub> with Sm filler also demonstrated an enhancement on the power factor for Sm<sub>0.1</sub>Co<sub>4</sub>Sb<sub>12</sub> about 23.7  $\mu$ W/cmK<sup>2</sup> at 568 K. The thermal conductivity of Sm<sub>x</sub>Co<sub>4</sub>Sb<sub>12</sub> was significantly reduced as compared to pure CoSb<sub>3</sub>, and the maximum value of ZT obtained is 0.55 at 711 K. Deng et al. (2011a) studied the multiple filling (Pb, Ba) with Te-doping on Co<sub>4</sub>Sb<sub>12</sub>, whereby the highest power factor of 31.64  $\mu$ W/cmK<sup>2</sup> was achieved by Pb<sub>0.03</sub>Ba<sub>0.27</sub>Co<sub>4</sub>Sb<sub>11.5</sub>Te<sub>0.5</sub> at 663 K among all of the filled samples, with its maximum ZT value reached 0.63 at 673 K. In the same year, Deng et al. (2011c) studied the Ti<sub>0.2</sub>Co<sub>4</sub>Sb<sub>11.5</sub>Te<sub>0.5</sub> skutterudite and found that the power factor was enhanced with increasing temperature and the figure of merit (ZT is about 0.702). A study conducted by Deng et al. (2012) on  $In_{0.5}Co_4Sb_{12-x}Ge_x$  skutterudites showed that the thermal conductivity decreased with the enhancement of Seebeck coefficient. Meanwhile, In<sub>0.5</sub>Co<sub>4</sub>Sb<sub>11.5</sub>Ge<sub>0.5</sub> compound recorded the maximum power factor of 21.98  $\mu$ W/cmK<sup>2</sup> at

615 K and the highest figure of merit (*ZT*) value of 0.58 at 663 K. Zhou *et al.* (2013) investigated double-filled skutterudites Yb<sub>x</sub>La<sub>y</sub>Fe<sub>2.7</sub>Co<sub>1.3</sub>Sb<sub>12</sub> compound and it was shown that the lattice thermal conductivity gradually reduced to 0.9 W/mK at high temperature. Nevertheless, the electrical conductivity of Yb<sub>0.25</sub>La<sub>0.6</sub>Fe<sub>2.7</sub>Co<sub>1.3</sub>Sb<sub>12</sub> compound increased with the maximum power factor of 27  $\mu$ W/cmK<sup>2</sup> along with the maximum *ZT* of 0.99 at 700 K. Xiong *et al.* (2010) studied the n-type Yb-filled skutterudite Co<sub>4</sub>Sb<sub>12</sub> composites with p-type GaSb nanoinclusions, which the results showed a low-energy electrons scattering by GaSb-related boundary energy barriers. After Yb-filling, the thermal conductivity of the Co<sub>4</sub>Sb<sub>12</sub> composite decreased whereas the figure of merit *ZT* improved to the highest value of 1.45 at 850 K.

Apparently, a significant reduction in the electrical resistivity and lattice thermal conductivity are the main driving factors to improve the performance of skutterudite materials through the optimization of carrier concentration and phonon scattering mechanism. Moreover, the theoretical and experimental research studies agreed that the substantial improvement on power factor and reduction of thermal conductivity can be achieved to enhance the figure of merit, *ZT*.

# 2.4 Electronic properties

#### 2.4.1 Scattering mechanism for carriers

In solids, an important transport behavior is the scattering caused by the carriers or phonons. The carrier scattering directly affects the electrical conductivity and the Seebeck coefficient, whereas phonon scattering affects the thermal conductivity (Joshi, 2010). Therefore, the transport properties of a semiconductor are strongly dependent on the scattering mechanisms such as acoustical phonon and optical phonon scatterings, ionized impurity scattering and neutral impurity scattering. When an external forces are applied to the semiconductor, the charged carriers will reach a steady-state conditions

by the aforementioned scattering mechanisms, and will eventually return to the equilibrium conditions when these forces are removed from the semiconductor (Li, 2006).

In the semiconductor carrier-phonon scattering process, there are many possibilities that a carrier can undergo a change in state; the availability of states, absorbing probability or phonon emitting, and the carrier-phonon interaction strength. Stationary defects (impurities and dislocations) and dynamic defects (electrons, holes, and lattice phonons) have a high possibility to scatter the charge carriers in a semiconductor. Therefore, the types of scattering mechanisms involved will determine the overall transport properties of the semiconductor (Li, 2006). Furthermore, the complex structures and high average atomic weight materials are preferable for improving the thermoelectric materials through the enhancement of phonon scattering and thus reducing the thermal conductivity.

#### 2.4.2 Carrier concentration

Generally, in the intrinsic semiconductor materials, there are two common types of charge carriers, either electrons or holes. The interrelationship between carrier concentration and Seebeck coefficient for degenerate semiconductors can be expressed by the relation below (Snyder *et al.*, 2008):

$$S = (8 \pi^2 K_B^2 / 3e h^2) \times m^* \times T \times (\pi / 3n)^{2/3}$$
(2-16)

where *n* is the carrier concentration and  $m^*$  is the effective mass of the carrier. An increase in the effective mass can yield a high Seebeck coefficient, thus increasing the power factor and consequently enhance the *ZT* value. Figure 2.3 reveals the maximum efficiency (*ZT*) of thermoelectric with the variations of  $\sigma$ , *S*,  $\kappa$  as a function of carrier concentration (*n*) (Snyder *et al.*, 2008; Valset, 2011). This implies that an increase in

carrier concentration not only increases the electrical conductivity but also increases the thermal conductivity and simultaneously, decreases the Seebeck coefficient.



**Figure 2.3:** Comparison of thermoelectric parameters Seebeck coefficient, electrical conductivity, thermal conductivity and figure of merit (Snyder *et al.*, 2008; Valset, 2011).

Moreover, the thermoelectric power factor,  $PF = S^2 \cdot \sigma$  reaches maximum at higher carrier concentration than ZT. The difference between the peak in  $S^2 \cdot \sigma$  and ZT is larger for the newer materials with lower  $k_L$ . The reduction of lattice thermal conductivity  $k_L$ can offer a two-fold benefit for the thermoelectric figure of merit, which is leading to a larger Seebeck coefficient and allows the carrier concentration to reoptimize (Snyder *et al.*, 2008). The carrier concentration can be measured using the Hall effect utilizing the following relationship (Du *et al.*, 2012):

$$R_{\rm H} = \frac{1}{\rm n \, e} \tag{2-17}$$

where  $R_H$  is the Hall coefficient and *e* is the electronic charge. Then, the carrier concentration (*n*) and carrier mobility ( $\mu$ ) are related to the electrical conductivity ( $\sigma$ ), which can be defined as (Snyder *et al.*, 2008):

$$\sigma = n e \mu \tag{2-18}$$

where  $\mu$  is the electron mobility that can be defined in terms of the conductivity  $\sigma$ , effective mass m<sup>\*</sup><sub>c</sub> and the relaxation time  $\tau$  by the following formula (Li, 2006):

$$\mu = \frac{q(\tau)}{m_c^*} \tag{2-19}$$

Equation (2-2) clearly shows that a good thermoelectric material must possess high carrier mobility (~ 1000 cm<sup>2</sup>/Vs for Bi<sub>2</sub>Te<sub>3</sub> and skutterudites) (Tritt, 1997), high effective mass, and low lattice thermal conductivity, leading to the formulation of the concept of "phonon-glass electron-crystal" as discussed previously. This phenomenon typically occurs in heavily doped semiconductors with optimum carrier concentrations between  $10^{19}$  and  $10^{21}$  carriers per cm<sup>3</sup> that falls in between the common metals and semiconductors (Wang *et al.*, 2011a).

The coupling between all thermoelectric parameters  $\sigma$ , *S*, and *k* makes the improvement of *ZT* becomes even more difficult. Heavily doped semiconductors are useful for modulating thermoelectric performance. However, the changes in the dopant and doping concentration in semiconductors may affect the corresponding changes in electrical conductivity and carrier type without much affecting other properties (Joshi, 2010). For example, doped semiconductor materials may achieve a higher electrical conductivity (~10<sup>5</sup> S/m) and remarkably higher Seebeck coefficient (~ 200  $\mu$ V/K), while the thermal conductivity still remains relatively insignificant (~ 0.5 W/mK) (Joshi, 2010). CoSb<sub>3</sub> binary skutterudite system could not be used in thermoelectric applications due to its very low carrier concentration, very high electrical resistivity and thermal conductivity (II-Ho *et al.*, 2010b). Generally, the thermoelectric properties

depend mainly on the carrier concentration, carrier mobility and carrier effective mass. It is noteworthy the carrier concentration and carrier mobility are inversely proportional to the Seebeck coefficient. Furthermore, a suitable filler can play an important role in the optimization of carrier concentration and the improvement of Seebeck coefficient, which can lead to a boost in the thermoelectric performance of the system. Several reports have been carried out on filled-skutterudite and it was demonstrated that the fillers can enhance the carrier concentration and carrier mobility, which in turn improves the power factor and ZT (Figure 2.4). Yu et al. (2012) conducted a study concerning Ge-doping on FeCo<sub>3</sub>Sb<sub>12</sub> multi fillers (Ba,In). The results showed that with increasing amount of Ge doping, the electrical conductivity is increased whereas Seebeck coefficient is suppressed, owing to the increase of carrier concentration and inversed material behaviors. In the case of Ba<sub>0.3</sub>In<sub>0.2</sub>FeCo<sub>3</sub>Sb<sub>11.7</sub>Ge<sub>0.3</sub> sample, the lattice thermal conductivity was considerably reduced and reached 1.0 W/mK whereas the highest dimensionless figure of merit ZT value achieved a mere 0.54 at 800 K. In the same year, Park et al. (2012) studied the YbzFe4-xCoxSb12 skutterudites and found that the electrical conductivity of the compound was slightly decreased whereas the Seebeck coefficient was increased in the range of 100  $\mu$ V/K to 150  $\mu$ V/K due to high carrier concentrations  $(10^{20} \text{ cm}^{-3} \text{ to } 10^{21} \text{ cm}^{-3})$ . Hence, the overall thermoelectric properties showed a better performance. In the following year, a study was carried out by Yang et al. (2013) on Mg-filled  $CoSb_3$ . The result showed that the Mg filling has considerably reduced the thermal conductivity of CoSb<sub>3</sub> and slightly enhanced the power factor and at the same time, enhanced the carrier concentration  $(5.3 \times 10^{18} - 1.4 \times 10^{19} \text{ cm}^{-3})$ . The highest ZT of 0.33 was achieved by Mg<sub>0.4</sub>Co<sub>4</sub>Sb<sub>12</sub> at 620 K. Another research was conducted by Kim *et al.* (2013a) on p-type  $Tl_xFe_1Co_3Sb_{12}$  skutterudites. The results showed that the thermal conductivity was reduced effectively by the addition of Tl and the carrier concentration is significantly reduced in the range of  $20.09 - 4.5 \times 10^{19}$  cm<sup>-3</sup>.

A maximum *ZT* value of 0.36 at 723 K has been obtained. In the same year, a study was conducted by Zhang *et al.* (2013) on Nd<sub>0.6</sub>Fe<sub>2</sub>Co<sub>2</sub>Sb<sub>12</sub> skutterudite doped with Ge. The results showed a remarkable suppression on the thermal conductivity and an increase in the carrier concentration  $(8.61 - 10.72 \times 10^{20} \text{ cm}^{-3})$  which lowered the power factor. The dimensionless figure of merit *ZT* improved to a maximum value of 1.1 at 670 K. A study carried out by Fu *et al.* (2013) on Yb<sub>0.2</sub>Co<sub>4</sub>Sb<sub>12</sub> based composites with AgSbTe<sub>2</sub> nanoinclusion showed that the carrier concentration of the composite decreases with an increase of the content of AgSbTe<sub>2</sub> nanoparticles in the range of 14.16 – 10.46 × 10<sup>19</sup> cm<sup>-3</sup>. The dimensionless figure of merit has been remarkably improved about to 1.27 at 300°C for Yb<sub>0.2</sub>Co<sub>4</sub>Sb<sub>12</sub>/4wt% AgSbTe<sub>2</sub>. Therefore, the literatures have revealed that the improvement of electrical conductivity of the filled-skutterudites CoSb<sub>3</sub> thermoelectric material is closely associated with the enhancement of the carrier concentration through the filler and/or heavy dopant, which will directly improve the dimensionless figure of merit.

## 2.4.3 Band gaps of thermoelectric materials

The band gap or energy gap is the difference in energy levels of a solid material where the electron states can exist (Elsheikh *et al.*, 2014). The band gap generally refers to the energy difference between the top of the valence band and the bottom of the conduction band in insulators and semiconductors. The band gap is a major factor in determining the electrical conductivity of a solid, where the substances with large band gaps are generally insulators and those with smaller band gaps are called semiconductors, while the conductors either will have very small band gaps or none due to the overlap in the valence and conduction bands (Elsheikh *et al.*, 2014; Ozpineci *et al.*, 2003). When the valence electrons are excited into the conduction band, the conductivity of a semiconductor increases. The energy gap for most semiconductors may vary between 0.1 and 6.2 eV (Li, 2006). However, a decrease in the band gap of

semiconductors can induce an exponential increase in charge carrier concentrations, which is considered most desirable (Nielsch *et al.*, 2011). Theoretical studies of the electronic structure of the thermoelectric materials including; CoSb<sub>3</sub> and Mg<sub>2</sub>Si–Sn systems have been carried out by several groups using the pseudopotential method. Theoretically, the energy gaps of CoSb<sub>3</sub> in the range between 0.003 and 0.22 eV (Rahnamaye Aliabad *et al.*, 2012). Moreover, a study reported that they found an indirect band gap of 0.51 eV for Mg<sub>2</sub>Si<sub>0.6</sub>Sn<sub>0.4</sub>, 0.77 eV for Mg<sub>2</sub>Si, and 0.35 eV for Mg<sub>2</sub>Sn (Chen *et al.*, 2011). Furthermore, CoSb<sub>3</sub> possesses a smaller band gap as compared to the Mg<sub>2</sub>Si–Sn systems which is very promising to obtaining a higher electrical conductivity (Liu *et al.*, 2011b). As a comparison, band gaps for well-known semiconductors are 1.12 eV for Silicon (Si), 0.7 eV for Germanium (Ge) and 0.08 eV for Tin (Sn) (Joshi, 2010; Li, 2006; Tripathi *et al.*, 2005). However, copper is the most conductive metals which the band overlaps with an empty band.

Nevertheless, the band gap of CoSb<sub>3</sub> group shows a slight change with doping elements or fillers. The experimental energy gap of CoSb<sub>3</sub> is about 0.031 – 0.55 eV was reported by several studies (Rahnamaye Aliabad *et al.*, 2012). Therefore, the important role not only focuses on the band gap width but also on the energy gap between the subbands (Godzhayev *et al.*, 2013). Two subbands of the conduction band are separated by a small gap ( $\Delta E < 0.5 \text{ eV}$ ) and they have been created from the states of Mg and of the element of the IV-group. In the CoSb<sub>3</sub> system, the gap between subbands is practically equal to zero. In this case, the electrons of both subbands will take part in the transport phenomena, which resulted in an increase in the thermoelectric figure of merit (Fedorov, 2009).



Figure 2.4: State-of-the-art comparison of *ZT* in the conventional bulk materials and nanostructured composite materials (Szczech *et al.*, 2011).

## 2.5 Fabrication techniques of thermoelectric materials

Several compaction techniques have been utilized to synthesize the thermoelectric materials. The fundamental principle behind most of the techniques is to apply high pressure for densification and frequently high temperature to soften the materials, to allow a better filling and material flow by diffusion in order to eliminate the remaining porosity. The challenge is to achieve a high material density which is close to the theoretical density, low porosity without losing the nanoscale microstructure and retaining the chemical purity of the material. There are several methods that can be used to consolidate thermoelectric materials such as mechanical alloying, microwave irradiation (Savary *et al.*, 2012), field-activated and pressure-assisted synthesis (FAPAS), hot pressing (HP) and spark plasma sintering (SPS) (Meng *et al.*, 2011; Tani *et al.*, 2007).

Hot pressing is one of the techniques used in powder consolidation and manufacturing processes for high performance thermoelectric materials. The hot pressing technique is mainly used to fabricate the powder materials by applying high pressure (80 MPa) with high temperature (900 – 1073K) to the specimen simultaneously (Zhang *et al.*, 2008; Zhu *et al.*, 2009). Preparing a homogeneous thermoelectric material is crucial by an extended time annealing in the hot pressing method. In addition, this method offers the platform to (a) improve mechanical properties, (b) enhance thermoelectric properties of materials, and (c) significantly simplify production of thermoelements (Samunin *et al.*, 2012).

Yang et al. (2006) studied the La<sub>x</sub>Co<sub>3.6</sub>Ni<sub>0.4</sub>Sb<sub>12</sub> filled skutterudites synthesized through mechanical alloying followed by hot pressing. The results demonstrated that the magnitude of Seebeck coefficient and electrical resistivity increased slightly with the increase of La filling fraction. Nevertheless, the thermal conductivity decreased to ~ 2.75 W/mK at 500°C for La<sub>0.6</sub>Co<sub>3.6</sub>Ni<sub>0.4</sub>Sb<sub>12</sub> compound but recorded the highest figure of merit, ZT value of ~ 0.31 at 400°C. Liu et al. (2011a) investigated that the CoSb<sub>3</sub> and Y<sub>0.18</sub>Co<sub>4</sub>Sb<sub>12</sub> compounds prepared via the hot-pressed process under vacuum condition. The electrical conductivity of the  $Y_{0.18}Co_4Sb_{12}$  sample had increased due to the increase in carrier concentration, while its thermal conductivity decreased can be ascribed to the enhancement of phonon scattering to 2.6 W/mK for Y<sub>0.18</sub>Co<sub>4</sub>Sb<sub>12</sub> sample at 673 K. The value of figure of merit, ZT, for the  $Y_{0.18}Co_4Sb_{12}$  sample was obviously enhanced due to the positive contribution of the electrical conductivity and the thermal conductivity to 0.18 at 623 K. A study conducted by Mallik et al. (2013) on p-type Co<sub>4</sub>Sb<sub>12-x</sub>Bi<sub>x</sub> showed that the electrical conductivity increased with increasing temperature, however, its thermal conductivity reduced with Bi doped fraction. The maximum value of ZT is 0.53 at 632 K, which is higher than that of  $Co_4Sb_{12}$ . In addition, hot pressing was found to be a very promising technique which can improve the thermoelectric properties of the materials. An improvement in Seebeck coefficient and power factor will yield a peak value of the thermoelectric figure of merit.

The development in thermal technology introduced the spark plasma sintering (SPS) technique, which is also known as field assisted sintering technique (FAST) and pulsed electric current sintering (PECS) process. SPS is a rapid sintering technique assisted by the pressure and the electric field which is commonly used to consolidate powder materials (Grasso et al., 2012). The main characteristic of the SPS technique is that it utilized a high pulsed current through the graphite mold to activate the consolidation and reaction-sintering of powder materials under a low voltage (Savary et al., 2012; Thiagarajan et al., 2010), then the electrical discharges will occur. The technical parameters required include high temperature, pressure and formation of good contact between the powder particles. SPS also has the advantage to eliminate the gases and moisture that may adsorb on the surface of the nanoparticles and arcs that can defeat the oxide layers of the material. SPS also has the unique advantage of using DC current to generate the internal heat, unlike the conventional hot pressing where the heat is provided by external heating elements. The clear benefits of SPS are the ability to retain nanostructures, energy and time (within a few minutes), whereas the traditional methods require hours to reach the peak temperature. Besides, the density of the material produced is very close to the theoretical density with excellent thermoelectric performances (Thiagarajan et al., 2010). Figure 2.5 shows the stoichiometric diagram of spark plasma sintering technology (Kopeliovich, 2013). In relation to this, the comparison between spark plasma sintering (SPS) and hot pressing (HP) techniques is shown in Table 2.1 (Kopeliovich, 2013).



Figure 2.5: Spark Plasma Sintering technology (Kopeliovich, 2013).

Table 2.1: Comparison of spark plasma sintering (SPS) and hot pressing (HP)
techniques (Kopeliovich, 2013).

Parameter	SPS	HP	
Heating rate	>2000C/min	Limited to 80C/min	
Productivity	Enhanced by high	Limited by long processing	
	heating rate	time	
Electric power consumption	Low	< 1/3 than required for SPS	
Control for the thermal	Enabled by punch	Not possible	
gradient for functional	die geometry and		
graded materials and	current distribution		
selective control of the			
density in specified regions			
Nanosintering and sintering	Promoted by the	Grain coarsening promoted	
under meta-stable conditions	high heating rate and	by the slow heating process	
	short sintering time		

A study was carried out by Liu *et al.* (2006) on the La<sub>x</sub>Co<sub>4</sub>Sb<sub>12</sub> thermoelectric materials fabricated via combining mechanical alloying followed by spark plasma sintering. The results indicated that a high value of *ZT* is 0.3425 at 500°C when x = 0.9. Another study was conducted by Duan *et al.* (2012a) on n-type double-substituted Co<sub>4</sub>Sb<sub>11.3</sub>Te<sub>0.7-x</sub>Se<sub>x</sub> skutterudites which were prepared by solid state reaction and spark plasma sintering. The results showed a decrease in the carrier concentration, electrical

conductivity and thermal conductivity with the Se-doping. Contrarily, the absolute Seebeck coefficient increased to ~ 239  $\mu$ V/K for Co<sub>4</sub>Sb<sub>11.3</sub>Te<sub>0.4</sub>Se<sub>0.3</sub> compound at ~ 750 K. The overall performance of Co<sub>4</sub>Sb<sub>11.3</sub>Te<sub>0.58</sub>Se<sub>0.12</sub> compound is enhanced to the highest ZT value of 1.11 at 800 K. In the following year, Ding et al. (2013) studied the thermoelectric properties of filled skutterudites  $Yb_{0.3}Co_4Sb_{12}$ with  $Yb_2O_3$ nanoinclusions, the results of the lattice thermal conductivity was reduced by about 19% at 850 K as compared to the Yb<sub>0.3</sub>Co<sub>4</sub>Sb<sub>12</sub> matrix, however, by the additional phonon scattering had lead to the maximum ZT of 1.3. Spark plasma sintering (SPS) techniques have revealed a large improvement in thermoelectric materials properties as compared to other techniques such as hot pressing and cold pressing. In addition, the advantages of the SPS technique include: very high density and controlled porosity, combination of the compaction and sintering stages in one operation, inexpensive operation cost, rapid cycle times and minimal grain growth (Kopeliovich, 2013). On the other hand, the disadvantages of spark plasma sintering are that only simple symmetrical shape can be prepared and the expensive pulsed DC generator is required (Kopeliovich, 2013).

## 2.6 Structure of skutterudite-based materials

Skutterudite is a natural mineral with CoAs<sub>3</sub> structure, which is discovered in Skutterud (Norway) at 1845. The general formulation of basic skutterudites is written as MX<sub>3</sub>, where M is a transition metal (Co, Ir, Rh) in the position site 8c (1/4,1/4,1/4) and X is a pnicogen atom (As, Sb, P) in the position site 24g (0, y, z) and 2a (0, 0, 0) for the void filler atom (Wojciechowski, 2002). The unit cell of a skutterudite is in a body-centered-cubic (BCC) structures with the space group Im-3, which consists of 32 atoms and two voids as shown in Figure 2.6 (Elsheikh *et al.*, 2014; Koza *et al.*, 2008).



Figure 2.6: Crystal structure of filled skutterudite (Elsheikh *et al.*, 2014; Koza *et al.*, 2008).

Generally, the binary skutterudites have a high power factor which gaining the interest in the field of thermoelectric materials. However, it is also has a very high thermal conductivity, which becomes the drawback factor to be used in the thermoelectric applications. However, by introducing the heavy atom guest into the voids able to rattle the cages and reduce the lattice conductivity, and hence improved the thermoelectric performance.

# 2.7 The strategies to improve the thermoelectric materials

In this section, the strategies of improving the skutterudite thermoelectric materials will be discussed in details. There are several strategies to improve the performance of skutterudite materials including; filling atoms into lattice cages, elemental substitutions into Co or Sb sites and nanostructure through a reduction of dimensionality.

## 2.7.1 Filling and doping modulation

Recently, element doping/filler has been employed to improve the thermoelectric performance of skutterudites materials by tuning the electrical and thermal behaviors of the materials (Zhou *et al.*, 2010). Moreover, by doping the semiconductors material is the promising technique to improve the electrical properties of thermoelectric materials without altering its thermal conductivity (Hou *et al.*, 2006). In this context, the

improvement of skutterudites thermoelectric materials performance due to the effect of filling atoms has been extensively investigated. Filling the voids with such atoms is the most effective way to reduce the thermal conductivity by improving the thermoelectric properties of skutterudite materials. Filling the skutterudites with rare earth elements has been widely studied in order to lower its lattice thermal conductivity. This can be ascribed to the filler atoms donate its electrons and rattle inside the voids, and thus improve the power factor. Moreover, the multi-filling approach has successfully enhanced the performance of thermoelectric materials more than single filler, and consequently increases the range of resonance phonon scattering frequencies, which is affected by the "rattling" provided the mass and vibration frequency of the filler species. In addition, the double filling method is more effective in reducing the thermal conductivity of the materials as compared to the single filling method (Yang *et al.*, 2009b).

Furthermore, several experimental studies have been conducted on CoSb<sub>3</sub> based composites and had shown the enhancement of thermoelectric properties by using the appropriate types of filling technique. Filling technique is considerably decreasing the lattice thermal conductivity, particularly in the mid-high temperature range. In 2009, a study was carried out by Chitroub *et al.* (2009) on n-type CoSb<sub>3</sub>-doped Pd and Te compounds prepared via the hot pressing method. The Pd and Te doping are the promising methods to enhance the performance of thermoelectric materials, where the figure of merit *ZT* had increased to the highest value of 1 for Co<sub>23.87</sub>Sb<sub>73.88</sub>Pd<sub>1.125</sub>Te<sub>1.125</sub> sample at 873 K. In the same year, Bai *et al.* (2009) had studied the single- and dual-filled skutterudites Ba<sub>x</sub>Ce<sub>y</sub>Co<sub>4</sub>Sb<sub>12</sub>. The results found that the Ba–Ce filling is more effective in reducing the lattice thermal conductivity than single Ba filling with the value less than 2.0 W/mK had achieved at room temperature. The highest *figure of merit of Ba*<sub>0.18</sub>Ce<sub>0.05</sub>Co<sub>4</sub>Sb<sub>12.02</sub> is 1.26 at 850 K. In the following year, Bai *et al.* (2010)

published a report on single-filled and double-filled of CoSb<sub>3</sub> skutterudites. The results possessed excellent thermoelectric properties and the Sr–Yb double filling was significantly suppressed the lattice thermal conductivity than the Sr-filled system. The highest power factor for Sr<sub>0.22</sub>Yb<sub>0.03</sub>Co<sub>4</sub>Sb<sub>12.12</sub> is 41  $\mu$ W/cmK<sup>2</sup> at room temperature and 57.5  $\mu$ W/cmK<sup>2</sup> at 850 K. The maximum dimensionless figure of merit value reaches 1.32 for Sr<sub>x</sub>Yb<sub>y</sub>Co<sub>4</sub>Sb<sub>12</sub>. Lee *et al.* (2012) reported a study on the multi-fillers CoSb<sub>3</sub> skutterudites prepared by spark plasma sintering. The results indicated that the Yb atoms were the most effective in suppressing the thermal conductivity. The peak of the figure of merit *ZT* value of 0.9 at 782 K was obtained for In<sub>0.1</sub>Yb<sub>0.2</sub>Co<sub>4</sub>Sb<sub>12</sub> specimen. Moreover, a recent study published by Ballikaya *et al.* (2012) on n-type skutterudite CoSb<sub>3</sub> with Yb, Ce, In double and triple fillers had showed that the double filling were able to enhance the power factor value to 57.7 mW/cmK<sup>2</sup> for Yb<sub>0.2</sub>Ce<sub>0.15</sub>Co<sub>4</sub>Sb<sub>12</sub>, while the triple fillers reduced the thermal conductivity to the lowest value of 2.82 W/mK corresponding to highest *ZT* value of 1.43 for Yb<sub>0.2</sub>Ce<sub>0.15</sub>In<sub>0.2</sub>Co<sub>4</sub>Sb<sub>12</sub> compound at 800K.

In addition, all of the results showed that the filled skutterudites displayed a much lower total thermal conductivity and lattice thermal conductivity than the unfilled CoSb<sub>3</sub> compound, which directly enhanced the performance of skutterudite thermoelectric material. Furthermore, the double filling technique significantly influences the thermal transport of the materials by decreasing the thermal conductivity more than single filling technique. In conclusion, it can be confirmed that the double and triple filling from the combination of different type filler atoms such as alkaline-earth element and rare-earth element (AE-RE) with different rattling frequencies are more effective way to suppress the lattice thermal conductivity than the single filler.

#### 2.7.2 Potential of nanostructuring

Traditional approaches of thermoelectric material properties were influenced by the types of dopants and their concentrations to maximize the power factor and enhance ZT(Ganguly et al., 2011). Both theoretical and experimental researches have tried the alternative approaches to develop thermoelectric materials by various distinct strategies such as exploring effective methods for phonon scattering, introducing nanostructured grain size, grain shape, secondary phases, dimension reduction and introduction of porosity to increase the performance of the bulk thermoelectric materials (Barron, 2005; Chen, 2006; Humphrey et al., 2005; Joannou et al., 2012; Kumpeerapun et al., 2010; Ni et al., 2005; Wang et al., 2011c). Therefore, as mentioned earlier, Hicks and Dresselhaus established the idea of nanoscale thermoelectric materials approach using reduction in dimensionality, which offers new strategies to vary S,  $\sigma$ , and k independently and enhance ZT (Hicks et al., 1993). For example, nanostructures such as quantum dots could cause a dramatic enhancement on the density of states near to E<sub>f</sub> which leads to the improvement of the Seebeck coefficient and increased carrier mobility, whereas nanocomposites and nanowires provide an enhanced boundary scattering of phonons at the barrier-well interfaces (Dresselhaus et al., 2007). Furthermore, the thermal conductivity of the quantum well structures is smaller as compared to the bulk counterparts. This finding can be attributed to the presence of quantum well/barrier interfaces which considerably enhanced the phonon-phonon scattering without significantly increasing the electron scattering (Je et al., 2009).

Given the ability of nanostructures to break through the barriers in thermoelectric material performance, development of bulk nanostructured materials for fabrication of large scale TEGs application has been a key area of research (Vaqueiro *et al.*, 2010). Mechanisms such as energy filtering at grain boundaries and phonon scattering are strategies that have been employed to improve the thermoelectric figure of merit

(Narducci *et al.*, 2012). For example, by employing the nanoparticles with a wide distribution of sizes will result in phonon scattering over both long and short wavelengths, thus further reducing the thermal conductivity of the material (Biswas *et al.*, 2012). Figure 2.7 shows a classification of the improvement of the nanocomposite morphologies in terms of parameters such as dimension reduction, size reduction of a second phase and grain refinement (Li *et al.*, 2010).



Figure 2.7: Summary of thermoelectric material structure from macro- to nanoscale. (a–d) Change in dimensionality. (a) bulk, (b) thin film, (c) nanowire, (d) atomic cluster. (e–h) Grain mixtures from micro- to nanoscale. (e) normal micro-grained bulk, (f) mixture of coarse and fine grains, (g) nano-grained bulk, (h) amorphous. (i–l) Size evolution of isolated distinct phases or atoms in the composite. (i) normal composite, (j) nanodispersions located inside grains or at grain boundaries, (k) nano-inclusions or nanodots, boundary modification, (l) atomic doping or alloying, and vacancies (Li *et al.*, 2010).

In particular, grain refinement is another viable strategy to achieve a higher *ZT*. Many nucleation sites are available during the solidification, which will result in a fine grain structure that is desirable for reduced thermal conductivity. The mechanism of grain formation is defined by the rate of cooling of the material, where a rapid cooling results in a smaller grain size and coarse-edged granules. The value of the figure of merit obtained with small grain size materials is significantly higher than that of large grain size with the same carrier concentration. Nanostructured and fine grain sized

thermoelectric materials can be achieved by mechanical alloying, rapid solidification, ball milling and hot pressing (Nakagawa *et al.*, 1997). The advantage of using ball milling includes handling ease and the ability to produce the nanostructured materials at room temperature (Ioannou *et al.*, 2012). Planetary ball milling is a simple yet cost effective method to break down the powder particles using mechanical impact and friction. The typical parameters of the ball milling process include milling time, milling speed, ball to powder weight ratio (BPR), ball size distribution and materials of the milling container (Suryanarayana, 2001). The properly executed ball milling with respect to the powder to ball ratio, time and under inert conditions will result in the formation of nanostructured materials with the significant *ZT* value, up to 250 % for both n- and p-type Si<sub>1-x</sub>Ge<sub>x</sub> alloys (Bux *et al.*, 2010).

Enhancement of thermoelectric performance through the reduction of grain sizes using the nanostructuring approaches have been demonstrated by several reported works. For example, Pshenai-Severin *et al.* (2013) reported that the thermoelectric materials with 30 nm grain size showed an increase in *ZT* about 38 % as compared to that of micro-sized grains. Bux *et al.* (2010) showed that the grain sizes reduced to 20 nm resulted in the decreased in lattice thermal conductivity about 90 %. The maximum *ZT* values of ~ 1.3 at 1275 K could be attained for Si<sub>0.8</sub>Ge<sub>0.2</sub> alloys. Table 2.2 shows a comparison of maximum *ZT* values for bulk and nanostructured thermoelectric materials (Vaqueiro *et al.*, 2010). Nanocomposite thermoelectric materials have also gained interest in large-scale commercial applications (Zhang *et al.*, 2010). For example, Eilertsen *et al.* (2012) introduced the InSb nanoinclusions and Pd-doped into In<sub>x</sub>Co<sub>4</sub>Sb<sub>12-x</sub> skutterudite-based nanocomposites. The results indicated that the nanoinclusions has successfully reduced the thermal conductivity, and consequently improved the thermoelectric figure of merit *ZT* to the highest value of ~ 0.56 for In<sub>0.1</sub>Pd<sub>0.15</sub>Co<sub>3.85</sub>Sb<sub>12</sub> sample at ~ 600°C. Figure 2.8 illustrates the grain size effect on the

electrical conductivity, thermal conductivity and figure of merit for Mg<sub>2</sub>Si thermoelectric material (Satyala *et al.*, 2012). Besides that, introducing an acoustically mismatched second phase in a matrix is another way to reduce the lattice thermal conductivity through the additional scattering mechanism. Figures 2.7(i)-(1) give an indication of the size reduction of isolated distinct phases or atoms in the composite, including sphere, plate and wire-shaped dispersed phases which could enhance the thermoelectric properties (Li *et al.*, 2010).



**Figure 2.8:** (a) Comparison of calculated electrical conductivity and thermal conductivity of nanostructured Mg<sub>2</sub>Si versus grain size (b) variation of figure of merit with grain size in Mg<sub>2</sub>Si (Satyala *et al.*, 2012).

	Bulk		Nano	ostructured
Material	ZT <sub>max</sub>	Temperature at which ZT <sub>max</sub> is observed	ZT <sub>max</sub>	Temperature at which ZT <sub>max</sub> is observed
Si	0.2	1200	0.7	1200
Si <sub>80</sub> Ge <sub>20</sub> (n- type)	1.0	1200	1.3	1173
Si <sub>80</sub> Ge <sub>20</sub> (p- type)	0.7	1200	0.93	1073
(Bi,Sb) <sub>2</sub> Te <sub>3</sub>	0.9	293	1.4	373
CoSb <sub>3</sub>	0.45	700	0.71	700

**Table 2.2:** Comparison of maximum ZT values for bulk and nanostructured thermoelectric materials (Vaqueiro *et al.*, 2010).

In conclusion, bulk nanostructuring has become a remarkable method to enhance the thermoelectric properties over those of bulk materials. Moreover, the approaches such as ball milling, nanocomposite fabrication and acoustical mismatch of secondary phases in a bulk material matrix are favorable strategies to improve the thermoelectric figure of merit.

# 2.8 Applications of thermoelectric materials

In 1996, the U.S. Air Force conducted a survey on thermal considerations on the performance of electronic systems. The results indicated that more than 50 % of the electronic failures are related to temperature (Yeh, 1995). For example, a significant waste heat is emitted from the domestic electronic appliances, automobile electronics, computers and portable electronics. The thermoelectric system is a promising method to convert these wasted heat energy into useful energy power without causing pollution or extra energy consumption during operation (Seo *et al.*, 2011). The utilization of waste heat as a potential source of electricity is a considered as "green" technology when the raw materials that are environmentally benign, fabrication processes are energetically conservative and the end of life issues are managed in an environmentally compatible

manner. Furthermore, tapping ambient waste heat cushions the effect of environmental warming as this waste heat is channeled into useful applications. As such, thermoelectric technology is being harnessed in applications such as thermoelectric cooling (TEC), thermoelectric heating (TEH) and thermoelectric power generation (TEG) (Caplain *et al.*, 2006; Leephakpreeda, 2012; Xi *et al.*, 2007).

For TEH and TEC configurations based on the Peltier effect, a voltage difference is applied through the object to enable the control of the temperature difference (Goupil et al., 2011). The majority of the applications of thermoelectric devices have been used for cooling purposes. Normally, the heat of the object is absorbed by the cold side of the thermoelectric module, while the hot side of the module is attached to a heat sink in order to dissipate this heat into the atmosphere. TEC devices have been widely used in electronic equipment such as diode lasers, IR detectors, car seats and refrigerators (Abdul-Wahab et al., 2009; Hirota et al., 2008; Yang et al., 2009a; Zhao et al., 2009), where the modules provide a fast and precise control of temperature and noise-free during operation (Li et al., 2003). On the other hand, semiconductor thermoelectric heat pumping (TEH) is an interesting technology that has the capability to compete with conventional heat pumping systems (Chen et al., 2007; Liu et al., 2010). The thermoelectric heat pump (TEH) is an energy friendly heating device due to its relatively high efficiency as compared to resistance heating device. TEH devices have been developed for applications such as clothes dryers, water heaters, and incubators (Luo, 2005). Furthermore, they have the potential to be used in specific applications including the military, aerospace, instrumentation, biology, medicine and industrial or commercial products (Barth et al., 2010; Riffat et al., 2003). On top of all, the thermoelectric heat pump has the advantages over the traditional heat pump in terms of lower noise level, compressor vibration and reduction in weight and size (Liu et al., 2010).

Thermoelectric generators (TEGs) modules for waste heat conversion typically consist of arrays of p-type and n-type semiconducting junctions which are connected electrically in series and thermally in parallel, as shown in Figure 2.9 (Gorsse *et al.*, 2011). Given its scalability, TEGs may be utilized to suit a range of power needs. On the milliwatt scale, TEGs have the potential to supply power to low power applications such as wireless sensors, mobile devices, and even medical applications (Schmitt *et al.*, 2012; Snyder, 2008). In 1998, Seiko incorporated thermoelectric technology into their wristwatches, which utilizes thin bulk thermoelectric devices driven by body heat, and hence the energy consumption is reduced by approximately 1  $\mu$ W (Kishi *et al.*, 1999). TEGs have also been used in domestic situations such as waste heat recovery for woodstoves and diesel power plants (Fergus, 2012). Bi-Te TEG modules are already commercially available, for instance, those manufactured by Komatsu and Ferrotec (Sano *et al.*, 2003). Since the recognition of the potential of CoSb<sub>3</sub> as thermoelectric materials, magnesium silicides based TEG modules are currently being developed by Murata Corporation (Kajitani *et al.*, 2013).



**Figure 2.9:** Basic thermoelectric device for (a) heat-to-electrical energy conversion, and (b) heat pumping (Gorsse *et al.*, 2011).

In order to develop a commercial CoSb<sub>3</sub> skutterudites TEG modules, balanced p-type and n-type materials must be readily available. Most of the CoSb<sub>3</sub> materials display favorable n-type thermoelectric properties in the temperature range of 500 – 800 K. On the other hand, the preparation of a stoichiometric composition with p-type filled skutterudites materials through the different types of doping/filler such as Ni and Ce elements was successfully synthesized. The highest *ZT* value reached ~0.8 for Ce<sub>0.9</sub>Fe<sub>3.9</sub>Ni<sub>0.1</sub>Sb<sub>12</sub> sample (Tan *et al.*, 2014). A study has been conducted by Nemoto *et al.* (2013) on thermoelectric modules with dimensions of 21 mm × 30 mm × 16 mm, which are composed only of n-type Sb-doped Mg<sub>2</sub>Si legs. The results showed that the module achieved a *ZT* value of 0.77 at 862 K, whereas the observed values of the opencircuit voltage and output power were 496 mV and 1211 mW, respectively, at  $\Delta T =$ 531. K. Kaibe *et al.* (2004) have successfully implemented a silicide thermoelectric modules consisting of p-MnSi<sub>1.73</sub> and n-Mg<sub>2</sub>Si<sub>0.4</sub>Sn<sub>0.6</sub>, in which both were doped with Sb. The results showed that the module attained the efficiency of more than 6.5 % at T<sub>h</sub> = 550°C with T<sub>c</sub> = 30°C.

## 2.9 Efficiency of thermoelectric devices

Despite the initial promising potential of TEGs in harvesting waste heat into electricity, currently, the applications are extremely limited by their low efficiency. As aforementioned, the efficiency of a thermoelectric device depends on several factors other than the maximum figure of merit, *ZT* of the materials. It is worth mentioning that the system efficiency at maximum power output is inversely proportional to the sum of the heat dissipation of the resistances of the hot and cold terminals in the TEG modules (Yazawa *et al.*, 2012). In conjunction with this, a technical report by Komatsu also mentioned that the conversion efficiency,  $\eta$  of their TEG modules are between 12 % to 15 % over a wide temperature range, i.e. from room temperature to around 600°C (Sano *et al.*, 2003). The overall efficiency of a thermoelectric generator device  $\eta$  is limited by

the Carnot cycle and the figure of merit ZT of the entire device. It depends on the temperature difference  $\Delta T = (T_h - T_c)$  across the device, which accounts for the individual ZT of the *n*- and *p*-type legs from the following equation (Müller *et al.*, 2003):

$$\eta = \left(\frac{\Delta T}{T_{\rm h}}\right) \cdot \frac{\left(\sqrt{(1+ZT)} - 1\right)}{\sqrt{(1+ZT) + \left(\frac{T_{\rm c}}{T_{\rm h}}\right)}}$$
(2-20)

 $\Delta T = (T_h - T_c)$  is the temperature difference between the hot and cold sides. Like all heat engines, the maximum power-generation efficiency of a thermoelectric generator is thermodynamically limited by the Carnot efficiency  $(\frac{\Delta T}{T_h})$ . Therefore, the efficiency of a thermoelectric device operating in a cooling or refrigeration method can be expressed by the following Coefficient of Performance (COP) (Rowe, 2005):

$$COP = \frac{\text{Heat absorbed}}{\text{Electrical power input}}$$
(2-21)

The COP of the thermoelectric cooling or refrigeration is lower than the conventional refrigeration techniques approximately by a factor of 0.5 (Gould *et al.*, 2009). For instance, an approximately 90 % of the commercially available thermoelectric modules are manufactured from bismuth telluride because it exhibits TE efficiency in the range of 6 - 8 % (Stranz *et al.*, 2011; Yang, 2005). However, the disadvantages of Bi<sub>2</sub>Te<sub>3</sub> compounds are difficult to overcome, including inherent toxicity and limited chemical stability at high temperatures in air (Gorsse *et al.*, 2011). For example, magnesium silicide has been considered as an alternative thermoelectric materials have demonstrated TEGs with an element efficiency of 6.4%, which was achieved by using a combination of microstructure-controlled MnSi<sub>1.73</sub> (p-type) and Mg<sub>2</sub>Si (n-type) (Kawamoto, 2009). Furthermore, the two-segmented thermoelectric modules fabricated from *n*-type Mg<sub>2</sub>(Si<sub>0.3</sub>Sn<sub>0.7</sub>)<sub>1-x</sub>Sb<sub>x</sub> based materials reached the highest efficiency of about 8.5 % in the temperature range of 323 – 773 K at a power of 19.9 W (Bilinsky-

Slotylo et al., 2013). In addition, Oiu et al. (2014) had reported that n-leg and p-leg of CoSb<sub>3</sub> doped materials possessed a higher efficiency than Mg<sub>2</sub>Si system, i.e. about 10.7%. To achieve the initial promise of TEGs as commercially viable energy harvesting devices, a dimensionless figure of merit ZT greater than unity and conversion efficiency higher than 10% are required (Yoshinaga et al., 2004). The beneficial effect of using the thermoelectric powered generator can be taken by example of its application in diesel engines, whereby around 43 MW/h or 167 GWh per annum of power savings can be achieved, corresponding to crude oil savings of 40,600 kiloliters per year and CO<sub>2</sub> emission reduction of approximately 20,200 tons per year (Sano et al., 2003). Given the promising potential of improvements on the global energy consumption and mitigation in greenhouse gases, CoSb<sub>3</sub> still remains a viable candidate for commercial thermoelectric materials. The main problem of CoSb<sub>3</sub> thermoelectric materials is its high thermal conductivity, which has an inverse impact on the TE performance. Scientist and researchers are trying to modify and develop a high performance thermoelectric materials, but to no avail thus far as the S, k and  $\sigma$ parameters are dependent. However, the filled-CoSb<sub>3</sub> is a great candidate for thermoelectric materials, which exhibits advantages in terms of raw resources availability and environmentally friendliness. Throughout this work, the addition of Al, In and Ni elements is expected to form new phases with free electrons in order to suppress the thermal conductivity and improve the overall TE performance. Moreover, Te dopant is expected to increase the Seebeck coefficient and enhance the dimensionless figure of merit, ZT.

#### **CHAPTER 3: METHODOLOGY**

The aim of this chapter is to describe the preparation, synthesis process of all the specimens and to elucidate different kinds of samples characterizations such as morphology, structural characterizations, thermoelectric properties, along with thermal and oxidation behaviors, as illustrated in the flowchart in Figure 3.1. In the first part, powdered raw materials were mixed and mechanically alloyed by ball milling, and then compacted via spark plasma sintering (SPS). In the second part, X-ray diffraction (XRD) and scanning electron microscope (SEM) techniques were used to examine the structural and morphological characterizations for the compositions, respectively. In the third part, the thermoelectric properties particularly the electrical resistivity and the Seebeck coefficient of the prepared samples were measured using the commercial instrument ZEM-3 system. The thermal conductivity of the sample was calculated from thermal diffusivity, which was measured by the laser flash method. In the last part, the thermal stability and oxidation behaviors of the samples were determined by simultaneous thermal analysis (STA) system. Summarily, the main focus of this chapter is to study the preparation and characterization of powder materials with different compositions, the thermoelectric properties of La<sub>x</sub>Co<sub>4</sub>Sb<sub>12</sub> and Yb<sub>y</sub>Co<sub>4</sub>Sb<sub>12</sub> system with the addition of different elements, namely Al, In, Ni and Te to improve the thermoelectric performance of the materials.

## **3.1** Preparation and synthesis of samples

## 3.1.1 Powder materials

The high purity starting elements powders, specifically Al (99.97%, 325 mesh), Co (99.8%, 1.6  $\mu$ m), In (99.99%, 325 mesh), La (99.9%, 200 mesh), Ni (99.8%, 325 mesh), Sb (99.5%, 200 mesh), Te (99.99%, 325 mesh) and Yb (99.9%, 200 mesh) were purchased from Alfa Aesar. The powders were weighed based on a stoichiometric ratio

for the nominal formula of  $M_x N_y Co_4 Sb_{12}$  (M = Al, In, Ni and Te, N = La and Yb) and values ( $0 \le x \le 0.5$ ) and (y = 0.25 and/or 0.5), as tabulated in Table 3.1.



Figure 3.1: Flowchart of material preparations and characterizations.

	No	Composition		No	Composition
Group 1	1	Yb <sub>0.25</sub> Co <sub>4</sub> Sb <sub>12</sub>		1	La0.25C04Sb12
	2	Yb <sub>0.25</sub> Co <sub>3.9</sub> Ni <sub>0.1</sub> Sb <sub>12</sub>	ıp 4	2	$In_{0.1}La_{0.25}Co_4Sb_{12}$
	3	Yb <sub>0.25</sub> Co <sub>3.7</sub> Ni <sub>0.3</sub> Sb <sub>12</sub>	Grot	3	$In_{0.3}La_{0.25}Co_4Sb_{12}$
	4	Yb <sub>0.25</sub> Co <sub>3.5</sub> Ni <sub>0.5</sub> Sb <sub>12</sub>		4	$In_{0.5}La_{0.25}Co_4Sb_{12}$
Group 2	1	La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>12</sub>		1	La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>12</sub>
	2	La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>11.9</sub> Te <sub>0.1</sub>	5	2	Al <sub>0.05</sub> La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>12</sub>
	3	La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>11.7</sub> Te <sub>0.3</sub>	roup	3	$Al_{0.1}La_{0.5}Co_4Sb_{12}$
	4	La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>11.5</sub> Te <sub>0.5</sub>	G	4	$Al_{0.3}La_{0.5}Co_4Sb_{12}$
	1	La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>12</sub>		5	$Al_{0.5}La_{0.5}Co_4Sb_{12}$
Group 3	2	$In_{0.1}La_{0.5}Co_4Sb_{12}$			<u> </u>
	3	In <sub>0.2</sub> La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>12</sub>			
	4	In <sub>0.3</sub> La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>12</sub>			

 Table 3.1: The nominal compositions

In this work, we investigated five groups of skutterudite materials through mechanical alloying and spark plasma sintering, namely;

- (a) Yb<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> doped with transition metals such as Ni to form a quaternary skutterudite material. Ni-doping has the potential to enhance the thermoelectric performance of skutterudite materials through substitution into Co sites in the Yb<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> system. The transition metal Ni dopant which substitutes into Co site is expected to act as electron donors. Therefore, Ni-doping is expected to improve the electrical conductivity of the material by increasing the carrier concentration, which will then lead to the enhancement of power factor and moderate increase of ZT.
- (b) Next, we investigate the potential of La-addition which partially fills the voids of polycrystalline skutterudite crystal structure to achieve a lower thermal

conductivity that that of Yb-filled skutterudite. In comparison with Yb filling (Yb<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> sample), La filling has resulted in 24% reduction of the thermal conductivity for skutterudite Co<sub>4</sub>Sb<sub>12</sub> at 404 K, as demonstrated by La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample. This phenomenon can be related to the lower density ( $\rho = 6.15 \text{ g/cm}^3$ ) and higher number of valence electrons ( $V_e=3$ ) of La than that of Yb ( $\rho =$ 6.90 g/cm<sup>3</sup>; V<sub>e</sub>= 3) (Barbalace, 2011; Dudy et al., 2013). Consequently, Lafilling may induce additional phonon scattering via inserting more La-filler atoms into the voids of the skutterudite structure. Simultaneously, the effect of Te doping into the partially filled La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> system is also studied. The Te dopant is expected to substitute the Sb sites and act as electron donors in the skutterudite system, owing to the higher number of valance electrons of Te ( $V_e =$ 6). As a result, Te-doping is anticipated to increase the electrical conductivity and Seebeck coefficient of the partially filled La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> system. The filling of La into Co<sub>4</sub>Sb<sub>12</sub> skutterudite is expected to contribute towards lowering the thermal conductivity of the system. On another note, the strategy of adding Te into La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> system is expected to produce a TE material with higher electrical conductivity and Seebeck coefficient.

(c) In-addition into partially filled La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> system. In which acts as filler is able to reduce the thermal conductivity of La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> formulation, thereby improving its thermoelectric properties. The density (ρ) and number of valence electrons (V<sub>e</sub>) of In filler are 7.31 g/cm<sup>3</sup> and 3, respectively (Barbalace, 2011). Considering from its material nature, In-filling is expected to give rise to secondary InSb phase in La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> skutterudite system, which helps to enhance phonon scattering and subsequently, reduce the electrical resistivity and lattice thermal conductivity of the system.

- (d) In-addition into partially filled La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> system. The addition of In is expected to contribute to the reduction of electrical resistivity and lattice thermal conductivity of the system, due to the presence of a secondary InSb phase. As discussed formerly, InSb phase could enhance phonon scattering in the system, thus enhancing the overall performance of the system.
- (e) Al-addition into partially filled La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> system. The density (ρ) and number of valence electrons (V<sub>e</sub>) of Al filler are 2.70 g/cm<sup>3</sup> and 3, respectively (Barbalace, 2011). Al-filler atoms are expected to rattle into the lattice voids and by this mean, enhance the carrier concentration and phonon scattering in the system. Therefore, both of the electrical resistivity and lattice thermal conductivity of the system are expected to reduce, leading to the improvement in the overall thermoelectric performance.

## 3.1.2 Mechanical alloying process

The nominal compositions were prepared through a mechanical alloying process (MA) via ball milling (BM), as seen in Table 3.1. This method is commonly performed by utilizing a high energy ball milling technique in which mechanical alloying occurs basically through a sequence of collision events inside a high energy ball mill. Moreover, ball milling process is simple and easy to handle for the formation of several alloys, which is difficult to achieve by any other technique. Besides, ball-milling process can also be used to prepare contamination-free powder under high purity argon gas atmosphere.

The stoichiometric materials were loaded into a Zirconia Jar (50 ml) with Zirconia balls (5 mm in diameter). The weight ratio of the balls to the powders was 20:1. The jar was placed into a ball mill (GOKIN Ltd., PLANET) with a rotation speed of 400 rpm, as depicted in Figure 3.2. All of the powders were dry milled for approximately 10

hours. To protect the as-prepared powdered material from atmospherical contamination during the milling process, an O-ring was used to seal the Jar's cover. After ball milling process, the mixed powders were transferred to SPS for consolidation.



Figure 3.2: Ball milling (GOKIN Ltd., PLANET)

# 3.1.3 Solidification of M<sub>x</sub>N<sub>y</sub>Co<sub>4</sub>Sb<sub>12</sub> skutterudites materials via spark plasma sintering (SPS)

Spark plasma sintering (SPS) is a state-of-the-art sintering method, which has been commonly utilized for the consolidation of  $M_xN_yCo_4Sb_{12}$  skutterudite materials. SPS has often been considered a good technique owing to their advantages which include significant time saving, energy saving, the ability to prepare samples with very high density and controlled porosity, and the ability to retain nanostructures as compared to the conventional method. In detail, stoichiometric amounts of the mixtures were loaded into a graphite die (10 mm diameter) after 10 hours of ball milling for solidification into dense bulk materials by using spark plasma sintering (SPS – Dr. Sinter Lab Series), as shown in Figure 3.3. The SPS was conducted at 600°C for 10 minutes in order to obtain a fully dense material. The pressure and heating rate of the sintering process were fixed
at 36 MPa and 100°C/min, respectively. A sintering atmosphere of ~4 Pa vacuum was used in order to evacuate ambient air from the mold. Then, the samples were mechanically cut using a fine cutting machine into appropriate sizes (bar shape) and the surface was grounded by Silicon carbide (SiC) sandpaper for subjection to the measurement of the thermoelectric properties. Most of the fabricated samples prepared herein possessed a sufficient density of more than 95% of the theoretical densities, whereby the density is measured using the Archimedes method.



**Figure 3.3:** (a) Spark plasma sintering (SPS), (b) graphite die and (c) graphite die inside the chamber

### **3.2 X-ray powder diffraction**

X-ray diffraction (XRD) is a rapid analytical and non-destructive method which is widely used in phase identification of a crystalline material. Besides, the lattice parameters information can also be determined via Jana2006 software. The X-ray diffraction peaks are produced from the constructive interference of a monochromatic X-rays. In detail, the elastically scattered X-rays is generated in a cathode ray tube and filtered to produce monochromatic radiation before collimated and directed toward the target sample. In this study, XRD measurement was performed using a Bruker AXS D8 Advance system to examine the overall structure of crystalline SPSed samples. Specifically, Cu K<sub>a1</sub> radiation ( $\lambda = 1.5418$  Å) was produced with generator parameters of 40mA and 40kV, while the step size was set at 0.020406° with measuring time 1 second per step. The specimens were placed into the holder for XRD measurement under ambient atmosphere at room temperature. The data was collected by Bruker AXS DIFFRAC.EVA V2.1 program in a continuous scan mode in the 2 $\theta$  range of 10° - 90° (where  $\theta$  represents the Bragg angles). The Bragg's law can be mathematically expressed by the following relationship:

$$2d\sin\theta = n\lambda \tag{3-1}$$

#### 3.3 Microstructure analysis

The SPSed samples were grounded and polished using a "Struers TegraPol-21" machine, which conducts microstructural analysis on the samples. The grinding method was carried out using different grit size for silicon carbide (SiC) sandpaper, namely 200, 800, 1200, 2400, and 4000 for all SPSed bulk samples. The speed range of holder and disc was in the range of 90-100 rpm for 1 min under 10 N of force and the rotation is at opposite direction. Water was used as a lubricant during the process. Then, the final step of the grinding process involved the abrasive suspension (particle size: 9.0 µm on MD-Largo) with Allegro Largo 9-Diapro as the lubricant during the process. After the grinding process, a polycrystalline diamond suspension was used for the polishing process, whereas an abrasive suspension (particle size: 3.0 µm) was used as a lubricant on MD-Dur and MD-Mol polishing cloth with (Mol R3 & OP-S NonDry), respectively. In the final polishing step with water, a MD-CHEM polishing cloth wetted with a

colloidal silica suspension was used. Thereafter, the sample surface was cleaned with distilled water and dried with a hot air blower to remove any remaining residue. Subsequently, the polished samples were placed into a scanning electron microscope (SEM) machine for microstructural analysis.

The microstructural analysis of SPSed samples was carried out using a scanning electron microscope (SEM) and an Energy Dispersive Spectroscopy (EDS) to study the crystallinity, composition, homogeneity and distribution of the doping/filler grain and grain boundaries. These parameters could considerably affect the thermoelectric properties of the consolidated bulk samples. SEM scanning is non-destructive in nature and during scanning, the surface of the sample is scanned with a high-energy beam of electrons, while the secondary electrons emitted from the sample are the primarily sources for image formation. The incident electrons interact with the atoms in the specimen to produce signals, which contain informative characterization of the sample's surface topography and composition. In this work, the microstructural images and elemental mapping of the samples were taken by a FEI Helios 450HP dual beam scanning electron microscopy (SEM) integrated with an energy-dispersive X-ray spectroscopy (EDS).

#### **3.4** Thermoelectric properties measurement

In this section, we describe the measurement of thermoelectric behaviors. A high performance thermoelectric materials typically possesses high electrical conductivity ( $\sigma$ ), high Seebeck coefficient (*S*) and low thermal conductivity (*k*), which can be found using *ZT* as shown in equation (2.1). The measurements of electrical resistivity ( $\rho$ ) and Seebeck coefficient were simultaneously carried out using the ZEM-3 system from room temperature to 800 K under Helium gas atmosphere. The thermal conductivity of

the sample is measured by a laser flash device in the temperature range of 300 - 800 K in vacuum.

### **3.4.1** Electrical resistivity measurement

Electrical resistivity can be defined as the specific electrical resistance of a material, which is the reciprocal of electrical conductivity. The measurement of the electrical resistivity ( $\rho$ ) of thermoelectric materials as a function of temperature was performed using the commercial instrument ZEM-3 (Ulvac-Riko), as shown in Figure 3.5(a). Moreover, in the ZEM-3 system, the electric resistivity is characterized using a four-probe AC technique, as shown in Figure 3.4, which can be calculated by the relation below:

$$\rho = \frac{A}{l} \left( \frac{dV}{dI} \right) \tag{3-2}$$

where (dV/dI) is the slope of the I-V plot, which is equal to the resistance (R). l is the distance between two voltage probes, while A is the cross-sectional area of the sample. The rectangular shaped sample (2 mm × 2 mm × 8 mm) was placed into the device as seen in Figure 3.5(b-d).



Figure 3.4: Schematic diagram of the four probe measurement in ZEM-3 system



**Figure 3.5:** (a) Commercial ZEM-3 system device, (b) chamber and sample in the device, and (c-d) the dimension of SPSed sample

# 3.4.2 Seebeck coefficient measurement

The Seebeck coefficient is otherwise known as the thermopower (S) of a material, which reflects the amount of potential induced by thermoelectric voltage regarding to the temperature gradient across the sample. In this study, cuboid shaped samples ( $8L \times 2W \times 2H$  mm) were used in mid-temperature range from room temperature to 800 K. The Seebeck measurement was performed using the same device to measure the electrical resistivity (ZEM-3 thermoelectric characterization system), as shown above in Figure 3.5(a). The Seebeck coefficient of the sample was measured under high purity Helium gas atmosphere condition. The SI unit of the Seebeck coefficient *S* is microvolts per kelvin ( $\mu$ V/K). It should be noted that while taking Seebeck coefficient measurements, the voltages and temperatures of the sample are measured simultaneously using the same thermocouple probes, as illustrated in Figure 3.4 above. Then, the voltage difference ( $\Delta$ V) between the two probes ( $\Delta$ T) was measured for a set of temperature differences to obtain the Seebeck coefficient. In this study, the Seebeck coefficient of the sample was estimated using the following equation:

$$S = S_1 - \frac{V_1}{V_1 - V_2} (S_1 - S_2)$$
(3-3)

where  $S_1$  and  $S_2$  represent S, and  $V_1$  and  $V_2$  represent the detected voltages of the Chromel and Constantan, respectively. The accuracy of the ZEM-3 system during Seebeck coefficient measurement is around 7%.

# 3.4.3 Thermal conductivity measurement

For thermoelectric materials, the thermal diffusivity is usually measured using a laser flash method TC-7000H (Ulvac-Riko) apparatus, as shown in Figure 3.6(a). The laser flash method can easily estimate the thermal conductivity (k) of a sample from its thermal diffusivity (D), density (d) and specific heat ( $C_p$ ) via following the relation. It should be mentioned that the density (d) of the sintered materials was measured by the Archimedes method.

$$k = D \times C_P \times d \tag{3-3}$$

The thermal diffusivity of the sample was measured in the temperature range of 300 - 800 K under high vacuum (less than  $10^{-5}$  torr) to reduce the heat loss as much as possible from the sample. Basically, the sample used for thermal conductivity

measurement should be in disk shape with a diameter and thickness of 10 mm and 1-3 mm, respectively. The two surfaces of the disk shape must be parallel and flat. During measurements, the thermocouples were attached to the sample using ceramic paste and the surface was coated with graphite, as demonstrated in Figure 3.6(b). This step is inevitable to avoid a high laser reflection, which may reduce the energy absorption and lead to a bad rear face signal. Finally, the sample was placed into the machine (Figure 3.6(c)).



**Figure 3.6:** (a) A laser flash system (TC-7000H), (b) sample with thermocouples and (c) SPSed sample in the device

# 3.5 Thermal and oxidation properties measurement

Thermal analysis is one of the crucial characteristic techniques used to determine and study the stability behavior of thermoelectric materials against temperature. The thermal stability behavior dictates the lifetime of a thermoelectric device. Thermal analysis was performed to examine the thermal and oxidation behavior for the sintered samples through Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) devices, respectively. TGA measurement is valuable for any reaction with weight changes during heating, which indicates mass loss or gain by decomposition and reduction, or absorption and reaction with oxygen. The weight of the sample is recorded as a function of increasing temperature. On the other hand, DSC technique is used to investigate the thermal effects associated with phase transitions, melting/crystallization behavior as a function of temperature.

The measurements were carried out using simultaneous thermal analyzer (STA 6000, PerkinElmer Instrument) in the temperature range from 25 to 1000°C. After the baseline was established, the samples (typically in 80 - 100 mg) were placed into Al<sub>2</sub>O<sub>3</sub> crucible with a heating rate of 10°C min<sup>-1</sup> and a cooling rate of 10°C min<sup>-1</sup> under consistent N<sub>2</sub> gas flow (100 mL min<sup>-1</sup>).

#### **CHAPTER 4: RESULTS AND DISCUSSION**

The goal of this chapter is to present the characterization results of the skutterudite materials which were synthesized using the combination of mechanical alloying (MA) followed by spark plasma sintering (SPS) process. In this research, SPSed skutterudite samples were prepared with different kinds of additions, namely Yb<sub>0.25</sub>Co<sub>4-x</sub>Ni<sub>x</sub>Sb<sub>12</sub>, La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12-x</sub>Te<sub>x</sub>, In<sub>x</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub>, In<sub>x</sub>La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> and Al<sub>x</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> compounds, in which x was fixed in the range of  $0 \le x \le 0.5$ . The characterization outcomes of the SPSed samples would be discussed individually in terms of their microstructural and thermoelectric properties as well as thermal and oxidation behaviors.

## 4.1 Ni<sub>x</sub>-addition Yb<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> compositions ( $0 \le x \le 0.5$ )

### 4.1.1 Microstructure properties

Figure 4.1 exhibits the XRD patterns of Yb<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> SPSed samples with different Ni-addition fraction content. From the results, it was found that all of the samples consisted of the dominant phase, i.e. skutterudite CoSb<sub>3</sub> (PDF 03-065-1791) structure (space group Im-3) and notably, a minor amount of secondary phases particularly CoSb<sub>2</sub> (PDF 03-065-4102) and Ni (PDF 00-001-1258) have also been identified in most of the doped samples. However, Yb<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> bulk sample only exhibits a single phase of skutterudite structure, mainly due to the limited filling of Yb in the void ( $0.2 \le x \le 0.3$ ), as suggested in the study of Park *et al.* (2014b).

Moreover, the Rietveld refinement analysis of XRD pattern was implemented on all of the bulk samples and the related lattice structures are shown in Figure 4.2. The initial input data of the cubic filled skutterudite were assumed to be 2a (0, 0, 0) for the void filler (La atoms), 8c (0.25, 0.25, 0.25) for the metal (Co and/or Ni atoms) and 24g (0, y, z) for pnicogen (Sb atoms) (Wojciechowski, 2002). Table 4.1 shows the refinement results of all SPSed samples at room temperature. Interestingly, it was found that the lattice parameters shrunk after Ni-doping, indicating that Ni-atoms have substituted Coatoms in the lattice structure. This phenomenon is viable to occur considering that the atomic radius of Ni is smaller than that of Co atom.



**Figure 4.1:** XRD pattern of  $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$  ( $0 \le x \le 0.5$ ) samples.

**Table 4.1:** Nominal compositions, actual compositions, lattice parameters and density of  $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$  ( $0 \le x \le 0.5$ ) samples.

Nominal composition	Actual composition	Lattice parameter (Å)	Density (%)
CoSb <sub>3</sub> (Wee <i>et c</i> 2010)	ıl.,	9.0350	
Yb <sub>0.25</sub> Co <sub>4</sub> Sb <sub>12</sub>	2 Yb <sub>0.25</sub> Co <sub>4</sub> Sb <sub>12</sub>	9.0412 (2)	99 %
Yb <sub>0.25</sub> Co <sub>3.9</sub> Ni <sub>0.1</sub> S	b <sub>12</sub> Yb <sub>0.25</sub> Co <sub>3.9</sub> Ni <sub>0.1</sub> Sb <sub>12</sub>	9.0349 (8)	96 %
Yb <sub>0.25</sub> Co <sub>3.7</sub> Ni <sub>0.3</sub> S	b <sub>12</sub> Yb <sub>0.25</sub> Co <sub>3.7</sub> Ni <sub>0.3</sub> Sb <sub>12</sub>	9.0443 (4)	96 %
Yb <sub>0.25</sub> Co <sub>3.5</sub> Ni <sub>0.5</sub> S	b12 Yb0.25C03.5Ni0.5Sb12	9.0404 (4)	99 %



Figure 4.2: Jana Refinement images of (a) Yb<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub>, (b) Yb<sub>0.25</sub>Co<sub>3.9</sub>Ni<sub>0.1</sub>Sb<sub>12</sub>, (c) Yb<sub>0.25</sub>Co<sub>3.7</sub>Ni<sub>0.3</sub>Sb<sub>12</sub> and (d) Yb<sub>0.25</sub>Co<sub>3.5</sub>Ni<sub>0.5</sub>Sb<sub>12</sub> SPSed samples.

Figures (4.3) – (4.5) display the SEM micrographs images of different Ni-added  $Yb_{0.25}Co_4Sb_{12}$  samples. It can be perceived that the microstructures for all of the samples have relatively high density (in the range of 96 % – 99 % of the theoretical density) as shown in Table 4.1. The microstructural images of the all samples have confirmed the dominate phase of the skutterudite  $CoSb_3$ , with a small amount of  $CoSb_2$  being detected as secondary phase. Elemental mapping results reveal the agglomeration of the Yb elements in certain regions as well. Interestingly, the agglomeration of the Yb elements was found to increase with increasing Ni-dopants, as depicted in Figure 4.3(d),

4.4(d) and 4.5(d). Figure 4.3(e) displays the homogenous distribution of Ni-element from the elemental mapping. However, the random distribution of Ni-element could be clearly observed in Figure 4.4(e) and Figure 4.5(e) along with some agglomerations. In addition, SEM and EDS also agrees well with the XRD analysis results. It can be revealed that the Ni is doped the Yb-filled skutterudite bulk material with some traces of Yb detected. The detailed EDS information for  $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$  ( $0.1 \le x \le 0.5$ ) samples can be seen in Table 4.2.

	Atomic percent (%)					
Compound	Yb0.25C03.9Ni0.1Sb12		Yb0.25C03.7Ni0.3Sb12		Yb0.25C03.5Ni0.5Sb12	
Element/Point	1	2	1	2	1	2
Со	21.69	28.83	22.61	24.5	21.86	32.97
Sb	71.87	64.61	74.27	56.61	71.7	62.93
Yb	2.38	0.4	1.07	0	4	1.33
Ni	4.06	6.16	2.05	11.74	2.44	2.77

**Table 4.2:** EDS points of  $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$  ( $0.1 \le x \le 0.5$ ) SPSed samples.



**Figure 4.3:** SEM-EDS images of Yb<sub>0.25</sub>Co<sub>3.9</sub>Ni<sub>0.1</sub>Sb<sub>12</sub>; (a) micrograph and (b-e) the elemental mapping of SPSed sample.



**Figure 4.4:** SEM-EDS images of Yb<sub>0.25</sub>Co<sub>3.7</sub>Ni<sub>0.3</sub>Sb<sub>12</sub>; (a) micrograph and (b-e) the elemental mapping of bulk sample.



**Figure 4.5:** SEM-EDS images of Yb<sub>0.25</sub>Co<sub>3.5</sub>Ni<sub>0.5</sub>Sb<sub>12</sub>; (a) micrograph and (b-e) the elemental mapping of SPSed sample.

# 4.1.2 Thermoelectric properties

Figure 4.6 displays the temperature dependence of electrical resistivity for  $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$  SPSed samples. In general, the electrical resistivity reduced with increasing Nidoping content and temperature, indicating a typical semiconductor behavior for all of the samples. Apparently, the reduction of electrical resistivity can be attributed to the generation of more charge carriers with increasing temperature. In detail, Yb<sub>0.25</sub>Co<sub>3.5</sub>Ni<sub>0.5</sub>Sb<sub>12</sub> sample showed the lowest electrical resistivity of 14.6  $\mu\Omega$ m at 785K among of the samples, which is a significant reduction from that of Ni-free sample (36.1  $\mu\Omega$ m) at the same temperature. This phenomenon arises from the excessive supply of electrons via Ni-doping which resulted in increased carrier concentrations. In comparison with previous research outcomes, Yang *et al.* (2006) reported an electrical resistivity of 50  $\mu\Omega$ m for Co<sub>3.6</sub>Ni<sub>0.4</sub>Sb<sub>12</sub> sample at room temperature, which is higher than the result herein. A recent research study on Yb<sub>0.2</sub>Co<sub>4-x</sub>Ni<sub>x</sub>Sb<sub>12</sub> compound also demonstrated that the electrical resistivity of the compound was significantly reduced after Ni doping and particularly, an electrical resistivity as low as ~ 8.5  $\mu\Omega$ m was obtained by 0.2 wt% Ni-added compound at room temperature (Fu *et al.*, 2015). The result of Ni-doping on Yb-filled skutterudite has improved the electrical resistivity of Co<sub>4</sub>Sb<sub>12</sub> bulk sample.



**Figure 4.6:** Temperature dependence of electrical resistivity of SPSed Yb<sub>0.25</sub>Co<sub>4-x</sub>Ni<sub>x</sub>Sb<sub>12</sub> ( $0 \le x \le 0.5$ ) samples; The insert enlarges the section of electrical resistivity at low values (10 to 40  $\mu\Omega$ m).

The temperature dependence of Seebeck coefficients for Yb<sub>0.25</sub>Co<sub>4-x</sub>Ni<sub>x</sub>Sb<sub>12</sub> SPSed samples is shown in Figure 4.7. Basically, the absolute Seebeck coefficient values improved with both the Ni-doping content and temperature. Among all of the samples, the highest absolute Seebeck coefficient value was achieved by Yb<sub>0.25</sub>Co<sub>3.7</sub>Ni<sub>0.3</sub>Sb<sub>12</sub> sample, reaching a remarkable 223  $\mu$ V/K at 592 K. In comparison, the pristine Yb<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> sample recorded a mere 153  $\mu$ V/K at the same temperature. The improvement here can be primarily ascribed to the additional supply of electrons via Nisubstitution. There is a decrease in Seebeck coefficient for x = 0.5 sample, maybe due to the appearance of Ni peak and more agglomeration of Yb element have been observed by XRD and SEM image, respectively. The present result is noticeably higher than that obtained in the previous studies, whereby the Seebeck coefficients for Co<sub>3.6</sub>Ni<sub>0.4</sub>Sb<sub>12</sub> compound (Yang *et al.*, 2006) and Yb<sub>0.17</sub>Co<sub>3.97</sub>Ni<sub>0.03</sub>Sb<sub>12</sub> compound (Da Ros *et al.*, 2007) was reported to be ~ 165 $\mu$ V/K for at 592 K and ~ 175 $\mu$ V/K at ~ 800 K, respectively.



Figure 4.7: Temperature dependence of Seebeck coefficient of SPSed Yb<sub>0.25</sub>Co<sub>4-x</sub>Ni<sub>x</sub>Sb<sub>12</sub> ( $0 \le x \le 0.5$ ) samples.

The temperature dependence of the power factors for Yb<sub>0.25</sub>Co<sub>4-x</sub>Ni<sub>x</sub>Sb<sub>12</sub> SPSed samples is depicted in Figure 4.8, in which the power factors were calculated from the Seebeck coefficients and electrical resistivity values. Similarly, it was found that the power factor improved with both the Ni-doping content and temperature. Yb<sub>0.25</sub>Co<sub>3.7</sub>Ni<sub>0.3</sub>Sb<sub>12</sub> sample reached the maximum power factor of  $2.41 \times 10^{-3}$  W/mK<sup>2</sup> at 592 K, owing to the increase of Seebeck coefficient which is higher at x = 0.3 and reduced electrical resistivity. In comparison, the Seebeck coefficient of Ni-doped sample is much higher than that of Ni-free sample, achieving only  $0.40 \times 10^{-3}$  W/mK<sup>2</sup> at the same temperature. The Seebeck coefficient of the optimum Ni-doped sample is slightly higher than that reported in the study of Park *et al.* (2012), i.e. ~  $2.2 \times 10^{-3}$  W/mK<sup>2</sup> for Yb<sub>0.9</sub>Fe<sub>3</sub>CoSb<sub>12</sub> compound at same temperature. However, the Seebeck coefficient of Ni-doped sample remains slightly lower than that attained by Ce<sub>0.8</sub>Fe<sub>3.5</sub>Ni<sub>0.5</sub>Sb<sub>12</sub> compound i.e.  $2.6 \times 10^{-3}$  W/mK<sup>2</sup> (Lee *et al.*, 2015).



Figure 4.8: Temperature dependence of power factor of  $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$  ( $0 \le x \le 0.5$ ) SPSed samples.

Figure 4.9(a) illustrates the temperature dependence of thermal conductivity (*k*) for  $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$  compounds. The total thermal conductivity is the sum of the electronic and lattice thermal conductivities  $k_{tot} = k_e + k_L$ . It was found that the thermal conductivity of the sample increased with increasing Ni-doping content at room temperature. For doped samples,  $Yb_{0.25}Co_{3.9}Ni_{0.1}Sb_{12}$  sample shows the lowest value of thermal conductivity of 2.91 W/mK at 500 K. This result is lower than that obtained for  $Co_{3.6}Ni_{0.4}Sb_{12}$  sample (Yang *et al.*, 2006) and Yb\_{0.17}Co\_{3.97}Ni\_{0.03}Sb\_{12} sample (Da Ros *et al.*, 2007), i.e. ~ 3.8 W/mK and 3.7 W/mK at the same temperature, respectively.

The lattice thermal conductivity was evaluated by subtracting the electronic contribution from the total thermal conductivity. The electronic contribution of the thermal conductivity can be determined via the Wiedemann–Franz law ( $k_e = L \times \sigma \times T$ , where L is Lorenz number). The Lorenz number can be calculated as the function of temperature dependence using single parabolic band model via the following equation (Rowe *et al.*, 1983):

$$L(T) = \left(\frac{K_{\rm B}}{e}\right)^2 \left[\frac{\left(\lambda + \frac{7}{2}\right)F_{\lambda+\frac{5}{2}}(\xi)}{\left(\lambda + \frac{3}{2}\right)F_{\lambda+\frac{1}{2}}(\xi)} - \left(\frac{\left(\lambda + \frac{5}{2}\right)F_{\lambda+\frac{3}{2}}(\xi)}{\left(\lambda + \frac{3}{2}\right)F_{\lambda+\frac{1}{2}}(\xi)}\right)^2\right]$$
(4-1)

where  $K_B$  is the Boltzmann constant, *e* is the electron charge,  $\lambda$  is scattering parameter,  $\xi = E_F/K_BT$  is the reduce Fermi energy and  $E_F$  is the Fermi energy.  $F_n(\xi)$  is the Fermi integral defined by

$$F_{n}(\xi) = \int_{0}^{\infty} \frac{x^{n}}{1 + e^{x - \xi}} dx$$
(4-2)

In this calculation, the scattering parameter is set to be -0.5 by assuming the acoustic phonon scattering is the dominant carrier scattering mechanism at measurement

temperature range. The reduced Fermi energy is extracted from the measured Seebeck coefficient values using the following expression (Rowe *et al.*, 1983):

$$S = \pm \frac{K_B}{e} \left[ \frac{\left(\lambda + \frac{5}{2}\right) F_{\lambda + \frac{3}{2}}(\xi)}{\left(\lambda + \frac{3}{2}\right) F_{\lambda + \frac{1}{2}}(\xi)} - \xi \right]$$
(4-3)

By using the extracted reduced Fermi energy, the Lorenz numbers are calculated to be  $1.63 \times 10^{-8}$ ,  $1.71 \times 10^{-8}$ ,  $1.65 \times 10^{-8}$ , and  $1.71 \times 10^{-8} \text{ V}^2/\text{K}^2$  for proportion of x = 0, 0.1, 0.3 and 0.5, respectively, near room temperature. The calculated Lorenz number are smaller than the degenerate limit of Lorenz number ( $2.44 \times 10^{-8} \text{ V}^2/\text{K}^2$ ) which is typically observed in thermoelectric materials with carrier concentrations between generate and non-degenerate semiconductor (Kim *et al.*, 2015).

Figure 4.9(b) presents the variation of lattice thermal conductivity ( $k_L$ ) for Yb<sub>0.25</sub>Co<sub>4-x</sub>Ni<sub>x</sub>Sb<sub>12</sub> specimens as a function of temperature. The results demonstrates that the lattice thermal conductivity reduced with Ni-doping content at room temperature. The lowest lattice thermal conductivity of 2.54 W/mK was achieved by Yb<sub>0.25</sub>Co<sub>3.7</sub>Ni<sub>0.3</sub>Sb<sub>12</sub> sample at 643 K, which can be primarily attributed to the phonon scattering by the rattling of filler into the voids of skutterudite.



Figure 4.9: Temperature dependence of (a) thermal conductivity and (b) lattice thermal conductivity of  $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$  ( $0 \le x \le 0.5$ ) SPSed samples.

The dimensionless figure of merit, ZT for Yb<sub>0.25</sub>Co<sub>4-x</sub>Ni<sub>x</sub>Sb<sub>12</sub> SPSed samples is displayed in Figure 4.10 as a function of temperature. It can be seen that the ZT values improved via increasing Ni-doped content and temperature. The maximum ZT value of 0.49 was attained by Yb<sub>0.25</sub>Co<sub>3.7</sub>Ni<sub>0.3</sub>Sb<sub>12</sub> sample at a temperature of 692 K, which is 88% higher than that of pristine Yb<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> sample at the same temperature. Comparatively, The *ZT* value obtained for Yb<sub>0.25</sub>Co<sub>3.7</sub>Ni<sub>0.3</sub>Sb<sub>12</sub> sample in this study is higher than that the *ZT* value obtained for Co<sub>3.6</sub>Ni<sub>0.4</sub>Sb<sub>12</sub> sample, i.e. ~ 0.15 at the same temperature (Yang *et al.*, 2006). The main reason of *ZT* enhancement can be associated with the increase of power factor and moderate reduction in the lattice thermal conductivity. Most notably, Ni-doped Yb<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> system exhibits more than 4% improvement when compared with Te-doped La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> system.



**Figure 4.10:** Temperature dependence of figure of merit for  $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$  ( $0 \le x \le 0.5$ ) SPSed samples.

# 4.1.3 Oxidation and thermal behaviors

Differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA) were conducted on  $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$  ( $0.1 \le x \le 0.5$ ) SPSed compounds to study their thermal and oxidation properties. The related results are illustrated in Figure 4.11 and Figure 4.12. Thermal analysis using DSC was utilized to study the reactions and formation of Yb<sub>0.25</sub>Co<sub>4-x</sub>Ni<sub>x</sub>Sb<sub>12</sub> as a function of temperature. The as-obtained results reveal that there are two endothermic peaks in the DSC curve, as seen in Figure 4.11. The first small endothermic peak was detected at 800°C, corresponding to the skutterudite phase and the decomposition of the materials. The second endothermic peak was observed near to 945°C, indicating the decomposition process of CoSb<sub>2</sub> secondary phase, of which its presence has been confirmed via SEM analysis Figure 4.3(a) to 4.5(a). The DSC results for all Yb<sub>0.25</sub>Co<sub>4-x</sub>Ni<sub>x</sub>Sb<sub>12</sub> samples suggest that the material is stable up to 800°C. Geng *et al.* (2013) studied La<sub>0.7</sub>Ba<sub>0.01</sub>Ga<sub>0.1</sub>Ti<sub>0.1</sub>Fe<sub>3</sub>CoSb<sub>12</sub> skutterudite and they found that the decomposition peak of the skutterudite phase

Figure 4.12 displays the TGA results for Yb<sub>0.25</sub>Co<sub>4-x</sub>Ni<sub>x</sub>Sb<sub>12</sub> ( $0.1 \le x \le 0.5$ ) samples. The results reveal that the residual moisture was evaporated at 480°C, 482°C and 486°C for Yb<sub>0.25</sub>Co<sub>3.9</sub>Ni<sub>0.1</sub>Sb<sub>12</sub>, Yb<sub>0.25</sub>Co<sub>3.7</sub>Ni<sub>0.3</sub>Sb<sub>12</sub> and Yb<sub>0.25</sub>Co<sub>3.5</sub>Ni<sub>0.5</sub>Sb<sub>12</sub> SPSed samples, respectively. Moreover, a total of three onset temperatures were detected at approximately 645, 830 and 925°C for all samples. The first temperature 645°C could be attributed to the evaporation antimony when exceeding the melting point of antimony (630°C). Subsequently, the following temperatures near to 875 and 930°C can be ascribed predominantly to the decomposition of skutterudite CoSb<sub>3</sub> (874°C) and CoSb<sub>2</sub> (931°C) phases, respectively (Leszczynski *et al.*, 2011). From these results, we found that the secondary phases that appeared on the microstructural images have no significant effect on the stability of the skutterudite materials. Additionally, Yb<sub>0.25</sub>Co<sub>4-x</sub>Ni<sub>x</sub>Sb<sub>12</sub> ( $0.1 \le x \le 0.5$ ) skutterudite thermoelectric material shows great thermal and oxidation stability for higher temperatures above 800 °C.



Figure 4.11: DSC thermographs upon heating of the; (a)  $Yb_{0.25}Co_{3.9}Ni_{0.1}Sb_{12}$ , (b)  $Yb_{0.25}Co_{3.7}Ni_{0.3}Sb_{12}$  and (c)  $Yb_{0.25}Co_{3.5}Ni_{0.5}Sb_{12}$  SPSed samples.



Figure 4.12: TGA thermographs upon heating of the; (a)  $Yb_{0.25}Co_{3.9}Ni_{0.1}Sb_{12}$ , (b)  $Yb_{0.25}Co_{3.7}Ni_{0.3}Sb_{12}$  and (c)  $Yb_{0.25}Co_{3.5}Ni_{0.5}Sb_{12}$  SPSed samples.

### 4.2 Te<sub>x</sub>-addition La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> compositions ( $0 \le x \le 0.5$ )

#### 4.2.1 Microstructure properties

Figure 4.13 demonstrates the XRD patterns of bulk  $La_{0.5}Co_4Sb_{12-x}Te_x$  ( $0 \le x \le 0.5$ ) specimens. It was found that the dominant phase of the skutterudite CoSb<sub>3</sub> (PDF 03-065-1791) structure is the (space group Im-3), whereas CoSb<sub>2</sub> (PDF 03-065-4102) and Sb (PDF 01-065-5920) exist as secondary phases. However, the XRD spectra did not reflect the detection of Te peak after doping, owing to the relatively similar energy of Sb and Te. To provide an in-depth analysis, the lattice parameters of  $La_{0.5}Co_4Sb_{12-x}Te_x$  samples was generated via Rietveld refinement using Jana2006 software at room temperature. The initial input data of the cubic filled skutterudite were assumed to be 2a (0, 0, 0) for the void filler (La atoms), 8c (0.25, 0.25, 0.25) for the metal (Co atoms) and 24g (0, y, z) for pnicogen (Sb and/or Te atoms) (Wojciechowski, 2002).

The crystal lattice of La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample was expanded to 9.0434 Å as compared to the unfilled Co<sub>4</sub>Sb<sub>12</sub> sample which has a lattice of 9.0350 Å. This indicates that the Laaddition has successfully filled the void of Co<sub>4</sub>Sb<sub>12</sub> material. Moreover, the shrinking of the lattice with the addition of Te clearly manifests that the Te-atoms had successfully substituted the Sb-atoms, as illustrated in Figure 4.14. Table 4.3 summarizes the refinement results of the XRD pattern for La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12-x</sub>Te<sub>x</sub> bulk samples. Next, the results of the lattice parameter are interpreted in terms of Te substitution on Sb sites in the skutterudite lattice structure. Te possesses a smaller atomic radius (1.43 Å) as compared to that of Sb (1.61 Å) (Shackelford *et al.*, 2015). The lattice parameter can be considered to be a function of not only atomic radius, but also valence state (Te: 4, 6, – 2 and Sb: 5, 3, – 3) and electron affinity (Te = 190.2 kJ/mol and Sb = 103.2 kJ/mol). The resulting lattice is a result of the interplay between the reduction of atomic radius through the substitution of Te for Sb and simultaneously, the increased electrostatic repulsion by Te.



**Figure 4.13:** XRD pattern of  $La_{0.5}Co_4Sb_{12-x}Te_x$  ( $0 \le x \le 0.5$ ) bulk samples.

Table 4.3: Nominal compositions, actual	compositions,	lattice parameters	and density
for La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>1</sub>	2-xTex bulk san	nples	

Nominal compositions	Actual compositions	Lattice parameter (Å)	Density (%)
CoSb <sub>3</sub> (Wee <i>et al.</i> , 2010)		9.0350	
La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>12</sub>	La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>12</sub>	9.0434 (3)	94 %
La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>11.9</sub> Te <sub>0.1</sub>	La0.52C03.96Sb11.96Te0.096	9.0467 (2)	97 %
La0.5Co4Sb11.7Te0.3	La <sub>0.52</sub> Co <sub>3.91</sub> Sb <sub>11.7</sub> Te <sub>0.3</sub>	9.0419 (1)	96 %
La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>11.5</sub> Te <sub>0.5</sub>	La <sub>0.49</sub> Co <sub>3.99</sub> Sb <sub>11.5</sub> Te <sub>0.5</sub>	9.0456 (1)	90 %



Figure 4.14: Jana Refinement images of (a)  $La_{0.5}Co_4Sb_{12}$ , (b)  $La_{0.5}Co_4Sb_{11.9}Te_{0.1}$ , (c)  $La_{0.5}Co_4Sb_{11.7}Te_{0.3}$  and (d)  $La_{0.5}Co_4Sb_{11.5}Te_{0.5}$  bulk samples.

Figures (4.15 - 4.17) exhibit SEM images of La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12-x</sub>Te<sub>x</sub> bulk samples. The results of the microstructures show that the relative density for all samples were in accordance with the range of theoretical density (90 – 97%), as shown in Table 4.3. In contrast, the SEM image of La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>11.5</sub>Te<sub>0.5</sub> sample confirms its higher porosity than the other samples that were generated via SPS process, as shown in Figure 4.17(a), which it has the lowest density of 90%. The microstructures clearly manifests the major phase of filled skutterudite for all doped samples, whereby small amounts of CoSb<sub>2</sub> and CoSb have been observed as secondary phases. The detailed composition breakdown of

the secondary phases were presented in the respective formulations listed in Table 4.5. Subsequently, EDS analysis was also conducted on the samples to correlate the chemical composition of the bulk skutterudite and secondary phases with the nominal composition obtained from the Rietveld refinement analysis of the XRD data. Points 1 and 2 in Figure 4.15 refer to the bulk skutterudite and secondary phase for the formulation of La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>11.9</sub>Te<sub>0.1</sub>, respectively. EDS data of La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12-x</sub>Te<sub>x</sub> ( $0.1 \le x \le 0.5$ ) bulk samples was extracted from these two points and the individual elemental compositions for each sample are listed in Table 4.4. The same routine was repeated for La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>11.7</sub>Te<sub>0.3</sub> and La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>11.5</sub>Te<sub>0.5</sub> formulations. A comparison of the chemical analysis as obtained from EDS for the three formulations against the nominal compositions are summarized in Table 4.4.

	Atomic percent (%)					
Compound	La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>11.9</sub> Te <sub>0.1</sub>		La0.5C04Sb11.7Te0.3		La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>11.5</sub> Te <sub>0.5</sub>	
Element/Point	1	2	1	2	1	2
Со	32.01	24.75	27.3	22.76	32.62	22.73
Sb	67.68	74.90	72.7	73.98	65.57	65.44
La	0.31	0.36	0	1.85	0	8.63
Te	0	0	0	1.41	1.82	3.19

**Table 4.4:** EDS points of La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12-x</sub>Te<sub>x</sub> ( $0.1 \le x \le 0.5$ ) bulk samples.

**Table 4.5:** The amount of secondary phases of La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12-x</sub>Te<sub>x</sub> ( $0.1 \le x \le 0.5$ ) bulk samples.

Compound	Secondary phase	Secondary phase (%)
La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>11.9</sub> Te <sub>0.1</sub>	CoSb <sub>2</sub>	1.04
La0.5Co4Sb11.7Te0.3	CoSb	0.32
La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>11.5</sub> Te <sub>0.5</sub>	CoSb <sub>2</sub>	0.87



**Figure 4.15:** SEM-EDS images of La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>11.9</sub>Te<sub>0.1</sub>; (a) micrograph and (b-e) the elemental mapping of bulk sample.



**Figure 4.16:** SEM-EDS images of La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>11.7</sub>Te<sub>0.3</sub>; (a) micrograph and (b-e) the elemental mapping of bulk sample.



**Figure 4.17:** SEM-EDS images of La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>11.5</sub>Te<sub>0.5</sub>; (a) micrograph and (b-e) the elemental mapping of bulk sample.

# 4.2.2 Thermoelectric properties

The temperature dependence of electrical resistivity for the  $La_{0.5}Co_4Sb_{12-x}Te_x$  ( $0 \le x \le 0.5$ ) bulk samples are presented in Figure 4.18. The electrical resistivity exhibits a declining trend with increasing Te-doping content fraction. This observation is highly anticipated as Te dopant could act as an electron donor and increase the charge carrier concentration along with increasing Te-doping content fraction, thus resulting in the

reduction of electrical resistivity. However, the electrical resistivity was slightly increased with the increase of temperature for the La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>11.5</sub>Te<sub>0.5</sub> skutterudite sample. For this formulation, there is a direct proportionality between resistivity and temperature, implying a semi-metallic behavior. These results agree well with the investigation by Peng *et al.* (2008) who discovered the electrical resistivity increment of the La<sub>y</sub>Co<sub>4-x</sub>Fe<sub>x</sub>Sb<sub>12</sub> compounds with increasing temperature. However, for x = 0, 0.1 and 0.3 samples, an inverse relationship was observed between the electrical resistivity of the sample and the temperature. This is a typical phenomenon for standard semiconductors. Furthermore, the lowest electrical resistivity in this work is 19.7  $\mu\Omega$ m for the La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>11.5</sub>Te<sub>0.5</sub> formulation can be correlated with the results presented by Duan *et al.* (2012b) who investigated and showed the purely semiconducting behavior for the formulation of Co<sub>4</sub>Sb<sub>12-x-y</sub>Te<sub>x</sub>Se<sub>y</sub>. With the increase of Te content fraction from x = 0.4 to x = 0.6, we have successfully altered the sample into a semi-metal, thus significantly boosting its electrical conductivity.

From the microstructural analysis, the presence of impurities and secondary phases may also result in scattering of electrons and hence modify the resulting electrical conductivity. Therefore, the presence of the secondary phases has been taken into consideration when calculating the resulting electrical conductivity of the sample, in accordance with the equation proposed by (Klemens, 1991);

$$\sigma_1 \approx \sigma_2 (1 + \frac{4f}{3}) \tag{4-4}$$

where  $\sigma_1$  and  $\sigma_2$  are the electrical conductivity of single and two phase material, respectively, and *f* is the volume fraction. Whilst it is impossible to estimate the volume fraction of the secondary phases, we have extrapolated the presence of the secondary phase using image analysis of the SEM micrographs. The details of the secondary phases and their corresponding area fraction are presented in Table 4.5. Based on literature study, the electrical resistivities for CoSb and CoSb<sub>2</sub> are reported in the range of (40.1 – 94.4)  $\mu\Omega$ m and (35 – 45)  $\mu\Omega$ m, respectively (Goto *et al.*, 2015; Penn *et al.*, 1973). Using equation 4.4, the electrical resistivity for a two-phase mixture was calculated. It was confirmed that the secondary phases of the sample has negligible influence on its electrical resistivity.



Figure 4.18: Temperature dependence of electrical resistivity of  $La_{0.5}Co_4Sb_{12-x}Te_x$  (0  $\leq x \leq 0.5$ ) bulk samples.

The Seebeck coefficient and temperature dependence of the La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12-x</sub>Te<sub>x</sub> bulk samples are shown in Figure 4.19. The Seebeck coefficients of all doped samples show a negative sign (n-type) over the entire measured temperature range whereas the Seebeck coefficient of undoped sample shows a positive (p-type). This finding indicates that for doped samples, the main charge carrier is electron and Te atoms have acted as electron donors. The magnitude of the Seebeck coefficient improved with the increase of Te-doping content and temperature, which can be attributed to the presence of

additional free electrons via the addition of Te. Specifically, the maximum absolute Seebeck coefficient for all doped samples, namely  $La_{0.5}Co_4Sb_{11.9}Te_{0.1}$  $La_{0.5}Co_4Sb_{11.7}Te_{0.3}$  and  $La_{0.5}Co_4Sb_{11.5}Te_{0.5}$  were recorded at  $157\mu V/K$  at 355 K, 300µV/K at 404 K and 245µV/K at 550 K, respectively. However, there was a reduction in the absolute Seebeck coefficient for Te = 0.5 sample, in opposition to the increasing trend of Seebeck coefficients for formulations up to Te = 0.3 sample. We interpret this anomaly for Te = 0.5 sample in terms of its semimetallic behavior, in comparison to the semiconducting behaviour of Te = 0.1 and Te = 0.3 samples. It is believed that the density of states for the Te = 0.5 sample has been modified and the electron occupancy at the Fermi level has been reduced, thus resulting in lower Seebeck coefficient for this formulation. The Seebeck coefficient maybe also have a correlation with the secondary phases as seen in table 4.3, which its decreased with increasing the secondary phases for Te = 0.5 sample. Among all of the samples, the highest Seebeck coefficient value was achieved by  $La_{0.5}Co_4Sb_{11.7}Te_{0.3}$  sample (- 300  $\mu$ V/K), which is 142% increment from that of undoped La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample. This finding has demonstrated showing the remarkable improvement in Seebeck coefficient through Te-doping and the introduction of n-type semiconducting behavior. For further reference, the Seebeck values of Co<sub>4</sub>Sb<sub>12</sub> system found in literature such as Co<sub>4</sub>Sb<sub>11.5</sub>Te<sub>0.5</sub> compound was reported to be 273.9 µV/K at a temperature of 610 K (Deng *et al.*, 2009).



Figure 4.19: Temperature dependence of Seebeck coefficient of  $La_{0.5}Co_4Sb_{12-x}Te_x$  ( $0 \le x \le 0.5$ ) bulk samples.

Figure 4.20 displays the temperature dependence of the power factor for bulk  $La_{0.5}Co_4Sb_{12-x}Te_x$  samples, which was calculated from the electrical resistivity and Seebeck coefficient values. The power factor clearly displays an improving trend with the increase of Te fraction content from  $0.13 \times 10^{-3}$  W/mK<sup>2</sup> to  $3.07 \times 10^{-3}$  W/mK<sup>2</sup> at a temperature of 598 K for  $La_{0.5}Co_4Sb_{12}$  and  $La_{0.5}Co_4Sb_{1.5}Te_{0.5}$  samples, respectively. However, the power factor of  $La_{0.5}Co_4Sb_{1.9}Te_{0.1}$  sample did not show any improvement. This is similar to the undoped  $La_{0.5}Co_4Sb_{12}$  sample, which exhibits high resistivity and relatively low absolute Seebeck coefficient values of 315 and 527  $\mu\Omegam$ , and 154 and 105  $\mu$ V/K, respectively at room temperature. Among all of the samples, the maximum power factor value of  $3.07 \times 10^{-3}$  W/mK<sup>2</sup> at 598 K was attained by  $La_{0.5}Co_4Sb_{11.5}Te_{0.5}$  sample. The enhancement of the power factor herein has been achieved via the reduction in electrical resistivity value and moderately high Seebeck coefficient value.


Figure 4.20: Temperature dependence of power factor of  $La_{0.5}Co_4Sb_{12-x}Te_x$  ( $0 \le x \le 0.5$ ) bulk samples.

Figure 4.21(a) presents the variation of the thermal conductivity of La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12-x</sub>Te<sub>x</sub> bulk samples. The total thermal conductivity is the sum of  $k_{tot} = k_e + k_L$ . From the figure, it can be seen the thermal conductivity decreased with increasing the temperature initially, however, it shows an increasing trend in the temperature regime above 600 K. This observation is consistent with the findings of Zhao *et al.* (2012) who studied the formulation Ga<sub>x</sub>Co<sub>4</sub>Sb<sub>11.7</sub>Te<sub>0.3</sub>. They attributed this observation to the bipolar conductivity was observed to gradually increase with the increase of Te-dopant fraction, reaching up to 4.73 W/mK value at 695 K for the Te = 0.5 sample.

A similar work treating the thermal conductivity of a two phase mixture was previously explored by Muta *et al.* (2003) for the formulation as:

$$k_1^{-1} \approx k_2^{-1} (1 + \frac{3f}{2})$$
 (4-5)

where  $k_1$  and  $k_2$  are the thermal conductivity of single and two phase material, respectively, and *f* is the volume fraction. We assumed the thermal conductivities of CoSb<sub>2</sub> phase to be ~ 9 W/mK (Penn *et al.*, 1973). It was found that accommodating the two phase mixture has resulted in a small modification of the thermal conductivity in the range of 0.5 to 1.6%, in which the effect is slightly more enhanced at higher temperatures.

The lattice thermal conductivity was evaluated by subtracting the electronic contribution from the total thermal conductivity. The electronic contribution of the thermal conductivity can be determined via the Wiedemann–Franz law ( $k_e = L \times \sigma \times T$ , where L is Lorenz number). The calculated Lorenz number of the La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12-x</sub>Te<sub>x</sub> samples as the function of temperature dependence can be calculated using Equations (4.1 – 4.3). By using the extracted reduced Fermi energy, the Lorenz numbers are calculated to be  $1.89 \times 10^{-8}$ ,  $1.72 \times 10^{-8}$ ,  $1.54 \times 10^{-8}$ , and  $1.60 \times 10^{-8} \text{ V}^2/\text{K}^2$  for proportion of x = 0, 0.1, 0.3 and 0.5, respectively, near room temperature. The calculated Lorenz number are smaller compared with the degenerate limit of Lorenz number ( $2.44 \times 10^{-8} \text{ V}^2/\text{K}^2$ ) which is typically observed in thermoelectric materials with carrier concentration between generate and non-degenerate semiconductor (Kim *et al.*, 2015). On another note, the results of the lattice thermal conductivity can be seen in Figure 4.21(b).

The magnitude of the thermal conductivity was comparable for La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub>, La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>11.9</sub>Te<sub>0.1</sub>, La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>11.7</sub>Te<sub>0.3</sub>, La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>11.5</sub>Te<sub>0.5</sub> samples. This can be mainly

attributed to the effect of La as the rattle atom in the void system. In addition, the smaller lanthanide ions may have an effective potential to increase the phononscattering which is reduced the lattice thermal conductivity ( $k_L$ ), and significantly improved the *ZT*. The lattice thermal conductivity for heavy La-filled skutterudite La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample is 2.25 W/mK, which is much lower than the binary CoSb<sub>3</sub> sample of ~ 10 W/mK at room temperature (Chubilleau *et al.*, 2013). This is in good agreement with the previous study of Park *et al.* (2014a) which reported that the lattice thermal conductivity of Co<sub>4</sub>Sb<sub>12</sub> sample was significantly reduced from 8.8 W/mK to 4.5 W/mK for La<sub>0.4</sub>Co<sub>4</sub>Sb<sub>12</sub> sample at room temperature, owing to the phonon scattering phenomenon by the rattling of La filler inside the voids of the skutterudite structure.

For higher temperatures above 650K, the strong dependence of the overall thermal conductivity on the lattice thermal conductivity, coupled with the fact that electrical conductivity is improved through Te addition, indicates that the addition of Te to  $La_{0.5}Co_4Sb_{12}$  is a useful strategy to simultaneously achieve high electrical conductivity and improved *ZT*.



**Figure 4.21:** Temperature dependence of (a) thermal conductivity and (b) lattice thermal conductivity of SPSed La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12-x</sub>Te<sub>x</sub> ( $0 \le x \le 0.5$ ) samples.

The dimensionless figure of merit *ZT* for the  $La_{0.5}Co_4Sb_{12-x}Te_x$  bulk samples is displayed in Figure 4.22 as a function of temperature. The results indicate that from 600 K to 792 K, the lowest electrical resistivity coupled with high Seebeck coefficient have the ability to improve the *ZT* value.  $La_{0.5}Co_4Sb_{11.5}Te_{0.5}$  reached the peak value of *ZT* = 0.47 at 792 K, which is greater than that of undoped  $La_{0.5}Co_4Sb_{12}$  sample, i.e. 0.04 at 550 K. The maximum value of *ZT* for La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>11.5</sub>Te<sub>0.5</sub> sample can be explained in terms of its semimetallic characteristic, which resulted in significantly higher thermal conductivity, as compared to Te addition at lower percentage. On the other hand, its Seebeck coefficient has reduced whereas the thermal conductivity has increased due to the increased number of charge carriers introduced by Te, resulting in a moderate overall *ZT*. Te addition is a useful strategy for identifying the optimal formulation of La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12-x</sub>Te<sub>x</sub>, which optimizes its electrical conductivity, whilst avoiding the disadvantages of reduced Seebeck coefficient and increased the thermal conductivity. Hence, the optimum Te doping range lies between x = 0.3 to x = 0.5, at the boundary between the semiconducting and semimetallic properties of the formulation.



Figure 4.22: Temperature dependence of figure of merit, ZT of  $La_{0.5}Co_4Sb_{12-x}Te_x$  (0  $\leq x \leq 0.5$ ) bulk samples.

# 4.2.3 Oxidation and thermal behaviors

A combination of two techniques of differential scanning calorimetry and thermogravimetry analysis (DSC–TGA) were carried out on to comprehensively study the thermal and oxidation properties of La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12-x</sub>Te<sub>x</sub> ( $0.1 \le x \le 0.5$ ) materials. The results of DSC and TGA were illustrated in Figure 4.23 and Figure 4.24, respectively. The thermal analysis using DSC was utilized to study the reactions and formation of  $La_{0.5}Co_4Sb_{12-x}Te_x$  as a function of temperature. The measurement reveals that there are two endothermic peaks on the DSC curve. The first small endothermic peak occurred at 880°C. 840°C for  $La_{0.5}Co_4Sb_{11.9}Te_{0.1}$ ,  $La_{0.5}Co_4Sb_{11.7}Te_{0.3}$ and 800°C and La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>11.5</sub>Te<sub>0.5</sub> samples, respectively, indicates the occurrence of skutterudite phase decomposition. Moreover, the decomposition temperatures were observed to decrease with increasing Sb secondary phase (as detected by XRD) because of it is low melting temperature of 630°C. The second endothermic peak was observed at approximately 945°C, which reflects the CoSb<sub>2</sub> secondary phase for most samples as seen in Figure 4.15(a) and 4.17(a). The DSC results show that all La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12-x</sub>Te<sub>x</sub> samples are stable up to  $800^{\circ}$ C.

Figure 4.24 presents the TGA results for La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12-x</sub>Te<sub>x</sub> ( $0.1 \le x \le 0.5$ ) samples. The results reveal that there was residual moisture being removed at 520°C, 550°C and 525°C for La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>11.9</sub>Te<sub>0.1</sub>, La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>11.7</sub>Te<sub>0.3</sub> and La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>11.5</sub>Te<sub>0.5</sub> samples, respectively. Furthermore, a total of three onset temperatures were detected at approximately 745°C, 880°C and 945°C for most samples. The first temperature 745°C could be attributed to antimony evaporation when exceeding the melting point of antimony (630°C), as seen from its small peak in XRD. Thereafter, the following temperatures near to 880°C and 945°C can be ascribed mainly to the decomposition of skutterudite CoSb<sub>3</sub> (874°C) and CoSb<sub>2</sub> (931°C) phases, respectively (Leszczynski *et al.*, 2011). From these results, we found that the secondary phases that appeared on the microstructural images have no significant effect on the stability of the skutterudite materials. Moreover, La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12-x</sub>Te<sub>x</sub> ( $0.1 \le x \le 0.5$ ) skutterudite thermoelectric material shows great thermal and oxidation stability at high temperature above 800°C.



Figure 4.23: DSC thermographs upon heating of the (a)  $La_{0.5}Co_4Sb_{11.9}Te_{0.1}$ , (b)  $La_{0.5}Co_4Sb_{11.7}Te_{0.3}$  and (c)  $La_{0.5}Co_4Sb_{11.5}Te_{0.5}$  sintered samples.



Figure 4.24: TGA thermographs upon heating of the (a)  $La_{0.5}Co_4Sb_{11.9}Te_{0.1}$ , (b)  $La_{0.5}Co_4Sb_{11.7}Te_{0.3}$  and (c)  $La_{0.5}Co_4Sb_{11.5}Te_{0.5}$  sintered samples.

### 4.3 In<sub>x</sub>-addition La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> compositions ( $0 \le x \le 0.3$ )

## 4.3.1 Microstructure properties

Figure 4.25 illustrates the XRD patterns of  $In_xLa_{0.5}Co_4Sb_{12}$  ( $0 \le x \le 0.3$ ) samples after the SPS process. In-addition into  $La_{0.5}Co_4Sb_{12}$  system is expected to act as filler, thus reducing the thermal conductivity. The results showed that the major phase of the skutterudite  $CoSb_3$  (PDF 03-065-1791) structure corresponds to the Im-3 space group. However, there are few impurity peaks of InSb (PDF 00-019-0579) and  $CoSb_2$  (PDF 03-065-4102) were detected as secondary phases. All of the In-addition bulk samples possessed the minor peaks of InSb phase. These results indicated the existence of the InSb secondary phase during the SPS process, the maximum In-filling limit fraction is 1.37 a.t.% (x = 0.22) according to Mallik *et al.* (2009). The peak of InSb phase increased with increasing In-addition fraction content. Moreover, a small amount of impurity peak of  $CoSb_2$  phase appeared in all bulk samples had decreased with increase in In-addition. Rietveld refinement analysis of XRD pattern was performed on SPSed samples, the proposed structure of  $In_xLa_{0.5}Co_4Sb_{12}$  ( $0 \le x \le 0.3$ ) compounds are presented in Figure 4.26.

The initial input data of the cubic filled skutterudite structure was assumed to be 2a (0, 0, 0) for the void filler (La and/or In atoms), 8c (0.25, 0.25, 0.25) for the metal (Co atoms) and 24g (0, y, z) for pnicogen (Sb atoms) (Wojciechowski, 2002). The Rietveld analysis shows the voids double-filled with In and La atoms. The occupancy of the filler atoms increases up to x = 0.3, and lead to an increase in lattice expansion. However, when x > 0.3, the lattice constant reduces along with the reduction of occupancy of filler atom. This can be ascribed to the electrostatic repulsion between the In atom and the lattice upon further loading of In (Shi *et al.*, 2005), where the electronegativity of an In and SB atom are 1.7 and 1.9, respectively (Kim *et al.*, 2013b). Thus, the results are in good agreements with the previous observations on the limit of filling in crystal voids

(Ballikaya *et al.*, 2011; Kim *et al.*, 2013b; Li *et al.*, 2009). Table 4.6 presents the nominal compositions, actual compositions, density and lattice parameters after SPS of  $In_xLa_{0.5}Co_4Sb_{12}$  samples.



**Figure 4.25:** XRD pattern of  $In_x La_{0.5}Co_4Sb_{12}$  ( $0 \le x \le 0.3$ ) sintered samples.

Nominal	Actual	Lattice	Density (%)		
composition	composition	parameters (Å)			
CoSb <sub>3</sub> (Wee <i>et al.</i> , 2010)		9.0350			
$La_{0.5}Co_4Sb_{12}$	La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>12</sub>	9.0433 (3)	94 %		
$In_{0.1}La_{0.5}Co_4Sb_{12}$	$In_{0.1}La_{0.5}Co_4Sb_{12}$	9.0588 (4)	96.4 %		
$In_{0.2}La_{0.5}Co_4Sb_{12}$	$In_{0.2}La_{0.5}Co_4Sb_{12}$	9.0678 (4)	95.9 %		
$In_{0.3}La_{0.5}Co_4Sb_{12}$	$In_{0.3}La_{0.5}Co_4Sb_{12}$	9.0615 (5)	97 %		

**Table 4.6:** Nominal composition, actual composition, the lattice parameters and density of In<sub>x</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> samples (determined by Jana)



Figure 4.26: Jana Refinement images of the (a)  $La_{0.5}Co_4Sb_{12}$ , (b)  $In_{0.1}La_{0.5}Co_4Sb_{12}$ , (c)  $In_{0.2}La_{0.5}Co_4Sb_{12}$  and (d)  $In_{0.3}La_{0.5}Co_4Sb_{12}$  sintered samples.

Figure 4.27(a), Figure 4.28(a) and Figure 4.29(a) show the surface topography of  $In_{0.1}La_{0.5}Co_4Sb_{12}$ ,  $In_{0.2}La_{0.5}Co_4Sb_{12}$  and  $In_{0.3}La_{0.5}Co_4Sb_{12}$  samples, respectively. The result of the microstructures showed that all of the SPSed samples are of very high density which is in the range of 96 – 97% as compared to theoretical density value as shown in Table 4.6. The microstructure image of  $In_{0.2}La_{0.5}Co_4Sb_{12}$  sample shows abundant of black spots which had lowered the density of about 95.9 % as compared to the other samples that were generated in the SPS process. The scanning electron microscope and energy-dispersive X-ray spectroscopy (SEM-EDS) results show the

main phase of skutterudite CoSb<sub>3</sub> for all bulk samples with a small amount of secondary phases containing both CoSb<sub>2</sub> and CoSb. SEM images indicated that the same compounds were presented in most of the bulk samples, which is represented by the dark grains in the microstructural images. Numerous small grains had observed in  $In_{0.1}La_{0.5}Co_4Sb_{12}$  sample (Figure 4.27(a)) as compared to the other samples. These small grains are the CoSb<sub>2</sub> phase and its decreased with increasing In-addition, which had agreed well with the XRD results. The results of EDS and mapping shows that Inelement was homogeneously distributed in the matrix for In<sub>0.1</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample, and the slight La-element was detected and distributed randomly within the matrix as observed in the EDS of  $In_{0.1}La_{0.5}Co_4Sb_{12}$  bulk sample. Furthermore, Figure 4.28(a) illustrates the SEM image of In<sub>0.2</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample, some dark grains were observed which can relate to the secondary phase of CoSb<sub>2</sub>. The In-element was homogeneously distributed in the grains and grain boundaries for In<sub>0.2</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample and a slight amount of In was concentrated along the grain boundaries by EDS mapping. Besides that, random distribution of the La-element was also detected in the matrix of In<sub>0.2</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample. Furthermore, the EDS results showed that In was homogeneously distributed in the grains and grain boundaries for In<sub>0.3</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample, and the larger dark grains correspond to the secondary phase of CoSb compound. Agglomeration of La-element was observed matrix mapping of In<sub>0.3</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample. Additionally, the EDS points for all SPSed samples were tabulated in Table 4.7.

	Atomic percent (%)							
Compound	Ino.1Lao.5Co4Sb12		Ino.2Lao.5Co4Sb12			Ino.3Lao.5Co4Sb12		
Element/Point	1	2	1	2	3	1	2	3
Со	22.14	31.42	21.87	32.12	19.9	22.87	19.92	44.47
Sb	72.51	67.6	72.06	67.69	68.95	72.58	75.07	55.53
La	4.5	0.81	3.98	0	9.37	2.88	3.10	0
In	0.86 0.17		2.09	0.19	1.78	1.67	1.91	0
							0	

Table 4.7: EDS points of In<sub>x</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sintered samples.



**Figure 4.27:** SEM-EDS images of In<sub>0.1</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub>; (a) micrograph and (b-e) the elemental mapping of sintered sample.



**Figure 4.28:** SEM-EDS images of In<sub>0.2</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub>; (a) micrograph and (b-e) the elemental mapping of sintered sample.



**Figure 4.29:** SEM-EDS images of In<sub>0.3</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub>; (a) micrograph and (b-e) the elemental mapping of sintered sample.

# 4.3.2 Thermoelectric properties

The temperature dependences of the electrical resistivity for  $In_xLa_{0.5}Co_4Sb_{12}$  bulk samples were illustrated in Figure 4.30, in which the inset shows a magnified graph. It was found that a substantial reduction in electrical resistivity occurred with the increase of In fraction content. The reduction in the electrical resistivity of the sample can be ascribed to the increase of charge carriers through In-addition. Moreover, the electrical resistivity of In<sub>0.2</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> and In<sub>0.3</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> samples shows a slight increment with increasing temperature, indicating the metal-like behavior of the sample. This phenomenon can be mainly caused by the shift of Fermi level and the increase of electron concentration through In-addition, which is in good agreement with a similar study carried out by Mallik *et al.* (2008) on In<sub>x</sub>Co<sub>4</sub>Sb<sub>12</sub> samples. Furthermore, the lowest electrical resistivity at room temperature (10.5  $\mu\Omegam$ ) was accomplished by In<sub>0.2</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample. This occurs mainly due to the influence of impurities such as InSb, which probably has relatively high electrical conductivity (Mallik *et al.*, 2009). These results are lower than that obtained by He *et al.* (2006), which recorded an electrical resistivity of ~ 12  $\mu\Omegam$  for In<sub>0.2</sub>SCo<sub>4</sub>Sb<sub>12</sub> sample at same temperature and ~ 15.4  $\mu\Omegam$  for In<sub>0.1</sub>Yb<sub>0.2</sub>Co<sub>4</sub>Sb<sub>12</sub> and In<sub>0.1</sub>Yb<sub>0.1</sub>La<sub>0.1</sub>Co<sub>4</sub>Sb<sub>12</sub> samples at 850 K (Lee *et al.*, 2012). However, for x = 0.3 sample electrical resistivity showed to increased due to increased CoSb and CoSb<sub>2</sub> phases as show in SEM images, which they have high electrical resistivities as mentioned above.



**Figure 4.30:** Temperature dependence of electrical resistivity of  $In_xLa_{0.5}Co_4Sb_{12}$  ( $0 \le x \le 0.3$ ) sintered samples; The insert enlarges the section of electrical resistivity at low values (5 to 30  $\mu\Omega$ m).

Figure 4.31 presents Seebeck coefficient as a function of temperature dependence of In<sub>x</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sintered samples. The results indicate that upon In-addition, the  $In_xLa_{0.5}Co_4Sb_{12}$  skutterudite changed from p-type to n-type, thus implying that the Inelement has acted as an electron donor in the skutterudite structure. These results have been confirmed from previous studies (Bao et al., 2006; Peng et al., 2008; Song et al., 2005). Specifically, In 2005, Song et al. (2005) studied La-filled skutterudites,  $La_vFeCo_3Sb_{12}$  which were prepared by mechanical alloving and hot pressing. The Seebeck coefficient results changed from p-type for (La = 0.2 - 0.6) samples to n-type for (La = 0.9) sample, respectively. In the following year, Liu *et al.* (2006) studied the partial filling of La in Co<sub>4</sub>Sb<sub>12</sub> skutterudite. Similarly, the results of Seebeck coefficient showed a p-type behavior for (La = 0.1 - 0.5) samples and changed to n-type for (La = 0.1 - 0.5)(0.7 - 2) samples, suggesting that the materials were indeed semiconducting. These findings were in agreement with our current work, which shows that (La = 0.5) sample remained as a p-type material. However, upon introduction of In, the semiconducting behavior of the sample changed from p-type to n-type, due to the presence of excessive electrons introduced by In-element. In particular, the absolute Seebeck coefficient showed significant improvement after In-addition, reaching a maximum value of 270µV/K at 548 K for In<sub>0.1</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample with low In content. InSb phase is highly conducted whilst lead to reduce the Seebeck coefficient with increasing In filling fraction. Generally, the Seebeck coefficient of a thermoelectric material is inversely proportional to its electrical conductivity.



Figure 4.31: Temperature dependence of Seebeck coefficient of  $In_xLa_{0.5}Co_4Sb_{12}$  ( $0 \le x \le 0.3$ ) sintered samples.

The power factors for  $In_xLa_{0.5}Co_4Sb_{12}$  bulk samples were calculated from the electrical resistivity and Seebeck coefficient values obtained from temperature dependence study, as shown in Figure 4.32. Apparently, the power factor of the sample increased with both In-element fraction content and temperature, owing to the reduction of electrical resistivity and the enhancement of Seebeck coefficient. Particularly, the maximum value of power factor  $(3.39 \times 10^{-3} \text{ W/mK}^2)$  was attained by  $In_{0.3}La_{0.5}Co_4Sb_{12}$  sample at a temperature of 644 K. This result is significantly higher than that of  $In_{0.3}Co_4Sb_{12}$  sample which achieved ~  $0.2 \times 10^{-3} \text{ W/mK}^2$  at the same temperature (Deng *et al.*, 2011b). The improvement in the power factor observed herein can be attributed to the reduction in electrical resistivity of the samples and the increase of Seebeck coefficient via the addition of In into the La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> material.



Figure 4.32: Temperature dependence of power factor of  $In_xLa_{0.5}Co_4Sb_{12}$  ( $0 \le x \le 0.3$ ) sintered samples.

Figure 4.33(a) shows the temperature dependence of thermal conductivity of the  $In_xLa_{0.5}Co_4Sb_{12}$  samples. It was found that at room temperature, the thermal conductivity of the sample was noticeably reduced after In-addition. Specifically,  $In_{0.3}La_{0.5}Co_4Sb_{12}$  sample exhibits the lowest thermal conductivity (1.81 W/mK) attained at a temperature of 499 K, which was relatively low as compared to the thermal conductivity of  $In_{0.3}Co_4Sb_{12}$  sample (3.8 W/mK) at the same temperature (Li *et al.*, 2012). This finding implies that the In-atom is immensely effective in reducing the thermal conductivity of  $La_{0.5}Co_4Sb_{12}$  material. On the other hand, Figure 4.33(b) presents the lattice thermal conductivity of  $In_xLa_{0.5}Co_4Sb_{12}$  samples as a function of temperature, which was estimated by subtracting the electronic contribution from the total thermal conductivity using Wiedemann–Franz law ( $k_e = L \times \sigma \times T$ ), whereby L represents Lorenz number. The calculated Lorenz number as the function of temperature dependence for  $In_xLa_{0.5}Co_4Sb_{12}$  samples were calculated using Equations (4.1 – 4.3). By

using the extracted reduced Fermi energy, the Lorenz numbers are calculated to be 1.89  $\times 10^{-8}$ ,  $1.58 \times 10^{-8}$ ,  $1.72 \times 10^{-8}$ , and  $1.65 \times 10^{-8} \text{ V}^2/\text{K}^2$  for proportion of x = 0, 0.1, 0.2 and 0.3, respectively, near room temperature. The calculated Lorenz number are smaller in comparison with the degenerate limit of Lorenz number  $(2.44 \times 10^{-8} \text{ V}^2/\text{K}^2)$ , which is typically observed in thermoelectric materials which exhibit carrier concentration between generate and non-degenerate semiconductor (Kim et al., 2015). From Figure 4.33(b), a significant reduction is observed in the lattice thermal conductivity of the sample with increasing In-addition fraction content. The lowest lattice thermal conductivity (1.18 W/mK) was attained by In<sub>0.2</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample at a temperature of 644 K. The lattice thermal conductivity of In<sub>0.2</sub>Co<sub>4</sub>Sb<sub>12</sub> system reported herein is much lower than that reported by Li et al. (2012) (3.75 W/mK) and Wang et al. (2009) (~ 2.2 W/mK) at approximately same temperature. This phenomenon is likely to arise from the increase of phonon scattering with increasing amount of In below the limit fraction (x << 0.22). Moreover, La and In atoms which functions as electron donors in Co<sub>4</sub>Sb<sub>12</sub> structure has in turn, led to the increment of carrier concentration of the sample. As a result, the electronic contribution to the total thermal conductivity has increased to as high as ~ 63 % for (x = 0.2) sample at a temperature of 644 K.



Figure 4.33: Temperature dependence of (a) thermal conductivity and (b) lattice thermal conductivity of  $In_xLa_{0.5}Co_4Sb_{12}$  ( $0 \le x \le 0.3$ ) sintered samples.

Finally, the ZT for  $In_xLa_{0.5}Co_4Sb_{12}$  bulk samples was studied as a function of temperature (Figure 4.34). As perceived from the figure, the ZT values of the sample show substantial improvement with increasing In fraction content and temperature,

arising from the significantly reduced electrical resistivity and lattice thermal conductivity of the sample. The maximum value of ZT = 1.15 was achieved by In<sub>0.3</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample at a temperature of 692 K, a remarkable 98% improvement from that of In-free La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample (ZT = 0.022) at same temperature. As a comparison, the ZT value obtained herein is considerably higher than that obtained in the study of Deng *et al.* (2011b) and Li *et al.* (2012), which reported  $ZT \sim 0.03$  and ZT= 0.66 for In<sub>0.3</sub>Co<sub>4</sub>Sb<sub>12</sub> sample at ~ 615 K, respectively. Other studies on skutterudites reported widely diversified ZT values for Co<sub>4</sub>Sb<sub>12</sub> sample at various temperature, including ZT = 0.67 for In<sub>0.35</sub>Co<sub>4</sub>Sb<sub>12</sub> sample at 600 K (Li *et al.*, 2012), ZT = 1.12 for In<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> sample at 650 K (Mallik *et al.*, 2008) and ZT = 1.13 for In<sub>0.15</sub>Ba<sub>0.075</sub>Co<sub>0.075</sub>Co<sub>4</sub>Sb<sub>12</sub> sample at ~ 750 K (Kim *et al.* 2013b). In addition, a significant 57% improvement of ZT was recorded by In-filled La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> system as compared to Ni-doped Yb<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> system.



**Figure 4.34:** Temperature dependence of *ZT* of  $In_xLa_{0.5}Co_4Sb_{12}$  ( $0 \le x \le 0.3$ ) sintered samples.

# **4.3.3** Oxidation and thermal behaviors

Differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA) results for  $In_xLa_{0.5}Co_4Sb_{12}$  ( $0 \le x \le 0.3$ ) sintered samples are illustrated in Figure 4.35 and Figure 4.36 to investigate their thermal and oxidation properties, respectively. Thermal analysis using DSC was utilized to study the influence of temperature on the formation  $In_xLa_{0.5}Co_4Sb_{12}$  and the measurements reveal the presence of two endothermic peaks in the DSC curve for all samples. The first endothermic peak observed at 880°C indicates the decomposition of skutterudite phase whereas the second endothermic peak observed at approximately 945°C can be related to the presence of CoSb<sub>2</sub> secondary phase, as discussed previously in XRD and SEM analysis previously.



**Figure 4.35:** DSC thermographs upon heating of the (a)  $La_{0.5}Co_4Sb_{12}$ , (b)  $In_{0.1}La_{0.5}Co_4Sb_{12}$ , (c)  $In_{0.2}La_{0.5}Co_4Sb_{12}$  and (b)  $In_{0.3}La_{0.5}Co_4Sb_{12}$  sintered samples.

Figure 4.36 depicts the TGA results for  $In_xLa_{0.5}Co_4Sb_{12}$  ( $0 \le x \le 0.3$ ) sintered samples. The results indicate that the materials are stable, in which two onset temperatures were identified at approximately 885°C and 945°C for most of the samples. The first temperature near to 885°C could be attributed mainly to the decomposition of skutterudite CoSb<sub>3</sub> phase when exceeding the melting point of (876°C) (Ikeda *et al.*, 2015). Subsequently, the following temperature near to 945°C can be ascribed mainly to the decomposition of CoSb<sub>2</sub> (931°C) phase (Leszczynski *et al.*, 2011). From these results, it was found that the presence of secondary phases detected in the microstructural images of the sample has no significant effect on the stability of skutterudite materials. Moreover,  $In_xLa_{0.5}Co_4Sb_{12}$  ( $0 \le x \le 0.3$ ) skutterudite thermoelectric material exhibits great thermal and oxidation stability in excessively high temperature regime (above 880°C).



**Figure 4.36:** TGA thermographs upon heating of the (a)  $La_{0.5}Co_4Sb_{12}$ , (b)  $In_{0.1}La_{0.5}Co_4Sb_{12}$ , (c)  $La_{0.2}Co_4Sb_{12}$  and (d)  $In_{0.3}La_{0.5}Co_4Sb_{12}$  sintered samples.

## 4.4 Inx-addition La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> compositions ( $0 \le x \le 0.5$ )

## 4.4.1 Microstructure properties

The XRD patterns of  $In_x La_{0.25} Co_4 Sb_{12}$  SPSed samples were presented in Figure 4.37. In-addition into La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> system is expected to act as filler, thus reducing the thermal conductivity. The results has confirmed that all of the samples were dominated by CoSb<sub>3</sub> structure of skutterudite phase with the space group of Im-3 (PDF 03-065-1791), which was successfully prepared via MA and SPS. The trace impurities detected in the spectra can be attributed to the tiny presence of secondary phases in the samples, mainly InSb (PDF 00-019-0579) and CoSb<sub>2</sub> (PDF 03-065-4102). InSb phase was detected in most of the filled samples, except In<sub>0.1</sub>La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> sample. The InSb impurity phase starts to appear for In<sub>0.3</sub>La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> sample which indicates the limit of indium filling into the voids of the skutterudite structure. The formation of InSb secondary phase originates from the SPS condition process, and also the addition of Infilling above the maximum filling limit of 1.37 at.% (x = 0.22), as reported by Mallik *et* al. (2009). On the other hand, the CoSb<sub>2</sub> phase was found to appear in all of the samples, however, its detection decreased drastically with increasing In-filling fraction content. In some cases, CoSb<sub>2</sub> peak overlapped with InSb peak. Rietveld refinement analysis of XRD pattern was applied to all SPSed samples. The initial input data of the cubic filled skutterudite were assumed to be 2a (0, 0, 0) for the void filler (La and/or In atoms), 8c (0.25, 0.25, 0.25) for the metal (Co atoms) and 24g (0, y, z) for pnicogen (Sb atoms), respectively (Wojciechowski, 2002). The lattice parameters show obvious increment after In-filling, suggesting that the In atoms has filled up the skutterudite voids, as seen in Figure 4.38. Table 4.8 summarizes the fundamental information on the refined lattice parameters, nominal compositions, actual compositions and density for all SPSed samples at room temperature.



Figure 4.37: XRD pattern of  $In_x La_{0.25}Co_4Sb_{12}$  ( $0 \le x \le 0.5$ ) SPSed samples.

Table 4.8: Nominal compositions, actual compositions, latt	ttice parameters and density
In <sub>x</sub> La <sub>0.25</sub> Co <sub>4</sub> Sb <sub>12</sub> SPSed samples.	3.

Nominal composition	Actual compositions	Lattice parameter (Å)	Density (%)
CoSb <sub>3</sub> (Wee <i>et al.</i> , 2010)		9.0350	
La <sub>0.25</sub> Co <sub>4</sub> Sb <sub>12</sub>	La <sub>0.25</sub> Co <sub>4</sub> Sb <sub>12</sub>	9.0411 (3)	97 %
In <sub>0.1</sub> La <sub>0.25</sub> Co <sub>4</sub> Sb <sub>12</sub>	$In_{0.1}La_{0.25}Co_4Sb_{12}$	9.0453 (3)	95 %
$In_{0.3}La_{0.25}Co_4Sb_{12}$	$In_{0.3}La_{0.25}Co_4Sb_{12}$	9.0580 (2)	97 %
$In_{0.5}La_{0.25}Co_4Sb_{12}$	$In_{0.5}La_{0.25}Co_4Sb_{12}$	9.0574 (2)	99 %



Figure 4.38: Jana Refinement images of (a)  $La_{0.25}Co_4Sb_{12}$ , (b)  $In_{0.1}La_{0.25}Co_4Sb_{12}$ , (c)  $In_{0.3}La_{0.25}Co_4Sb_{12}$  and (d)  $In_{0.5}La_{0.25}Co_4Sb_{12}$  SPSed samples.

Figures 4.39(a) – 4.41(a) display the SEM micrographs of  $In_xLa_{0.25}Co_4Sb_{12}$  (0.1  $\leq x \leq$  0.5) SPSed samples. The microstructural results show that all filled samples have a relatively high density (in the range of 95% – 99% of theoretical density), as tabulated in Table 4.8. The microstructural image shows some pores in the  $In_{0.1}La_{0.25}Co_4Sb_{12}$  sample, which was observed to have the lowest density of 95% that was generated during SPS process. The SEM–EDS results show the main phase of skutterudite CoSb<sub>3</sub> for all SPSed samples with small amount of secondary phases, namely CoSb<sub>2</sub> and CoSb.

Specifically, the detection of CoSb<sub>2</sub> phase decreased with increasing In-addition and this finding agrees well with previous XRD results. Moreover, the CoSb<sub>2</sub> phase was also detected by EDS on In<sub>0.1</sub>La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> sample. The EDS result of In<sub>0.3</sub>La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> sample detected a tiny amount of CoSb as secondary phase. Furthermore, EDS results reflect that the In-filler was homogeneously distributed in the grains and grain boundaries of In<sub>0.5</sub>La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> sample, accompanied by the presence of a small amount of CoSb as secondary phase. The EDS analysis outcomes for all SPSed samples have been summarized in Table 4.9. The elemental mapping results clearly demonstrate that In-element was randomly distributed in the sample and a slight amount of In appeared in the grains and grain boundaries of all Consolidated samples. Additionally, the presence of agglomerated La-element in the matrix of all SPSed samples has also been confirmed by elemental mapping analysis.

	Atomic percent (%)								
Compound	In0.1La0.25C04Sb12			In0.3La0.25C04Sb12			In0.5La0.25Co4Sb12		
Element/Point	1	2	3	1	2	3	1	2	3
Со	21.06	16.07	32	22.74	42.22	18.61	22.30	34.58	9.18
Sb	69.17	55.29	68	70.91	57.56	51.59	71.39	64.14	59.08
La	6.55	15.9	0	2.28	0	15.57	2.72	0	0.99
In	3.22	12.74	0	3.97	0.21	14.23	3.60	1.28	30.76
<b>S</b>									

**Table 4.9:** EDS points of In<sub>x</sub>La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub>SPSed samples.



**Figure 4.39:** SEM-EDS images of In<sub>0.1</sub>La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub>; (a) micrograph and (b-e) the elemental mapping of SPSed sample.



**Figure 4.40:** SEM-EDS images of In<sub>0.3</sub>La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub>; (a) micrograph and (b-e) the elemental mapping of SPSed sample.



**Figure 4.41:** SEM-EDS images of In<sub>0.5</sub>La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub>; (a) micrograph and (b-e) the elemental mapping of SPSed sample.

# 4.4.2 Thermoelectric properties

Figure 4.42 displays the temperature dependence of the electrical resistivity for SPSed samples of  $In_xLa_{0.25}Co_4Sb_{12}$  ( $0 \le x \le 0.5$ ). The result of electrical resistivity shows a clear trend, there is a rapid decrease of electrical resistivity with increasing Infilling fraction at room temperature. Moreover, the electrical resistivity of the sample

was observed to be decreasing with the increase of temperature of In<sub>0.1</sub>La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> sample which possesses a semiconducting transport behavior, but in In<sub>0.3</sub>La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> and In<sub>0.5</sub>La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> samples, the electrical resistivity were observed to be increased with increase in temperature, which shows that it has a metallic conduction behavior. This occurrence is likely due to the presence of In impurities of present and the secondary phase of InSb as shown by XRD and EDS results, which shows they have an essential impact on improving the electrical conductivity. The lowest electrical resistivity at room temperature was achieved by In<sub>0.5</sub>La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> sample (9.67  $\mu\Omega$ m), mainly due to the presence of InSb phase which is relatively higher conductivity, as discussed in section 4.3.2. This result is superior than that achieved by In<sub>0.2</sub>Co<sub>4</sub>Sb<sub>11.2</sub>Te<sub>0.8</sub> compound (~ 9  $\mu\Omega$ m) at same temperature (Jung *et al.*, 2010).



**Figure 4.42:** Temperature dependence of electrical resistivity for  $In_xLa_{0.25}Co_4Sb_{12}$  ( $0 \le x \le 0.5$ ) SPSed samples; The insert enlarges the section of electrical resistivity at low values (0 to 100  $\mu\Omega$ m).

The temperature dependence of Seebeck coefficient for In<sub>x</sub>La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> SPSed samples are presented in Figure 4.43. The results of all In-filled samples exhibits a negative sign (n-type) of the Seebeck coefficients over the entire measured temperature range, indicating that the majority of charge carriers in the samples are electron, as opposed to the In-free La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> sample which exhibits a positive sign (p-type). These result indirectly reveals that the In-atoms has acted as electron donors, which agrees well with the findings of Liu et al. (2006). It was also found with increasing La fraction content in La<sub>x</sub>Co<sub>4</sub>Sb<sub>12</sub> from 0.1 to 0.5, the Seebeck coefficient shows p-type semiconducting material behavior. The magnitude of the Seebeck coefficients were inversely proportional to the electrical conductivity of the In-filled skutterudites. With increasing In-filling content at room temperature, the absolute Seebeck coefficient decreased whereas the electrical conductivity increased, mainly due to increase of the electron carrier concentrations. This is because In and La-filling contributes additional electrons to the conduction band of  $In_xLa_{0.25}Co_4Sb_{12}$  sample. At x = 0.3 and x = 0.5, the Seebeck coefficient of the sample increased gradually with temperature. On the contrary, at x = 0.1, it reached a maximum value over measured samples was 252  $\mu$ V/K at 495 K, which is higher than that reported by Mallik et al. (2009) ~ 205  $\mu$ V/K at 673 K for In<sub>0.4</sub>Co<sub>4</sub>Sb<sub>12</sub> compound. InSb phase is highly conducted whilst lead to reduce the Seebeck coefficient with increasing In filling fraction. Generally, the Seebeck coefficient of a thermoelectric material is inversely proportional to its electrical conductivity.



Figure 4.43: Temperature dependence of Seebeck coefficient for  $In_xLa_{0.25}Co_4Sb_{12}$  ( $0 \le x \le 0.5$ ) SPSed samples.

The power factors were estimated from the electrical resistivity and Seebeck coefficient values, as plotted in Figure 4.44. The power factor was remarkably improved with increasing In-element fraction content, and simultaneously, it became higher with the temperature rising to the maximum peak. The highest power factor  $(3.85 \times 10^{-3} \text{ W/mK}^2)$  was obtained by In<sub>0.5</sub>La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> sample at a temperature of 543 K, which is relatively higher than that reported by II-Ho *et al.* (2010a). In their study, was ~ 3.5 × 10<sup>-3</sup> W/mK<sup>2</sup> has been obtained for In<sub>0.25</sub>Co<sub>3.9</sub>La<sub>0.1</sub>Sb<sub>12</sub> compound at 600 K, and that obtained by Lee *et al.* (2012) was ~ 3.2 × 10<sup>-3</sup> W/mK<sup>2</sup> for In<sub>0.1</sub>Yb<sub>0.1</sub>La<sub>0.1</sub>Co<sub>4</sub>Sb<sub>12</sub> compound. The InSb impurity maybe the reason for the enhancement of the power factor, which in turn contributes to the reduction of electrical resistivity.



Figure 4.44: Temperature dependence of power factor for  $In_xLa_{0.25}Co_4Sb_{12}$  ( $0 \le x \le 0.5$ ) SPSed samples.

Figure 4.45(a) presents the variation of thermal conductivity (*k*) of the  $In_xLa_{0.25}Co_4Sb_{12}$  SPSed samples at different temperature. Generally, the thermal conductivity of the sample was reduced after In-filling, but it rose slightly for (x = 0.3) sample. For all of the samples, the thermal conductivity reduced marginally with increasing temperature. Particularly, the lowest thermal conductivity value of 1.27 W/mK was attained by  $In_{0.1}La_{0.25}Co_4Sb_{12}$  sample at 495K, which was observed to be much lower in comparison with that of  $In_{0.05}Co_4Sb_{12}$  compound (~ 1.6 W/mK) attained at 580 K (He *et al.*, 2006). In addition,  $In_{0.1}La_{0.25}Co_4Sb_{12}$  sample exhibits the lowest density among all of the samples, thus contributing to the reduction of thermal conductivity. This result correlates well with the reported findings of Yang *et al.* (2004).

The lattice thermal conductivity of the sample was obtained by subtracting the electronic contribution from the overall thermal conductivity. The electronic thermal conductivity is calculated via Wiedemann–Franz law ( $k_e = L \times \sigma \times T$ , whereby L
represents Lorenz number). The calculated Lorenz number as the function of temperature dependence of the In<sub>x</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> samples was calculated using Equations (4.1 - 4.3). By using the extracted reduced Fermi energy, the Lorenz numbers were calculated to be (2.08, 1.61, 1.62 and 1.67)  $\times 10^{-8} \text{ V}^2/\text{K}^2$  for proportion of x = 0, 0.1, 0.3 and 0.5, respectively, near room temperature. In general, the calculated Lorenz numbers are smaller than the degenerate limit of Lorenz number  $(2.44 \times 10^{-8} \text{ V}^2/\text{K}^2)$  that is typically observed in thermoelectric materials with carrier concentrations between generate and non-degenerate semiconductor (Kim et al., 2015). Concurrently, the lattice thermal conductivity  $(k_L)$  for In<sub>x</sub>La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> compounds was studied as a function of temperature, as displayed in Figure 4.45(b). As a result of In-addition, the values of  $k_L$ were greatly reduced, reflecting that the lattice parameters of the sample were expanded after In-addition. This phenomenon could be attributed to the occupation of In-element into the voids in the skutterudite, which accounted for the reduced lattice thermal conductivity observed herein. The lowest lattice thermal conductivity value of 1.23W/mK was achieved by In<sub>0.5</sub>La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> compound at 639 K and in comparison, it is considerably lower than that of In<sub>0.35</sub>Co<sub>4</sub>Sb<sub>12</sub> compound, which recorded a conductivity of 2.86 W/mK at 550 K (Li et al., 2012). Besides, Jung et al. (2010) also reported an approximately conductivity of ~ 2.6 W/mK for In<sub>0.25</sub>Co<sub>4</sub>Sb<sub>11.9</sub>Te<sub>0.1</sub> compound at room temperature.



Figure 4.45: Temperature dependence of (a) thermal conductivity and (b) lattice thermal conductivity of  $In_xLa_{0.25}Co_4Sb_{12}$  ( $0 \le x \le 0.5$ ) SPSed samples.

Figure 4.46 illustrates the temperature dependence of the thermoelectric dimensionless figure of merit (*ZT*) of  $In_xLa_{0.25}Co_4Sb_{12}$  SPSed samples. From the figure, it can be observed that *ZT* values were considerably enhanced with increasing In-filling fraction content and temperature, owing to the substantial reduction in lattice thermal

conductivity. The maximum value of *ZT* (1.25) was recorded by In<sub>0.5</sub>La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> sample at a temperature of 688 K, which is significantly higher than that of In-free La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> sample. As a comparison, the obtained *ZT* value in this study is relatively higher than that attained by In<sub>0.1</sub>Co<sub>4</sub>Sb<sub>12</sub> (*ZT* = 0.79 at 643 K) and In<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> composition (~ 1.2 at 573 K) in the study of Wang *et al.* (2009) and He *et al.* (2006), respectively. From here, it can be inferred that InSb phase is a key factor in the maximization of *ZT*. Therefore, In-filled skutterudites with La partially filler seems to exhibit remarkably enhanced thermoelectric properties and electrical resistivity, which renders them a superior material in thermoelectric applications in medium temperature regime. Furthermore, the improvement of *ZT* in In-filled La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> system is approximately 8% higher than that of In-filled La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> system.



Figure 4.46: Temperature dependence of dimensionless figure of merit for  $In_xLa_{0.25}Co_4Sb_{12}$  ( $0 \le x \le 0.5$ ) SPSed samples.

# 4.4.3 Oxidation and thermal behaviors

As illustrated in Figure 4.47 and Figure 4.48, differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA) are conducted to study the thermal and oxidation properties of  $In_xLa_{0.25}Co_4Sb_{12}$  ( $0 \le x \le 0.5$ ) SPSed samples. For further elucidation, thermal analysis via DSC technique was utilized to study the influence of temperature on the formation of  $In_xLa_{0.25}Co_4Sb_{12}$ . The measurement reveals that there are two endothermic peaks in the DSC curve for all of the samples. The first endothermic peak was observed at 847°C, corresponding to the decomposition of skutterudite phase. Meanwhile, the second endothermic peak which was observed near 958°C arises from the decomposition process of CoSb<sub>2</sub> phase, as supported by previous XRD and SEM analysis. The obtained DSC results for all of the  $In_xLa_{0.25}Co_4Sb_{12}$  samples indicate that the material is stable up to as high as 847°C.



Figure 4.47: DSC thermographs upon heating of the (a)  $La_{0.25}Co_4Sb_{12}$ , (b)  $In_{0.1}La_{0.25}Co_4Sb_{12}$ , (c)  $In_{0.3}La_{0.25}Co_4Sb_{12}$  and (d)  $In_{0.5}La_{0.25}Co_4Sb_{12}$  SPSed samples.

Figure 4.48 represents the TGA results for  $La_{0.25}Co_4Sb_{12}$ ,  $In_{0.1}La_{0.25}Co_4Sb_{12}$ ,  $In_{0.3}La_{0.25}Co_4Sb_{12}$  and  $In_{0.5}La_{0.25}Co_4Sb_{12}$  samples. The results show the detection of two onset temperatures at approximately 885°C and 950°C for most of the samples. The first temperature 885°C could be primarily attributed to the decomposition of skutterudite CoSb<sub>3</sub> phase when exceeding the melting point of (876°C) (Ikeda *et al.*, 2015). The following temperature near to 950°C can be ascribed mainly to the decomposition of CoSb<sub>2</sub> secondary phase when exceeding the melting point of (931°C) (Leszczynski *et al.*, 2011). From these results, it can be noticed that the secondary phases detected from the microstructural images have no significant influence on the stability of the skutterudite materials, which agrees well with the DSC analysis outcomes. Simultaneously, the DSC and TGA results also demonstrate that the  $In_xLa_{0.25}Co_4Sb_{12}$  samples have a great stability up to 840 °C.



Figure 4.48: TGA thermographs upon heating of the (a)  $La_{0.25}Co_4Sb_{12}$ , (b)  $In_{0.1}La_{0.25}Co_4Sb_{12}$ , (c)  $In_{0.3}La_{0.25}Co_4Sb_{12}$  and (d)  $In_{0.5}La_{0.25}Co_4Sb_{12}$  SPSed samples.

## 4.5 Al<sub>x</sub>-addition La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> compositions ( $0 \le x \le 0.5$ )

#### 4.5.1 Microstructure properties

Figure 4.49 presents the XRD patterns of La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> compacted specimens with different Al additions. Al-addition into La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> system is expected to act as filler, thus reducing the thermal conductivity. The XRD patterns demonstrate that all of the Al-added SPSed samples displayed main phase of CoSb<sub>3</sub> skutterudite (PDF 03-065-1791) structure with Im-3 as space group. Furthermore, all of the Al<sub>x</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> ( $0 \le x$  $\leq$  0.5) compounds synthesized via MA and SPS methods exhibit minor amount of secondary phases, namely CoSb<sub>2</sub> (PDF 03-065-4102) and Al (PDF 00-004-0787) except for Al<sub>0.05</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample which contains only a single phase of CoSb<sub>3</sub> skutterudite. However, CoSb<sub>2</sub> phase was found to decrease with increasing Al-filling fraction content (x) from 0.1 to 0.5. Noticeably, a subtle peak of Al-phase was only detected at x = 0.5. indicating that the fraction amount of Al-filler has exceeded the filling limit. In addition, Rietveld refinement analysis of XRD patterns were performed on all specimens using Jana2006 software. The initial input data of the cubic filled skutterudite were assumed to be 2a (0, 0, 0) for void filler (La and/or Al atoms), 8c (0.25, 0.25, 0.25) for metal (Co atoms) and 24g (0, y, z) for pnicogen (Sb atoms) (Wojciechowski, 2002). The results of the refinement analysis reveal that the lattice parameters were increased after Al filling, as shown in Table 4.10. Furthermore, Table 4.10 also contains information concerning the nominal compositions, actual compositions and density of the sample at room temperature. The expansion of the lattice parameters suggests that the Aluminum has occupied the skutterudite void-site, as illustrated in Figure 4.50.



**Figure 4.49:** XRD pattern of  $Al_xLa_{0.5}Co_4Sb_{12}$  ( $0 \le x \le 0.5$ ) samples.

 Table 4.10: Nominal compositions, actual compositions, lattice parameters and density of Al<sub>x</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> SPSed samples

Nominal composition	Actual composition	Lattice parameter (Å)	Density (%)	
CoSb <sub>3</sub> (Wee <i>et al.</i> , 2010)		9.0350		
La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>12</sub>	La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>12</sub>	9.0434 (3)	94 %	
$Al_{0.05}La_{0.5}Co_4Sb_{12}$	$Al_{0.05}La_{0.5}Co_4Sb_{12}$	9.0591 (3)	93 %	
Al <sub>0.1</sub> La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>12</sub>	Al <sub>0.1</sub> La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>12</sub>	9.0584 (3)	89 %	
Al <sub>0.3</sub> La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>12</sub>	Al <sub>0.3</sub> La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>12</sub>	9.0591 (3)	79 %	
Al <sub>0.5</sub> La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>12</sub>	Al <sub>0.5</sub> La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>12</sub>	9.0524 (3)	88%	



**Figure 4.50:** Jana Refinement images of (a) Al<sub>0.05</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub>, (b) Al<sub>0.1</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub>, (c) Al<sub>0.3</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> and (d) Al<sub>0.5</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> SPSed samples.

Figures 4.51(a) - 4.54(a) display the SEM micrographs of  $Al_xLa_{0.5}Co_4Sb_{12}$  bulk samples. The microstructural results show that most of the samples are relatively high dense, typically in the range of 88 - 94% of the theoretical density. SEM was used to study the microstructures of the sintered pellets and the results show that the microstructure contains numerous pores that were generated during the SPS process, which is in good agreement with the variation of density. Besides, the microstructural images also confirms that CoSb<sub>3</sub> skutterudite exists as the major phase for all of the samples whereas a small amount of CoSb was detected by EDS as secondary phase in most of the samples. For Al<sub>0.05</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample, the SEM results illustrated in Figure 4.51(a) did not show any detection of secondary phases whereas EDS analysis reveals that Al-element was homogeneously distributed in the matrix, as seen from Figure 4.51(b) - (e). Simultaneously, the EDS mapping of Al<sub>0.05</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample reveals the abundancy of Al-element at the grain boundaries. Figure 4.52(a) illustrates SEM results for Al<sub>0.1</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample that reveals the presence of small dark grains in its microstructure, which can be associated with the CoSb phase. The elemental mapping also shows the homogeneous distribution of Al-element in the grains and the grain boundaries, as seen in Figure 4.52(b) - (e). Apparently, from EDS characterization, it can be noticed that the distribution of Al-element was concentrated at the grain boundaries. Next, Figure 4.53(a) displays the SEM results for Al<sub>0.3</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample. Interestingly, SEM-EDS characterization did not detect any secondary phase. Nevertheless, the elemental mapping confirms the homogeneous distribution of Alelement in the matrix. Similarly, the EDS results show more concentration of Al at the grain boundaries. Subsequently, Figure 4.54(a) depicts the SEM results for Al<sub>0.5</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample, in which CoSb exists as secondary phase in the sample. The elemental mapping analysis for this particular sample reveals that the Al-elements have undergone slight agglomeration and exhibit random distribution. Comparatively, the distribution of Al-element in Al<sub>0.5</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample is more heavily concentrated at the grain boundaries than the rest, arising from the excessive Al-addition which breaks the Al-filling limit in the compound. In the case of La-addition, the elemental mapping analysis also shows the random distribution and certain agglomeration of La-element at the grains and grain boundaries for most of the samples. The dark grains of CoSb phase decreased with increasing Al-addition. Additionally, the findings from SEM and EDS characterization correlates well with previous XRD analysis results. It can be confirmed that the Al-element has partially filled the skutterudite bulk material. The detailed

information for all SPSed samples extracted from EDS characterization have been summarized in table 4.11.

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	Atomic percent (%)										
Compound	Al <sub>0.05</sub> La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>12</sub>		Al <sub>0.1</sub> La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>12</sub>			Al <sub>0.3</sub> La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>12</sub>			Al <sub>0.5</sub> La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>12</sub>		
Element/Point	1	2	1	2	3	1	2	3	1	2	3
Со	22.89	22.6	23.72	20.31	47.56	22.48	24.14	18.65	14.71	18.94	47.78
Sb	74.12	73.99	75.82	69.69	52.44	73.53	70.24	66.72	67.46	70.94	51.83
La	2.47	2.21	0.46	4.91	0	2.26	2.11	6.62	10.24	5.13	0
Al	0.51	1.2	0	5.09	0	1.73	3.51	8.01	7.59	5.02	0.39

# **Table 4.11:** EDS points of Al<sub>x</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> SPSed samples.

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**Figure 4.51:** SEM-EDS images of Al<sub>0.05</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub>; (a) micrograph and (b-e) the elemental mapping of SPSed sample.



**Figure 4.52:** SEM-EDS images of Al<sub>0.1</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub>; (a) micrograph and (b-e) the elemental mapping of SPSed sample.



**Figure 4.53:** SEM-EDS images of Al<sub>0.3</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub>; (a) micrograph and (b-e) the elemental mapping of SPSed sample.



**Figure 4.54:** SEM-EDS images of Al<sub>0.5</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub>; (a) micrograph and (b-e) the elemental mapping of SPSed sample.

## 4.5.2 Thermoelectric properties

Figure 4.55 depicts the temperature dependence of electrical resistivity for  $Al_xLa_{0.5}Co_4Sb_{12}$  ( $0 \le x \le 0.5$ ) SPSed bulk compounds. The results demonstrates that there was a substantial reduction in electrical resistivity of the compound after the Aladdition. However, the electrical resistivity slightly rose back at excessively high Alfilling fraction content. Therefore, the electrical resistivity fluctuates based on Al-filling fraction content. On another note, the electrical resistivity shows relatively weaker dependency on temperature, in which there was a tiny rise of temperature after Alfilling while displaying a metal-like behavior. In this study, it was found that the electrical resistivity of the sample reduced most significantly at low Al-filling fraction content. Particularly, Al<sub>0.05</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample which has a high density (93%) (low porosity) and constituted by a single phase of skutterudite recorded the lowest electrical resistivity, i.e. 7  $\mu\Omega m$  at room temperature. On the contrary, Al<sub>0.3</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample which has the lowest density (79%) (high porosity) exhibits relatively higher electrical resistivity, i.e. 15  $\mu\Omega m$  at same temperature. This result agrees well with the study carried out by Yang et al. (2004) which reported higher electrical resistivity for La<sub>0.75</sub>Fe<sub>3</sub>CoSb<sub>12</sub> compound, i.e. ~ 7.2  $\mu\Omega m$  and ~ 17  $\mu\Omega m$  at room temperature for sample with the lowest and highest porosities, respectively. Lee et al. (2012) also obtained higher resistivity value for  $In_{0.1}Yb_{0.1}La_{0.1}Co_4Sb_{12}$  compound, i.e. ~ 15.4  $\mu\Omega m$ at 850 K.



**Figure 4.55:** Temperature dependence of electrical resistivity for  $Al_xLa_{0.5}Co_4Sb_{12}$  ( $0 \le x \le 0.5$ ) samples; The insert enlarges the section of electrical resistivity at low values (0 to  $20 \ \mu\Omega m$ ).

The temperature dependence of Seebeck coefficient for  $Al_xLa_{0.5}Co_4Sb_{12}$  ( $0 \le x \le 0.5$ ) bulk samples are illustrated in Figure 4.56. It can been seen that all samples displayed a negative sign (n-type) thermoelectric material behavior over the entire measured temperature range after Al-filling. This observation suggests that electrons make up the majority of charge carrier and Al atoms has acted as electron donors in the system. Contrarily, the Al-free  $La_{0.5}Co_4Sb_{12}$  sample shows a positive sign (p-type) thermoelectric material behavior, indicating that the dominant charge carriers are holes. This result is in good agreement with the findings of Liu *et al.* (2006), which reported that the Seebeck coefficient results shows a positive sign (p-type) semiconducting materials with increasing La content from 0.1 to 0.5 in  $La_xCo_4Sb_{12}$  system. Furthermore, the results of Seebeck coefficient were further enhanced through Al-addition. The absolute Seebeck shows a decrement in value with increasing Al-filling, arising from the donation of additional electrons by Al-atoms which resulted in the increase of

carrier concentration. Moreover, the Seebeck coefficients of all samples demonstrate a visible increasing trend with increasing temperature. At room temperature, the Seebeck coefficient was observed to increase from – 138  $\mu$ V/K with a high density to – 112 $\mu$ V/K for Al<sub>0.05</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> and Al<sub>0.3</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> samples with low density, respectively. This result also agrees well with the findings of Yang *et al.* (2004), which reported that the Seebeck coefficient for La<sub>0.75</sub>Fe<sub>3</sub>CoSb<sub>12</sub> compound increased from ~ 80  $\mu$ V/K to ~ 90  $\mu$ V/K for samples with the lowest and highest porosities, respectively at the same temperature. This phenomenon was found to arise from the decreasing number of carrier mobility and carrier concentrations. In this study, Al<sub>0.05</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> specimen possessed the highest absolute Seebeck coefficient of 193  $\mu$ V/K at a temperature of 789 K, which is marginally lower than literature findings, i.e. 222  $\mu$ V/K at 527 K for La<sub>0.1</sub>Co<sub>4</sub>Sb<sub>12</sub> specimen (Park *et al.*, 2014a) and 202.6  $\mu$ V/K at 573 K for La<sub>0.7</sub>Co<sub>4</sub>Sb<sub>12</sub> specimen (Liu *et al.*, 2006). However, after x = 0.05 the Seebeck coefficient values decreased maybe doe to the appearance of the secondary phases detected via XRD and SEM.



Figure 4.56: Temperature dependence of Seebeck coefficient for  $Al_xLa_{0.5}Co_4Sb_{12}$  ( $0 \le x \le 0.5$ ) samples.

Figure 4.57 presents the temperature dependence of the power factor for compacted  $Al_xLa_{0.5}Co_4Sb_{12}$  samples, in which the power factor is calculated using the Seebeck coefficient and electrical resistivity values. The power factor was obviously improved after Al-filling, however, it appeared to be decreasing with Al-filling fraction content. Besides that, the increment of power factor was also driven by the increase of temperature. Among all of the samples,  $Al_{0.05}La_{0.5}Co_4Sb_{12}$  sample possessed the highest power factor of  $4.02 \times 10^{-3}$  W/mK<sup>2</sup> that was attained at a temperature of 789 K. This result is much higher than the power factor reported for  $La_{0.9}Co_4Sb_{12}$  (Liu *et al.*, 2006) and  $La_{0.75}Fe_3Cob_{12}$  composition (Yang *et al.*, 2004), i.e. ~  $2.8 \times 10^{-3}$  W/mK<sup>2</sup> at 773 K and  $2.2 \times 10^{-3}$  W/mK<sup>2</sup> at 723 K, respectively. The improvement of power factor originates from the significant reduction of electrical resistivity which subsequently leads to the enhancement of the dimensionless figure of merit *ZT*.



Figure 4.57: Temperature dependence of power factor for  $Al_xLa_{0.5}Co_4Sb_{12}$  ( $0 \le x \le 0.5$ ) samples.

The variation of thermal conductivity as a function of temperature for  $Al_xLa_{0.5}Co_4Sb_{12}$  compositions is presented in Figure 4.58(a). The thermal conductivity was remarkably suppressed with increasing Al-filling content. Conversely, at x = 0.5, the thermal conductivity increased slightly with increasing temperature for most of the samples. The lowest value of thermal conductivity was achieved by  $Al_{0.3}La_{0.5}Co_4Sb_{12}$  sample which recorded 1.1 W/mK at room temperature. It should be noted that  $Al_{0.3}La_{0.5}Co_4Sb_{12}$  sample has the lowest density (73%), high porosity and therefore, capable of increasing phonon scattering via pores, leading to the least value of thermal conductivity. This result is in good agreement with the study of Yang *et al.* (2004), which reported a thermal conductivity of 1.48 W/mK at 300 K for La<sub>0.75</sub>Fe<sub>3</sub>CoSb<sub>12</sub> specimen with the highest porosity.  $Al_{0.5}La_{0.5}Co_4Sb_{12}$  sample exhibits the highest thermal conductivity at room temperature because of the appearance of Al-phase which is highly conductive.

The lattice thermal conductivity was obtained by subtracting the electronic contribution from the overall thermal conductivity. The electronic thermal conductivity is calculated through the Wiedemann–Franz law ( $k_e = L \times \sigma \times T$ , where L represents Lorenz number). The calculated Lorenz number of the Al<sub>x</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> samples can be calculated using Equations (4.1 - 4.3). By using the extracted reduced Fermi energy, the Lorenz numbers are calculated to be  $1.89 \times 10^{-8}$ ,  $1.76 \times 10^{-8}$ ,  $1.85 \times 10^{-8}$ ,  $1.86 \times 10^{-8}$ , and  $1.80 \times 10^{-8} \text{ V}^2/\text{K}^2$  for proportion of x = 0, 0.05, 0.1, 0.3 and 0.5, respectively, near room temperature. The calculated Lorenz number are smaller than the degenerate limit of Lorenz number (2.44  $\times$  10<sup>-8</sup> V<sup>2</sup>/K<sup>2</sup>), which is typically observed in thermoelectric materials with carrier concentration between generate and non-degenerate semiconductor (Kim et al., 2015). Additionally, Figure 4.58(b) interprets the lattice thermal conductivity  $(k_L)$  as a function of temperature for Al<sub>x</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> samples. The lattice thermal conductivity was dramatically reduced due to the increasing Al-filling fraction at room temperature. However, in the case of Al<sub>0.5</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample, the lattice thermal conductivity only increased partially. On another note, the lattice thermal conductivity of all of the samples reduced with increasing temperature. In particular, the lowest lattice thermal conductivity was accomplished by Al<sub>0.3</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> compound, i.e. 0.64 W/mK, at a temperature of 595 K.



**Figure 4.58:** Temperature dependence of (a) thermal conductivity and (b) lattice thermal conductivity of  $Al_xLa_{0.5}Co_4Sb_{12}$  ( $0 \le x \le 0.5$ ) samples.

Finally, Figure 4.59 demonstrates the temperature dependence of the dimensionless figure of merit, ZT for Al<sub>x</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> SPSed samples. The result reveals that the ZT value was considerably increased with Al-filling and it appears to be on monotonically increasing trend with increasing temperature up to a maximum temperature limit. When

exceeding the limit, the *ZT* value begins to reduce with increasing Al-filling fraction content. Among all of the samples,  $Al_{0.05}La_{0.5}Co_4Sb_{12}$  sample which exhibits a single phase of skutterudite CoSb<sub>3</sub> structure recorded the highest *ZT* value, i.e. 1.36 at a temperature 789 K. This result is much higher than the *ZT* values previously reported for La<sub>0.2</sub>Co<sub>4</sub>Sb<sub>12</sub> composition (Park *et al.*, 2014a) and La<sub>0.5</sub>Ce<sub>0.5</sub>Fe<sub>3</sub>CoSb<sub>12</sub> composition (Lu *et al.*, 2010), i.e. 0.35 in the temperature range from 623 to 823 K and 0.82 at 773 K, respectively. In addition, the improvement of *ZT* in Al-filled La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> system is more than 8% higher as compared to the In-filled La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> system.



Figure 4.59: Temperature dependence of dimensionless figure of merit for  $Al_xLa_{0.5}Co_4Sb_{12}$  ( $0 \le x \le 0.5$ ) samples.

# 4.5.3 Oxidation and thermal behaviors

Differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA) results were conducted to investigate the thermal and oxidation properties for  $Al_xLa_{0.5}Co_4Sb_{12}$  (0.05  $\leq x \leq$  0.5) sintered samples, as illustrated in Figure 4.60 and Figure 4.61. The analysis using DSC was utilized to study the reactions and influence of

temperature on the formation of  $Al_xLa_{0.5}Co_4Sb_{12}$ . The measurement reveals that there are two endothermic peaks in the DSC curve for all of the samples. The first small endothermic peak was detected near 845°C for all of the samples, corresponding to the decomposition of skutterudite phase. The second endothermic peak was observed near 945°C, which identified the decomposition process of CoSb<sub>2</sub> phase, as confirmed via XRD and SEM analysis. The DSC results for  $Al_xLa_{0.5}Co_4Sb_{12}$  samples show that the material is stable up to a temperature as high as 845°C.



**Figure 4.60:** DSC thermographs of the (a) Al<sub>0.05</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub>, (b) Al<sub>0.1</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub>, (c) Al<sub>0.3</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> and (d) Al<sub>0.5</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> samples.

Figures 4.61(a)-(d) represents the distinctive TGA results for  $Al_{0.05}La_{0.5}Co_4Sb_{12}$ ,  $Al_{0.1}La_{0.5}Co_4Sb_{12}$ ,  $Al_{0.3}La_{0.5}Co_4Sb_{12}$  and  $Al_{0.5}La_{0.5}Co_4Sb_{12}$  samples. The results of  $Al_{0.05}La_{0.5}Co_4Sb_{12}$  sample reveal that there are clear two onset temperatures detected at approximately 890°C and 950°C. The first temperature 890°C could be attributed

mainly to the decomposition of skutterudite  $CoSb_3$  phase when exceeding the melting point of 876°C (Ikeda *et al.*, 2015). The following temperature near to 950°C can be ascribed mainly to the decomposition of  $CoSb_2$  secondary phase when the temperature exceeded the melting point of 931°C (Leszczynski *et al.*, 2011).

For Al<sub>0.3</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub>, Al<sub>0.3</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> and Al<sub>0.5</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> samples, a total of four onset temperatures were detected at approximately 525°C, 715°C, 880°C and 945°C for most of the samples. The first temperature 525°C reveals the presence of residual impurities such as moisture which were not removed from the samples. The second temperature 715°C could be attributed to aluminum evaporation when exceeding the melting point of antimony (660°C). Subsequently, the following temperatures near to 880°C and 945°C can be ascribed mainly to the decomposition of skutterudite CoSb<sub>3</sub> (874°C) and CoSb<sub>2</sub> (931°C) phases, respectively (Leszczynski *et al.*, 2011). From these results, it can be confirmed that the secondary phases existed on the microstructural images with no significant effect on the stability of the skutterudite materials. The combinatorial results of these two techniques (TGA-DSC) demonstrate that the Al<sub>x</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> skutterudite thermoelectric materials have a great stability in high temperature regime up to 800°C.



Figure 4.61: TGA thermographs upon heating of the (a)  $Al_{0.05}La_{0.5}Co_4Sb_{12}$ , (b)  $Al_{0.1}La_{0.5}Co_4Sb_{12}$ , (c)  $Al_{0.3}La_{0.5}Co_4Sb_{12}$  and (d)  $Al_{0.5}La_{0.5}Co_4Sb_{12}$  samples.

#### **CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS**

### 5.1 Conclusions

In conclusions of this thesis, we formulate five groups of skutterudite materials namely, Te<sub>x</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12-x</sub>, Ni<sub>x</sub>Yb<sub>0.25</sub>Co<sub>4-x</sub>Sb<sub>12</sub>, In<sub>x</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub>, In<sub>x</sub>La<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> and Al<sub>x</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> skutterudite. The formulation materials were successfully synthesized via mechanical alloying method followed by spark plasma sintering techniques. XRD and SEM-EDS analysis of all samples have successfully identified the major phase and secondary phases of the CoSb<sub>3</sub> skutterudite structure. The results of thermoelectric properties obtained are summarized for the five groups as follows:

- 1. The electrical resistivity for all five groups was drastically reduced due to improving the carrier concentration, and minimized to 7.6  $\mu\Omega$ m at room temperature for Al<sub>0.05</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample.
- 2. Seebeck coefficient was significantly enhanced, and the highest absolute Seebeck coefficient (300  $\mu$ V/K) was recorded for La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>11.7</sub>Te<sub>0.3</sub> sample at 404 K. This due to the optimum carrier concentration and high carriers' effective mass.
- 3. The thermal conductivity and lattice thermal conductivity were considerably reduced, which can be attributed to the improved phonon scattering phenomenon. The lowest thermal conductivity (1.1 W/mK) was recorded for Al<sub>0.3</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample at room temperature. At a temperature of 789 K, a great increment in the figure of merit (*ZT*) was observed in Al<sub>0.05</sub>La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> sample, which peaked at the value of 1.36.

Summarily, the addition of Al and In fillers into  $La_xCo_4Sb_{12}$  systems provides a pathway to improve the overall thermoelectric performance of skutterudites materials through significant enhancement in the power factor and substantial reduction in the lattice thermal conductivity. Additionally, the thermal and oxidation analysis results

have demonstrated that the skutterudites materials prepared in the studies exhibit great stability at high temperature regime, up to as high as 800°C.

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No	Compound	Exp. density (g/cm <sup>3</sup> )	Th. density (g/cm <sup>3</sup> )	$ \rho_{min} (\mu \Omega m) $	S <sub>max</sub> (µV/K)	P.F <sub>max</sub> (10 <sup>-3</sup> × W/K <sup>2</sup> m)	Ktot,min (W/mK)	K <sub>Lmin</sub> (W/mK)	ZT <sub>max</sub>
1	$La_{0.5}Co_4Sb_{12}$	7.42	7.93	36@ 792 K	130@ 501 K	0.13@ 598 K	1.95@ 402 K	1.9@ 499 K	0.037@ 596 K
2	Al <sub>0.05</sub> La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>12</sub>	7.38	7.93	7 @ 314 K	-193@ 789 K	4.02@ 789 K	1.95@ 314 K	0.26@ 789 K	1.36@ 789 K
3	$Al_{0.1}La_{0.5}Co_4Sb_{12}$	7.02	7.9	8 @ 314 K	-175@ 789 K	2.4@ 643 K	1.69@ 314 K	0.57@ 643 K	0.87@ 789 K
4	$Al_{0.3}La_{0.5}Co_4Sb_{12}$	6.24	7.93	15 @ 314 K	-174@ 789 K	1.54@ 789 K	1.1 @ 314 K	0.4@ 643 K	0.86@ 789 K
5	$Al_{0.5}La_{0.5}Co_4Sb_{12}$	6.84	7.78	14 @ 314 K	-190@ 789 K	2.09@ 740 K	2.22@ 314 K	1.17@ 789 K	0.71@ 789 K
6	$La_{0.25}Co_4Sb_{12}$	7.535	7.78	42.1 @ 789 K	124 @ 495 K	0.14@ 591 K	1.98 @ 495 K	1.92@ 400 K	0.04@ 591 K
7	$In_{0.1}La_{0.25}Co_4Sb_{12}$	7.43	7.82	36.5 @ 789 K	-252@ 495 K	1.09 @ 543 K	1.27 @ 495 K	1.07@ 495 K	0.44@ 543 K
8	In <sub>0.3</sub> La <sub>0.25</sub> Co <sub>4</sub> Sb <sub>12</sub>	7.66	7.89	17.5 @ 400 K	▶ -243@ 688 K	3.2 @ 591 K	1.98 @ 495 K	1.29@ 543 K	0.94@ 639 K
9	In <sub>0.5</sub> La <sub>0.25</sub> Co <sub>4</sub> Sb <sub>12</sub>	7.88	7.995	9.7 @ 314 K	-231@ 688 K	3.85 @ 543 K	1.92 @ 495 K	0.83@ 639 K	1.25@ 789 K
10	$In_{0.1}La_{0.5}Co_4Sb_{12}$	7.65	7.94	25.8@ 792 K	-270@ 548 K	2.71@ 596 K	1.91@ 402 K	1.47@ 499 K	0.78@ 688 K
11	$In_{0.2}La_{0.5}Co_4Sb_{12}$	7.64	7.97	10.5@ 314 K	-203@ 741 K	3.19@ 644 K	1.90@ 402 K	0.78@ 644 K	1.05@ 789 K
12	$In_{0.3}La_{0.5}Co_4Sb_{12}$	7.8	8.037	13.1@ 314 K	-229@ 692 K	3.39@ 644 K	1.81@ 402 K	0.81@ 644 K	1.15@ 692 K
13	La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>11.9</sub> Te <sub>0.1</sub>	7.72	7.92	42@ 792 K	-157@ 355 K	0.12@ 453 K	2.1@ 501 K	2.2@ 598 K	0.03@ 453 K
14	La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>11.7</sub> Te <sub>0.3</sub>	7.59	7.92	34@ 792 K	-300@ 404 K	1.51@ 501 K	2.21@ 501 K	2.0@ 501 K	0.39@ 598 K

 Table 5.1: Summary of TE analysis results for all samples

15	La <sub>0.5</sub> Co <sub>4</sub> Sb <sub>11.5</sub> Te <sub>0.5</sub>	7.13	7.93	19.7@ 501 K	-250@ 598 K	3.07@ 598 K	3.02@ 313 K	2.65@ 313 K	0.47@ 792 K	
16	Yb <sub>0.25</sub> Co <sub>4</sub> Sb <sub>12</sub>	7.75	7.82	36.1@ 789 K	211@ 402 K	0.44@ 547 K	2.53@ 314 K	2.4@ 498 K	0.09@ 547 K	
17	Yb <sub>0.25</sub> Co <sub>3.9</sub> Ni <sub>0.1</sub> Sb <sub>12</sub>	7.54	7.81	16.1@ 789 K	-174@ 498 K	1.12@ 498 K	2.91@ 498 K	2.47@ 498 K	0.19@ 547 K	
18	Yb <sub>0.25</sub> Co <sub>3.7</sub> Ni <sub>0.3</sub> Sb <sub>12</sub>	7.52	7.82	18.4@ 789 K	-223@ 595 K	2.41@ 595 K	2.92@ 498 K	2.30@ 595 K	0.49 @ 692 K	
19	Yb <sub>0.25</sub> Co <sub>3.5</sub> Ni <sub>0.5</sub> Sb <sub>12</sub>	7.74	7.8	14.6@ 789 K	-197@ 595 K	2.38@ 643 K	3.22@ 402 K	2.29@ 498 K	0.41@ 692 K	
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# **5.2** Recommendations for the future work

There are still some works that can be done to further develop the materials prepared in this thesis including;

- Based on the present experiment works, further treatments should be done on the synthesis process such as using annealing method for longer duration with SPS instead of SPS only in order to enhance the phase purity and density of materials.
- 2. The filling concentration of In-element can be increased in both La-filled skutterudite series and it is believed that this will increase the distribution of In-filler at grain boundaries. Consequently, a further reduction in the electrical resistivity and lattice thermal conductivity of the material can be anticipated, leading to additional improvements on the TE performance.
- 3. The temperature-dependence of TE parameters measurement can be done in high range of temperature for Al-filled with La- skutterudite system. It shows highly plausible to increase the Seebeck coefficient and reduce the lattice thermal conductivity with increasing temperatures. Simultaneously, a larger *ZT* can be anticipated.

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## LIST OF PUBLICATIONS

## **Published Article:**

- Bashir, M.B.A., Said, S.B.M., Sabri, M.F.M., Shnawah, D.A. and Elsheikh, M.H. Recent advances on Mg<sub>2</sub>Si<sub>1-x</sub>Sn<sub>x</sub> materials for thermoelectric generation. Renewable and Sustainable Energy Reviews 37 (2014) 569–584.
- S.B.M. Said, M.B.A. Bashir, M.F.M. Sabri, Y. Miyazaki, D.A. Shnawah, A.S. Hakeem, M. Shimada, A.I. Bakare, N.N.N. Ghazali and M.H. Elsheikh. Enhancement of thermoelectric behaviour of La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12-x</sub>Te<sub>x</sub> skutterudite materials, Metallurgical and Materials Transactions A. (2017) 1-9.

## **Submitted Article:**

- 1. High thermoelectric figure of merit of La<sub>0.5</sub>Co<sub>4</sub>Sb<sub>12</sub> skutterudite with In-filler, Journal of Electronic Materials. 2016.
- 2. Enhancement of thermoelectric properties of Yb<sub>0.25</sub>Co<sub>4</sub>Sb<sub>12</sub> skutterudites through Ni substitution, Sains Malaysiana. 2016.

## **Conferences:**

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