

# MATERIALS SYNTHESIS AND FABRICATION OF THERMOELECTRIC GENERATOR APPLIED TO ICE PRODUCTION INDUSTRY

DISSERTATION BY PANIDA PILASUTA

A Dissertation Submitted in Partial Fulfillment of the Requirements for The Doctor of Philosophy in Physics Program at Sakon Nakhon Rajabhat University December 2021 All Rights Reserved by Sakon Nakhon Rajabhat University

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# DISSERTATION APPROVAL SAKON NAKHON RAJABHAT UNIVERSITY DOCTOR OF PHILOSOPHY PROGRAM IN PHYSICS

Thesis Title: Materials Synthesis and Fabrication of Thermoelectric Generator Applied to Ice Production Industry

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ชื่อเรื่อง	การสังเคราะห์วัสดุและการประดิษฐ์เครื่องกำเนิดไฟฟ้า
	เทอร์โมอิเล็กทริกประยุกต์ใช้กับอุตสาหกรรมการผลิตน้ำแข็ง
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#### บทคัดย่อ

วัสดุเทอร์โมอิเล็กทริกมีความน่าสนใจสำหรับการเปลี่ยนความร้อนเหลือทิ้งเป็น พลังงานไฟฟ้าได้โดยตรงด้วยปรากฏการณ์ของซีเบก งานวิจัยนี้ได้ศึกษาเทอร์โมอิเล็กทริก ใน 3 ช่วงอุณหภูมิ สำหรับนำไปใช้กับความร้อนเหลือทิ้งตามอุณหภูมิที่เหมาะสมในโรงงาน อุตสาหกรรม ซึ่งจะทำให้ได้พลังงานหมุนเวียนกลับมาใช้กับระบบแสงสว่าง เพื่อเป็นวิธีการ ประหยัดพลังงานอีกทางหนึ่ง

วัตถุประสงค์ของงานวิจัยนี้คือการสังเคราะห์ การประดิษฐ์เทอร์โมอิเล็กทริก มอดูล 3 ช่วงอุณหภูมิ และศึกษาความเป็นไปได้ในการใช้เทอร์โมอิเล็กทริกมอดูลกับ อุตสาหกรรมโรงน้ำแข็งในการผลิตไฟฟ้า การแบ่งช่วงอุณภูมิของวัสดุเทอร์โมอิเล็กทริก แบ่งได้ 3 ช่วงอุณหภูมิคังนี้ ได้แก่ช่วงอุณหภูมิต่ำ ใช้อยู่ในช่วง 323–573 เคลวิน ช่วง อุณหภูมิกลาง อยู่ในช่วง 523–973 เคลวิน และช่วงอุณหภูมิสูง อยู่ในช่วง 743–1173 เคลวิน ในการปรับปรุงการประดิษฐ์และการเชื่อมวัสดุฐานรองให้สามารถทนความร้อนสูง มีความสำคัญเนื่องจากเพิ่มความทนทานเหมาะสมสำหรับการใช้งานกับวัสดุ เทอร์โมอิเล็กทริกทั้ง 3 ช่วงอุณหภูมิ

วัสดุฐานรองได้เตรียมมาจากแผ่นอะลูมินา 96 % ขนาด 50x50x1 mm<sup>3</sup> ใช้กาว เงินเป็นขั้วไฟฟ้าด้วยการทาลงไปบนแผ่นอะลูมินาจากนั้นอบที่อุณหูมิ 953 เคลวิน พบว่า สามารถทนความร้อนได้สูงถึง 953 เคลวินซึ่งเหมาะสมกับการประดิษฐ์อุปกรณ์ เทอร์โมอิเล็กทริกทั้ง 3 ช่วงอุณหภูมิ การประดิษฐ์เทอร์โมอิเล็กทริกมอดูลช่วงอุณหภูมิต่ำ ใช้วัสดุชนิดพีเป็น Sb<sub>2</sub>Te<sub>3</sub> และใช้วัสดุชนิดเอ็นเป็น Bi<sub>2</sub>Te<sub>3</sub> สังเคราะห์ด้วยเครื่องบดและผสมสารและวิธีอัดร้อน โดยค่า ZT สูงสุดของวัสดุชนิดพี Sb<sub>2</sub>Te<sub>3</sub> และวัสดุชนิดเอ็น Bi<sub>2</sub>Te<sub>3</sub> คือ 0.51 และ 0.54 ที่อุณหภูมิ 473 เคลวินตามลำดับ การต่อขั้วไฟฟ้าแบบ p–n โดยอนุกรมทางไฟฟ้าบนวัสดุฐานรองที่ทำ ขั้วด้วยกาวเงินและขั้วไฟฟ้าแผ่นเงินหนา 0.05 มิลลิเมตร ด้วยกระบวนการบัดกรีจำนวน 16 คู่ พบว่า มีค่าความต้านทานรวมประมาณ 1.7 โอห์ม ทดสอบการผลิตไฟฟ้าแรงดันไฟฟ้า วงจรเปิดมีค่า 0.5 โวลต์ กำลังไฟฟ้าสูงสุด 8.75 มิลลิวัตต์ที่อุณหภูมิด้านร้อน 523 เคลวิน และผลต่างอุณหภูมิ 100 เคลวิน

เทอร์โมอิเล็กทริกมอดูลช่วงอุณหภูมิกลางแบบรอยต่อแบบพีและเอ็น ใช้วัสดุ ชนิดพีเป็น MnSi<sub>1.75</sub> และใช้วัสดุชนิดเอ็นเป็น Mg<sub>2</sub>Si ที่ถูกสังเคราะห์ด้วยเครื่องบดและผสม สารและวิธีอัดร้อน ซึ่งค่า ZT สูงสุดของวัสดุชนิดพี และ ชนิดเอ็นคือ 0.44 และ 0.73 ที่ อุณหภูมิ 773 เคลวิน ตามลำดับ การต่อวัสดุเทอร์โมอิเล็กทริกจำนวน 16 คู่ พีและเอ็นแบบ อนุกรมทางไฟฟ้าบนวัสดุฐานรองที่ทำขั้วด้วยกาวเงินและเชื่อมต่อกันด้วยกาวเงิน นำไปเผา ในเครื่องอัดร้อน ในบรรยากาศอาร์กอน ที่อุณหภูมิ 823 เคลวิน เป็นเวลา 1 ชั่วโมง พบว่า มี ค่าความต้านทานรวมประมาณ 570 โอห์ม ทดสอบการผลิตไฟฟ้าได้แรงดันไฟฟ้าวงจรเปิดมี ค่า 0.39 โวลต์ กำลังไฟฟ้าสูงสุดมีค่า 6.4 มิลลิวัตต์ที่อุณหภูมิด้านร้อน 723 เคลวิน ที่ ผลต่างอุณหภูมิ 100 เคลวิน

กระบวนการประดิษฐ์เทอร์โมอิเล็กทริกมอดูลสำหรับช่วงอุณหภูมิสูงแบบ รอยต่อพีและเอ็น ใช้วัสดุชนิดพีเป็น Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> และใช้วัสดุชนิดเอ็นเป็น Zn<sub>0.98</sub>Al<sub>0.02</sub>O ที่ถูก สังเคราะห์ด้วยวิธีปฏิกิริยาสถานะของแข็งและอัดร้อน ซึ่งได้ค่า ZT สูงสุด 0.108 และ 0.2044 ที่อุณหภูมิ 973 เคลวิน ตามลำดับ การต่อวัสดุเทอร์โมอิเล็กทริกจำนวน 16 คู่ พี และเอ็นแบบอนุกรมทางไฟฟ้าบนวัสดุฐานรองที่ทำขั้วด้วยกาวเงินและเชื่อมต่อกันด้วยกาว เงิน นำไปเผาในเตาเผา 953 เคลวิน ในบรรยากาศเป็นเวลา 15 นาที พบว่า มีค่าความ ต้านทานรวมประมาณ 35 เมกะโอห์ม ทดสอบการผลิตไฟฟ้าได้แรงดันไฟฟ้าวงจรเปิด 0.1418 โวลต์ กำลังไฟฟ้าสูงสุด 0.61 มิลลิวัตต์ที่อุณหภูมิด้านร้อน 923 เคลวิน และผลต่าง อุณหภูมิ 100 เคลวิน

การประยุกต์ใช้เทอร์โมอิเล็กทริกโมดูลสำหรับอุณหภูมิต่ำจำนวน 24 โมดูลโดย มีจานรวมแสงอาทิตย์แบบพาราโบลาที่สามารถสร้างแหล่งความร้อนและใช้แหล่งระบาย ความร้อนด้วยน้ำจากน้ำเย็นในการผลิตน้ำแข็งของ ห้างหุ้นส่วนจำกัดกรเดชน้ำแข็งหลอด สกลนคร เพื่อผลิตกระแสไฟฟ้า ความต่างศักย์ กระแส และกำลังไฟฟ้าสูงสุดมีค่า 5.87 โวลต์ 0.512 แอมป์ และ 3 วัตต์ ในเวลา 13.00 น. สามารถชาร์จหลอดไฟ LED ได้ 2 ดวงใน 5 ชั่วโมงและเปิดหลอดไฟประมาณ 2.30 ชั่วโมง

**คำสำคัญ:** วัสดุเทอร์โมอิเล็กทริก 3 ช่วงอุณหภูมิ อุปกรณ์เทอร์โมอิเล็กทริก การผลิตไฟฟ้า จานรวมแสงอาทิตย์แบบพาราโบลา

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#### ABSTRACT

Thermoelectric materials are attractive for turning waste heat directly into electrical energy, thanks to the phenomenon of Seebeck. This research studied thermoelectric in 3 temperature ranges for applying waste heat from industrial plants with appropriate temperatures.

The purposes of this dissertation are synthesis and fabrication of thermoelectric modules in 3 temperature ranges, then studying the feasibility of using thermoelectric modules with the ice mill industry to generate electricity. Thermoelectric material has a low-temperature range (323–573 K), medium-temperature range (523–973 K), and high-temperature ranges (743–1173 K).

The substrate was prepared from a 96% alumina sheet, in size of  $50 \times 50 \times 1 \text{ mm}^3$  using silver paste as an electrode by applying it on the alumina sheet and then heating at 953 K. It was found that it withstands heat up to 953 K, which is suitable for the invention of thermoelectric devices in all three temperature ranges.

The thermoelectric module fabrication for low-temperature using p-type material of Sb<sub>2</sub>Te<sub>3</sub> and n-type material of Bi<sub>2</sub>Te<sub>3</sub> as synthesized by Planetary Ball Mill and hot-pressing methods. The maximum ZT of Sb<sub>2</sub>Te<sub>3</sub> and Bi<sub>2</sub>Te<sub>3</sub> materials are 0.51 and 0.54 at 473 K, respectively. P-n materials were connected by serial junction on silver paste electrodes 0.05 mm of thickness with 16 pairs by soldering processes.

The resistance of the module is approximately 1.7  $\Omega$ . The maximum open-circuit voltage and output powers are 0.5 V and 8.75 mW, respectively, at a hot temperature of 523 K, and the temperature difference was 100 K.

The thermoelectric module fabrication for medium-temperature using ptype material of MnSi<sub>1.75</sub> and n-type material of Mg<sub>2</sub>Si as synthesized by Planetary Ball Mill and hot-pressing methods. The maximum ZT of MnSi<sub>1.75</sub> and Mg<sub>2</sub>Si materials are 0.44 and 0.73 at 773 K, respectively. P-n materials were connected by serial junction on silver paste electrodes 0.05 mm of thickness with 16 pairs by soldering processes. P and N on base materials are terminalized with silver paste and connected by silver paste. Burn in a hot press in the Argonne atmosphere, at 823 K for an hour. The resistance of the module is approximately 570  $\Omega$ . The maximum open-circuit voltage and output powers are 0.39 V and 6.4 mW, respectively, at a hot temperature of 723 K, and the temperature difference was 100 K.

The thermoelectric module for high-temperature ranges with P and N joints uses p-type material Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and n-type is Zn<sub>0.98</sub>Al<sub>0.02</sub>O as synthesized by Planetary Ball Mill hot-pressing methods. The maximum ZT of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and Zn<sub>0.98</sub>Al<sub>0.02</sub>O are 0.108 and 0.2044 at 973 K, respectively. Sixteen pairs of thermoelectric materials electrically serialized P and N on base materials terminalized with silver paste and connected by silver paste. Burned in kiln 953 K. In the atmosphere for 15 minutes, the resistance of the module is approximately 35 M $\Omega$ . The maximum open-circuit voltage and output powers are 0.1418 V and 0.61 mW at a hot-side temperature of 923 K and a temperature difference of 100 K.

Low-temperature thermoelectric modules (24 modules) were connected with solar concentration parabola for heat sources and used cool water from Kordej Ice industry Sakon Nakhon Limited for the cooling system. The maximum electrical, voltage, current are 5.87, V 0.512 A, and 3 W, respectively; at 1 p.m., 2 LED lamps can be charged in 5 hours and about 2.30 hours.

#### **Keywords:** Thermoelectric Material 3 Temperature Range, Thermoelectric Device, Power Generation, Solar Concentration Parabola

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#### CHAPTER 1

#### INTRODUCTION

#### MOTIVATION

Thailand has developed continuously in both industry and economy, which increases demand for resources and energy and has an effect on electricity cost. According to the demand response, the increasing energy output is required to reduce the cost. Thus, finding new electricity–generating technology or using renewable energy can help reduce fuel usage. One is finding new clean, sustainable, highly efficient energy sources and optimization such as solar thermal, solar cells, hydrogen technology (fuel cells), wind turbines, vibration, etc. which have been developed and enhance efficiency for an increased energy source. Leading to new and important research regimes needed to convert heat to electrical energy is waste heat recovery, this is the process of collecting waste heat which is called thermoelectric (TE) technology. The thermoelectric materials for the 3 temperature ranges can be applied to the source of waste heat from an industrial factory (Michitaka Ohtaki, 2010), this will restore the energy circulation for it to be reused which another way to save energy.



Figure 1 Schematic comparison of various TE materials in terms of the applicable temperature range

Figure 1 shows a schematic comparison of various TE materials in terms of the applicable temperature range. The thermoelectric material that has the best application properties can be divided into 3 groups according to the operating temperature.

The low temperature range is alloy material groups such as BiTe, PbTe, SbTe (Lowhorn, 2011; Hsu, 2004) in the range of 323–573 K, which is heated from a hob, small fireplace, and small fuel engine. The medium temperature range is the silicide groups such as MnSi and MgSi in the range 523–973K which is heated from the combustion of cars, and incinerators. The last is the high temperature range, the oxide group such as CCO ZNO in the range of 743–1173K that is heated from the iron smelting industry in large furnaces.

Thermoelectric materials are materials that can convert heat into electrical energy. The difference between the temperatures of the material-based electrons and holes that are moving from a high to a low temperature inside causing voltage and electrical energy power by changing the heating and cooling waste from different sources to get the maximum benefit (Fergus, J. W., 2012).

TE devices consist of 4 parts, they are p-type material, n-type material, an electrode, and substrate shown in Figure 2. The p and n materials are connected electrically in series by using a metal electrode on the substrate, so that the performance of TE devices depends on conversion efficiency of the TE materials. The conversion efficiency of TE materials is evaluated by using dimensionless figure of merit (ZT) which is the key in this research. It correlates the three most important proprieties of a TE material, Seebeck coefficient (*s*), electrical resistivity ( $\rho$ ), and thermal conductivity ( $\kappa$ ) as shown in Eq.1; (Rowe, 2006, p. 1).

$$ZT = \frac{S^2 T}{\rho \kappa}$$
(1.1)



Figure 2 The Schematic illustration of a thermoelectric device (Srinivasan, B. 2018, and Le, P. H., & Jian, S. R. 2021)

According to a survey, the country's use of electricity is rising every year, but the production capacity remains the same, insufficient for use in Thailand. This results in Thailand having to buy electricity from neighboring countries to meet the needs of people (purchase 95,747.44 million kWh/year http://www.egat.co.th/2020). The researcher needed to find alternative energy sources to reduce importing electricity from abroad.

Therefore, the researcher is interested in studying thermoelectric materials suitable for different heat applications to generate electricity for use in Thailand. The researcher conducted a survey and data search of operators and industrial plants which had the sources of waste heat and cold–water leftover from the ice machines with high temperature and plenty of cooled wastewater. KORNDECH–ICE Part., Ltd., is a small ice production industry that got the idea to bring the heat source and cooling waste to maximize efficiency. The researcher thus fabricated thermoelectric modules for the applicable temperature range to be of the highest efficiency and install a generator to produce thermoelectric to be applied to the heat source and cooling

waste to bring power back to new industrial factories, which is another way to save energy. Thermoelectric can also be used with numerous other heat sources.

#### DISSERTATION OBJECTIVES

1. To synthesis Thermoelectric materials for 3 temperature ranges are:		
Low temperature	(323–573 K)	
Medium temperature	(523–973 K)	
High temperature	(743–1173 K)	

2. To study crystal structure, chemical composition, microstructure and thermoelectric properties.

3. To fabricate of thermoelectric modules from thermoelectric materials in 3 temperature ranges.

4. To apply thermoelectric modules with a heat source and cold source in industry Ice production.

#### SCOPE AND LIMITATION OF THE DISSERTATION

1. Synthesis thermoelectric materials by hot pressing method (HP).		
2. Low temperature	(323–573 K) p– $\rm Sb_2Te_3$ and n– $\rm Bi_2Te_3$	
Medium temperature	(523–973 K) p– MnSi <sub>1.75</sub> and n–Mg <sub>2</sub> Si	
High temperature	(743–1173 K) p-Ca <sub>3</sub> Co <sub>4</sub> O <sub>9</sub> and n-Zn <sub>0.98</sub> Al <sub>0.02</sub> O.	

3. Application with industry ice production.

#### OUTCOMES OF THE DISSERTATION

- 1. Knowledge of the thermoelectric materials in 3 temperature ranges.
- 2. Petty patent or patent of thermoelectric application.
- 3. The articles were published in international journals.

#### DISSERTATION STRUCTURE

The dissertation structure includes 5 chapters, namely, introduction, literature reviews, materials and methods, results and discussions, and conclusions and suggestions. Chapter 1 introduction consists of rationale and motivation, dissertation objectives, scope and limitation of the dissertation, outcomes of the dissertation, and dissertation structure. The literature reviews of the thermoelectricity theorem, thermoelectric materials, and thermoelectric devices are present in Chapter 2. Chapter 3 is thermoelectric materials synthesis, crystal structure analysis, microstructure analysis, thermoelectric properties, as well as the fabrication of thermoelectric modules and applications. The results and discussion of the experiments are present in Chapter 4. In the final chapter, Chapter 5, presents the conclusions and suggestions of the work. In addition, the references and appendix are presented after Chapter 5.

All work was carried out in the Thermoelectric Research Laboratory (TRL), Center of Excellence on Alternative Energy (CEAE) at Sakon Nakhon Rajabhat University, Sakon Nakhon, Thailand. This work has been supported by Project research and researcher for industries (RRi), Grant No. PHD59I0003 and KORNDECH–ICE Part., Ltd. Sakon Nakhon, Thailand.

#### CHAPTER 2

#### THEORETICAL BACKGROUND

#### THEOREM OF THERMOELECTRICITY

#### THERMOELECTRIC EFFECT

The thermoelectric phenomena are comprised of three reversible effects, Seebeck, Peltier, and Thomson. Moreover, these three effects have a relationship with the function of a thermoelectric device and performance of materials are estimated by Dimensionless Figure of Merit (ZT). Then the thermoelectric device was discussed on mechanism and efficiency.



#### Seebeck effect

Figure 3 Schematic illustration of Seebeck effect between two dissimilar materials with junctions held at different temperatures where  $T_h > T_c$ . Arrow indicates the direction of current flow

The Seebeck effect was discovered in 1823 by Thomas Johann Seebeck results in an electromotive force (e.m.f.) in a circuit composed of two different homogeneous materials if the junctions of the materials are at different temperatures. For small temperature differences, the e.m.f. depends on the temperature difference and is a function of the material used. The Seebeck coefficient between the materials a and b is Sab and both Eab and Sab are positive if conventional current flow is from a to b at the hot junction (Russche, 1964, pp. 4–5) as illustrated in Figure 3.

$$E_{AB} = S_{AB} \Delta T = \left(S_A - S_B\right) \Delta T \tag{2.1}$$

Seebeck effect is the phenomena of heat transfer into electricity. The physical significance is determined by the phenomenon of a constant temperature gradient. Initially, the conductor controls the uniform distribution of charge carriers, under temperature gradients. The carriers where the heated end is more kinetic than the cold end and tends to spread to the cold end. The formation of the charge causes the electric current to reverse, which is the opposite of the charge flow. The open-circuit voltage, when there is no current, is called the Seebeck voltage. Equation of the Seebeck coefficient, if written in the form of difference in electric potential and temperature effect, is that;

$$-\frac{dV}{dx} = S \frac{dT}{dx}$$
  
$$-\Delta V = S \Delta T$$
  
$$S = -\frac{\Delta V}{\Delta T}$$
  
is Seebeck coefficient (V K<sup>-1</sup>), (2.2)

where

S

 $\Delta V$  is Voltage difference (V),

 $\Delta T$  is Temperature difference (K).

A material has Seebeck coefficient not equal to zero is considered a thermoelectric materials. The positive and negative Seebeck coefficient depend on the properties of the material. In the case of the n-type semiconductor, the Seebeck coefficient is negative, but the p-type semiconductor has a positive coefficient.



Peltier effect

Figure 4 Schematic illustration of Peltier effect in a thermocouple. The electron current flow in p and n materials which generate the heat current flow. The  $T_h$  and  $T_c$  are the temperature of hot end and cold end, respectively
The Peltier effect was discovered in 1832 by Jean Charles Athanase Peltier. Whenever a circuit composed of two dissimilar materials carries an electric current, heat is absorbed at one junction and released at the other at a rate that is proportional to the current. This is called the Peltier effect it is illustrated in Fig. 4., and the heat transferred is called the Peltier heat. Resistance heating is of course nonreversible and proportional to the square of the current. The Peltier coefficient,  $\Pi_{AB}$ , is positive if the current flow is from A to B at the junction where heat is absorbed, and the coefficient is really the difference of the absolute coefficients as in the Seebeck effect (Russche, 1964, pp. 5–6).

$$\frac{dQ_{AB}}{dt} = \Pi_{AB}I = \left(\Pi_A - \Pi_B\right)I$$
(2.3)

where

Q	is the return heat absorption rate. (W),
$\Pi_A$	is the Peltier coefficient of the conductor A. (W $\ensuremath{A^{-1}}\xspace),$
$\Pi_B$	is the Peltier coefficient of the conductor B. (W $\ensuremath{A^{-1}}\xspace),$
Ι	Is the current supplied from conductor A to B (A)

The relationship between the Seebeck phenomenon and the Peltier phenomenon can be written as Equation;

$$\Pi = ST \tag{2.4}$$

#### Thomson effect

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

$$\frac{dQ_A}{dt} = \tau_A I \frac{dT}{dx}$$
(2.5)

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



Figure 5 Schematic illustration of Thomson effect

The Seebeck potential generated  $EMF = S_{AB}\Delta T$ The energy required per unit charge is E = EMF / I

$$EMF = I \int_{T_2}^{T_1} \tau_B dT - \Pi_1 I - I \int_{T_1}^{T_2} -\tau_A dT + \Pi_2 I \qquad (2.6)$$
$$E = \frac{EMF}{I} = \Pi_2 - \Pi_1 + \int_{T_2}^{T_1} (\tau_B - \tau_A) dT$$
$$Let \ \Pi_1 - \Pi_2 = \Delta \Pi \qquad \therefore \qquad \Delta E = -\Delta \Pi + (\tau_B - \tau_A) \Delta T$$

The second law requires that the total change in entropy of the system due to the passage of unit charge under reversible conditions is zero.

$$0 = \frac{\Pi_1}{T_1} + \frac{\Pi_2}{T_2} + \int_{T_1}^{T_2} \frac{\tau_B - \tau_A}{T} dT$$
(2.7)

Differentiating Eq. 2.6 and 2.7 with respect to temperature gives

$$S = \frac{dE}{dT} = \frac{d\Pi}{dT} + \tau_{B} - \tau_{A}$$
(2.8)

$$0 = \frac{d\Pi}{dT} - \frac{\Pi}{T} + \tau_{\scriptscriptstyle B} - \tau_{\scriptscriptstyle A} \tag{2.9}$$

Subtract Eq. 2.8 from 2.9.

$$S = \frac{d\Pi}{dT} - \frac{d\Pi}{dT} + \frac{\Pi}{T}$$
$$ST = \Pi$$
(2.10)

Differentiating 
$$\tau_A - \tau_B = T \frac{dS}{dT}$$
  $dS = (\tau_A - \tau_B) \frac{dT}{T}$ 

$$S_A = \int_0^T \frac{\tau_A dT}{T} \qquad d\Pi = SdT + TdS \qquad (2.11)$$

$$\Pi_A = TS_A \tag{2.12}$$

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

# DIMENSIONLESS FIGURE OF MERIT AND THERMOELECTRIC PARAMETERS

#### **Dimensionless Figure of Merit**

In 1949 the concept of a thermoelectric figure of merit, ZT, was developed by Abram Fedorovich loffe (Vedernikov, & lordanishvili, 1998, pp. 37–42). The figure of merit (FOM) presented in Eq. 2.13 describes the relationship between the three quantities determining the TE proprieties of a material: (Ohtaki., 2011, pp. 770–775)

$$ZT = \frac{\sigma S^2 T}{\kappa_{tot}} = \frac{S^2 T}{\rho \kappa_{tot}}$$
(2.13)

where S is the Seebeck coefficient,

 $\sigma$  is the electrical conductivity,

 $\kappa_{tot}$  is the total thermal conductivity,

ho is the electrical resistivity,

and T is the absolute temperature.

In principle z is the thermoelectric figure of merit a material, however since it is temperature dependent it is more meaningful to use it in its dimensionless form ZT. The ultimate goal is to have as high ZT as possible which implies that a good TE should possess (i) large Seebeck coefficient, in order to efficiently convert heat into electricity, (ii) high electrical conductivity to minimize Ohmic losses and Joule heating due to electrical resistance and (iii) low thermal conductivity to minimize heat losses and maintain the thermal gradient (Molinari, M., Tompsett, D. A., Parker, S. C., Azough, F., & Freer, R., 2014, pp. 14109–14117). The three thermoelectric parameters are functions of the carrier concentration and they are interrelated in a conflicting manner.

#### Seebeck coefficient

In an earlier section, the Seebeck coefficient was defined as the relation between the induced voltage and the temperature difference, Eq. 2.2. By utilizing thermodynamics of irreversible processes, the Seebeck coefficient can be expressed.

as; 
$$S = \frac{8\pi^2 k_B^2}{3eh^2} m * T \left(\frac{\pi}{3n}\right)^{\frac{3}{2}}$$
(2.14)

where	$k_{B}$	is the Boltzman constant,
	е	is electron charge,
	h	is Planck's constant,
	<i>m</i> *	is the effective carrier mass,
	Т	is the absolute temperature,

and *n* is charge carrier concentration.

Assuming that S is measured at constant temperature, the only variable in this equation will be carrier concentration *n* that can be varied through doping. By looking at the equation we can see that S will decrease when n increases. The reason for this is the fact that the Seebeck effect is caused by the induced voltage in the material. The higher the carrier concentration to begin with the lower the induced voltage as it takes less new electron–hole pairs to induce current flow through the material.

#### Electrical conductivity

Electrical conductivity is obviously strongly affected by the carrier

concentration. It is derived from the Ohm law and expressed as: (Hilaal Alama, 2012, pp. 190–212)

$$\sigma = \frac{1}{R} = ne\mu \tag{2.15}$$

where  $\mu$  is this case is the carrier mobility,

*n* is the carrier concentration,

and e is the electron charge.

This equation illustrates very well that  $\sigma$  increases with increasing carrier concentration simultaneously decreasing the electrical resistivity of the material. In addition, electrical conductivity can be expressed through the Arrhenius equation: (Kabir, R., et al, 2014, 7522–7528)

$$\sigma = \frac{A}{T} \exp\left(\frac{=E_a}{k_B T}\right)$$
(2.16)

where A

is the pre-exponential factor,

 $k_B$  is Boltzmann's constant,

T the absolute temperature,

and  $E_a$  the activation energy of conduction.

#### Thermal conductivity

In a crystalline solid, heat can be carried through the motion of charge carriers described as the electronic thermal conductivity,  $\kappa_l$ , and through the lattice vibrations, i.e., phonon thermal conductivity,  $\kappa_e$ . As a result, the total thermal conductivity,  $\kappa_{intal}$  is defined as a sum of the electronic and lattice component, Figure 6.



Figure 6 Thermal conductivity dependence on carrier concentration

$$\kappa_{total} = \kappa_l + \kappa_e \tag{2.17}$$

The electronic thermal conductivity can be expressed as (Bhaskar, A., Liu, C.–J., Yuan, J. J., & Chang, C.–L., 2013, pp. 236–239)

$$\kappa_{el} = L\sigma T \tag{2.18}$$

where

L is the Lorentz number,

 $\sigma$  is the electrical conductivity,

and T is the temperature.

Another illustrative equation is the Wiedemann–Franz relationship

(Fergus, J.W., 2014, pp. 525–540):

$$\frac{\kappa_{el}}{\sigma} = \left(\frac{\pi^2 k_B^2}{3e^2}\right) T \tag{2.19}$$

where

*e* is charge of an electron,

and  $k_B$  is the Boltzman's constant.

Both equations indicate that the ratio between  $\sigma$  and  $\kappa_{el}$  is constant at a given temperature and that any improvement in electrical conductivity leads to an offsetting increase in the electronic thermal conductivity.

The lattice thermal conductivity dominates the heat conduction process in insulators and its contribution becomes less significant the more metallic material is. Although lattice vibrations are independent of the carrier concentration the lattice thermal conductivity increases rapidly and becomes less significant in materials with high carrier concentration because the electronic thermal conductivity is the dominating process. Lattice thermal conductivity corresponds to the propagations of phonons in the three space dimensions through the crystal lattice and can be expressed as; (Sootsman, Chung, & Kanatzidis, 2009, pp. 8616–8639).

$$\kappa_{ph} = \frac{1}{3} C_V v l_{ph} \tag{2.20}$$

where  $C_{V}$  is the heat capacity at constant volume,

v is the concentration and velocity of phonons,

and  $l_{ph}$  is the phonon mean free path,

which is defined as the average distance a phonon travels before colliding with another particle. The evolution of  $\kappa_{ph}$  with the temperature depends on the dominating interactions occurring in the lattice. At low temperatures those limitations are caused by the grain size and the defect concentration while at high temperatures, collisions between phonons are the dominant factor limiting heat conduction.

## ENERGY CONVERSION EFFICIENCY

In every heat engine, including the thermoelectric generator, the energy conversion efficiency is governed by the Carnot efficiency.

$$\eta_c = \frac{\Delta T}{T_h} \tag{2.21}$$

The amount of electrical energy produced is dependent on the thermoelectric conversion efficiency of the device and heat flux. The conversion efficiency is a function of the temperature gradient and the thermoelectric figure of merit (ZT), defined as;

$$\eta_{\max} = \frac{P}{Q} = \frac{T_h - T_c}{T_h} \frac{\sqrt{1 + Z\overline{T}} - 1}{\sqrt{1 + Z\overline{T}} + \frac{T_c}{T_h}}$$
(2.22)

where 
$$\overline{T} = \frac{T_h + T_c}{2}$$

To maximize power generation efficiency, ZT should be as high as possible, and the temperature differential between the hot and cold sides should be as large as possible. This relation is well illustrated in Figure 7.







For practical applications Z = 1 is chosen as a benchmark then as the efficiency reaches approx. 10% (Ohtaki, Tokunaga, Eguchi, & Arai, 1997, pp. 224–227). Although it is less than more traditional technologies that can achieve 30% conversion efficiency it still is a viable addition to traditional energy production techniques. In the end the goal is not to replace existing technologies but to provide a supplement that would reduce energy losses mainly in industry where they are largest (Vining, 2009, pp. 83–85).

If it is assumed that the electrical conductivities, thermal conductivities, and Seebeck coefficients of a and b are constant within an arm, and that the contact resistances at the hot and cold junctions are negligible compared with the sum of the arm resistance, then the efficiency can be expressed as;

$$\eta = \frac{I^2 R}{S_{ab} I T_h + \kappa' (T_h - T_c) - \frac{1}{2} I^2 R} 8$$
(2.23)

where  $\kappa'$  is the thermal conductance of a and b in parallel and R is the series resistance of a and b. In thermoelectric materials  $\sigma$ ,  $\kappa'$ , and S change with temperature, and in both, generation and refrigeration should be taken into account.

However, the simple expression obtained for the efficiency can still be employed with an acceptable degree of accuracy, if approximate averages of values are adopted for these parameters over the temperature range of interest. Appropriate allowances can also be made for contact resistance. Efficiency is clearly a function of the ratio of the load resistance to the sum of the generator arm resistances, and at maximum power output it can be shown that;

$$\eta_P = \frac{T_H - T_C}{\frac{3T_H}{2} + \frac{T_C}{2} + \frac{4}{Z_C}}$$
(2.24)

while the maximum efficiency

$$\eta_{\max} = \eta_C \gamma \tag{2.25}$$

(2.26)

 $\eta_{c} = \frac{T_{H} - T_{c}}{T_{H}}$   $\gamma = \frac{\sqrt{1 + Z_{c}\overline{T}} - 1}{\sqrt{1 + Z_{c}\overline{T}} + \frac{T_{c}}{T_{H}}}$ 

(2.27)

$$Z_C$$
 (Figure of Merit of the couple)  $= \frac{S_{ab}^2}{R\kappa'}$  (2.28)

The maximum efficiency is thus the product of the Carnot efficiency, which is clearly less than unity, and  $\gamma$ , which embodies the parameters of the materials. If the geometries of a and b are matched to minimize heat absorption, then;

$$Z_{C} = \frac{S_{ab}^{2}}{\sqrt{\kappa_{a} / \sigma_{a}} + \sqrt{\kappa_{b} / \sigma_{b}}}$$
(2.29)

where

In practice, the two arms of the junction have similar material constants, in which case the concept of a Figure of Merit for a material is employed and given by;

$$Z = \frac{S^2 \sigma}{\kappa} \tag{2.30}$$

where  $S^2\sigma$  is referred to as the electrical power factor.

## THERMOELECTRIC MATERIALS



Figure 8 Schematic dependence of electrical conductivity, Seebeck coefficient, power factor, and thermal conductivity on concentration of free carriers (David Michael Rowe, 2005)

One of the parameters used in the classification of materials is electrical conductivity. Metals have high electrical conductivity, while insulators have very low conductivity which under normal conditions is taken as zero. Semiconductors occupy an intermediate position between the two. Electrical conductivity reflects the charge carrier concentration. All three parameters which occur in the figure of merit are functions of carrier concentration (Spies, P., Pollak, M., & Mateu, L. (Eds.). (2015). Electrical conductivity increases with an increase in carrier concentration as shown in Figure 8, while the Seebeck coefficient decreases, and the electrical power factor maximizes at a carrier concentration of around  $10^{19}$  cm<sup>-3</sup>. The electronic contribution to the thermal conductivity, also increases with carrier concentration. Evidently the Figure of Merit optimizes at carrier concentrations which corresponds to semiconductor materials. Consequently, semiconductors are the materials most researched for thermoelectric applications.

Thermoelectric phenomena are exhibited in almost all conducting materials (except for superconductors below  $T_c$ ). Because the Figure of Merit varies with temperature, a more meaningful measure of performance is the Dimensionless Figure of Merit ZT, where T is absolute temperature. However, only those materials which possess a ZT > 0.5 are usually regarded as thermoelectric materials.

State of the art materials



Figure 9 Summary of the temperature dependence of ZT of (a) thermoelectric p– type material and (b) thermoelectric n–type materials.

Currently one of the most popular TE materials that are available on the market is the tellurides base. Those alloys are good at low temperatures (<523 K, ZT  $\approx$  1.1) when composed of PbTe and TAG-85 materials for medium-range temperatures (523 K to 923 K). In high-temperature applications, meaning above 923 K, SiGe alloys are most used, both as n- and p-type materials. Figure 9 (a) shows the p-type thermoelectric materials in 3 temperature ranges consisting of low-temperature, medium-temperature, and high temperature. The low-temperature range is Sb<sub>2</sub>Te<sub>3</sub> group has a ZT value of about 0.3–0.35. The medium-temperature range is high-temperature is Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> has a ZT value of about 0.07–0.2. Figure 9 (b) shows the p-type thermoelectric materials in 3 temperature ranges consisting of low-temperature, medium-temperature, and high temperature. The low-temperature range is Bi<sub>2</sub>Te<sub>3</sub> group has a ZT value of about 0.48–0.62. The medium-temperature range is  $Mg_2Si$  has a ZT value of about 0.41–0.65. The last temperature range is high-temperature is  $Zn_{0.98}Al_{0.02}O$  has a ZT value of about 0.09–0.21.

Furthermore, for commercialization, industries are interested in cheap materials for the price, durability, and that they are effective enough to use for industrial plants. Therefore, the development of polymer, silicide, oxide, and other TE materials is heavily motivated by the need to lower costs and to improve the commercial viability of TEGs. The relation between raw materials ' costs associated with sample materials of the main types of TE material classifications is shown in Figure 10.



Figure 10 Cost of various TE materials based on the raw material costs of the constituent elements.



Antimony Telluride

Figure 11 Crystal structure of  $Sb_2Te_3$  Gary ball =Sb and Yellow ball = Te (Ma, Y., et al., 2012)

Antimony telluride (Sb<sub>2</sub>Te<sub>3</sub>) is a narrow–gap semiconductor with a band gap 0.21 eV, topological insulator, and thermoelectric material. The layers are stacked together via Van der Waals interactions and can be exfoliated into thin 2D layers (Eschbach, et al., 2015). Antimony telluride belongs to the group–15 metalloid trichalcogenides. Sb<sub>2</sub>Te<sub>3</sub> material has high–performance thermoelectric properties because Sb<sub>2</sub>Te<sub>3</sub> has a small bandgap that leads to a high Seebeck coefficient, electrical conductivity, and thermal conductivity is very low. Sb<sub>2</sub>Te<sub>3</sub> has a rhombohedral crystalline structure (Anderson, T. L., Krause, H. B. (1974). The crystalline material comprises atoms covalently bonded to form 5 atom thick sheets (in order: Te–Sb–Te–Sb–Te), with sheets held together by Van der Waals attraction. Due to its layered structure and weak inter–layer forces, bulk antimony telluride may be mechanically exfoliated to isolate single sheets.

Yang, H. Q., et al. (2014) were study on Low–Temperature, Solution– Based, Scalable Synthesis of Sb<sub>2</sub>Te<sub>3</sub> Nanoparticles with an Enhanced Power Factor. in this work, he reports an alternative versatile solution–based method for synthesis of plate–like Sb<sub>2</sub>Te<sub>3</sub> nanoparticles in a flask using SbCl<sub>3</sub> and Te powders as raw materials, EDTA–Na<sub>2</sub> as complexing agent, and NaBH<sub>4</sub> as reducing agent in the solvent (distilled water). To investigate their thermoelectric transport properties, the obtained powders were cold compacted into cuboid prisms then annealed under a protective N<sub>2</sub> atmosphere. The results showed that both the electrical conductivity ( $\sigma$ ) and the power factor (S<sup>2</sup> $\sigma$ ) can be enhanced by improving the purity of the products and by increasing the annealing temperature. The highest power factor was 2.04 µW cm<sup>-1</sup> K<sup>-2</sup> at 140°C and electrical conductivity remained in the range 5–10 × 10<sup>3</sup> S m<sup>-1</sup>. This work provides a simple and economic approach to preparation of large quantities of nanostructured Sb<sub>2</sub>Te<sub>3</sub> with excellent TE performance, making it a fascinating candidate for commercialization of cooling devices.

D. Das, et al. (2016) were study on tuning of thermoelectric properties with changing Se content in  $Sb_2Te_3$  were synthesized by the solid–state reaction method. Found that the increase of Se content increases the resistivity of the samples. The variation of phonon frequencies, observed from the Raman spectroscopic study, depicts an anomalous behavior around x = 0.2. The sample Sb<sub>2</sub>Te<sub>2.8</sub>Se<sub>0.2</sub> also shows maximum Seebeck coefficient, carrier concentration and thermoelectric power factor. The nature of the scattering mechanism controlling the thermopower data has been explored. The thermoelectric properties of the synthesized materials have been analyzed theoretically in the frame of the Boltzmann equation approach.

Masato Kitamura and Kazuhiro Hasezaki (2016) were study on Effect of Mechanical Alloying on Thermal Conductivity of Bi<sub>2</sub>Te<sub>3</sub>–Sb<sub>2</sub>Te<sub>3</sub>. A Bi<sub>2</sub>Te<sub>3</sub>–Sb<sub>2</sub>Te<sub>3</sub> solid solution was prepared by mechanical alloying (MA) followed by hot pressing (HP). X–ray diffraction indicated that all samples which were removed at a depth below the surface of approximately 1 mm were single–phase and isotropic Bi<sub>2</sub>Te<sub>3</sub>–Sb<sub>2</sub>Te<sub>3</sub> solid solution. Reduction of the phonon thermal conductivity as a result of the ne–grains caused by MA predominated over the solid–solution effect caused by melt growth. The Seebeck coefficient and electrical and thermal conductivities fluctuated between those for (Bi<sub>2</sub>Te<sub>3</sub>)<sub>0.15</sub>(Sb<sub>2</sub>Te<sub>3</sub>)<sub>0.85</sub> and (Bi<sub>2</sub>Te<sub>3</sub>)<sub>0.2</sub>(Sb<sub>2</sub>Te<sub>3</sub>)<sub>0.8</sub> at room temperature. A (Bi<sub>2</sub>Te<sub>3</sub>)<sub>0.15</sub>(Sb<sub>2</sub>Te<sub>3</sub>)<sub>0.85</sub> solid solution with a dimensionless figure of merit ZT = 1.16 at 367 K was obtained by MA–HP. These results indicate that the maximum ZT of the Bi<sub>2</sub>Te<sub>3</sub>)<sub>0.25</sub>(Sb<sub>2</sub>Te<sub>3</sub>)<sub>0.75</sub>, which has the minimum phonon thermal conductivity in the case of melt growth.

Aniruddha Mahajan, et al. (2018) Study and Characterization of Thermoelectric Material (TE) Bismuth. Three different materials; Bismuth Telluride, (Bi<sub>0.75</sub>Sb<sub>0.25</sub>)<sub>2</sub>Te<sub>3</sub>, and (Bi<sub>0.5</sub>Sb<sub>0.5</sub>)<sub>2</sub>Te<sub>3</sub> were synthesized. XRD and TEM analysis was carried out to confirm the results. The particle size of the material was determined by using FESEM analysis. The two alloys of Bismuth Telluride such prepared were converted in the pellet form using vacuum hydraulic pressure and their Seebeck coefficients were determined to test the material suitability for its use as a thermoelectric device. Their power factor measurement and Hall effect measurements were carried out at room temperature. Hyun Soo Shin, et al. (2018) studied the Thermoelectric properties of  $Bi_2Te_3$  and  $b_2Te_3$  solid solution prepared by the hot-pressing method. It has been found that the mechanical deformation during pulverization or pressing processes is very important in controlling the Seebeck coefficient. The role of the anion vacancies formed by the mechanical deformation as well as the change of the antistructure defect concentration was discussed. By optimizing particle size and hot-pressing temperature.

#### Bismuth Telluride

Bismuth telluride (Bi<sub>2</sub>Te<sub>3</sub> material) is discussed as high-performance thermoelectric properties because the Bi<sub>2</sub>Te<sub>3</sub> small bandgaps lead to a high Seebeck coefficient, electrical conductivity and thermal conductivity is very low, a maximum ZT value of 0.75 at 300 K (Kim H, Han M–K, & Kim S–J, 2012). Thus, Bi<sub>2</sub>Te<sub>3</sub> is one of the best thermoelectric materials since it has a capability to convert waste heat energy into the beneficial electrical energy (Culebras M, Uriol B, Gómez & CM, Cantarero, 2016). In recent years, many studies have been carried out to obtain high efficiency thermoelectric materials through the development of Bi<sub>2</sub>Te<sub>3</sub> (Antonenko AO, Charnaya EV, & Marchenkov YV, 2017; Luo B, Deng Y, & García–Cañadas J, 2016). Bi<sub>2</sub>Te<sub>3</sub> is a material from the group of space group 166 and lattice parameter a = b = 4.38 Å and c = 30.48 Å (Guo W, Ma J, & Zheng W, 2016). Bi–Te is a compound of bismuth (Bi) and tellurium (Te), with composition Bi<sub>2</sub>Te<sub>3</sub> show in Figure 12.



Figure 12 Crystal structure of Bi<sub>2</sub>Te<sub>3</sub> Purple ball =Bi and Orange ball =Te (https://materialsproject.org/materials/mp=34202/)

Bismuth telluride ( $Bi_2Te_3$ ) is a gray powder that is a compound of bismuth and tellurium also known as bismuth (III) telluride physically behaves like metal and is atomic number 83. It is a semiconductor, which, when alloyed with antimony or selenium, is an efficient thermoelectric material for refrigeration or portable power generation.  $Bi_2Te_3$  is a topological insulator, and thus exhibits thickness–dependent physical properties. Bismuth telluride is a narrow–gap layered semiconductor with a trigonal unit cell. The valence and conduction band structure can be described as a many–ellipsoidal model with 6 constant–energy ellipsoids that are centered on the reflection planes (Haynes and William M, 2011).

Bi<sub>2</sub>Te<sub>3</sub> cleaves easily along the trigonal axis due to Van der Waals bonding between neighboring tellurium atoms. Due to this, bismuth-telluride-based materials used for power generation or cooling applications must be polycrystalline. Furthermore, the Seebeck coefficient of bulk Bi<sub>2</sub>Te<sub>3</sub> becomes compensated around room temperature, forcing the materials used in power-generation devices to be an alloy of bismuth, antimony, tellurium, and selenium. The melting point and transition temperature of the materials increases, crystallization speed decreases and data retention increase, the melting point of  $Bi_2Te_3$  materials is 580 °C (1,076 °F; 853 K). The crystalline of  $Bi_2Te_3$  has two possible configurations hexagonal and trigonal.

 $Bi_2Te_3$  has transition temperature of around < 25 °C a maximum ZT value of 0.8 at 48 °C when it is doped antimony (Sb) then it behaves like a semiconductor p-type a maximum ZT value 1.86 at 47 °C (Jiang Q, Yan H, & Simpson, 2014) and selenium (Se) alloy then it behaves like a semiconductor p-type a maximum ZT value 1.15 at 97 °C It can be used for some applications like thermoelectric refrigeration, TEG, and TEC (Gaikwad M, 2016).

H.L. Ni et al. (2005) were study Thermoelectric properties of hydrothermally synthesized and hot-pressed n-type  $Bi_2Te_3$  alloys with different contents of Te. Nanosized  $Bi_2Te_3$  based powders with the designed compositions of  $Bi_2Te_x$  (x = 2.85, 3.00, 3.15, 3.30, 3.45) have been synthesized by hydrothermal method. Bulk thermoelectric materials with crystal sizes smaller than 200 nm have been obtained by hot pressing of the hydrothermally synthesized  $Bi_2Te_3$  based powders. It was found that all samples are n-type. A maximum power factor of 2.35 × 10<sup>-3</sup> Wm<sup>-1</sup> K<sup>-2</sup> was obtained at 312 K in the sample with a nominal composition of  $Bi_2Te_{3.30}$ 

X.H. Ji et al. (2005) reported the synthesis and properties of rare earth containing  $Bi_2Te_3$  based thermoelectric alloys prepared by solvothermal and hot pressing the powders in a vacuum of about 0.1 Pa with a pressure of 65 MPa at 300 ° C for 30 min. They occupy the Bi-position in the  $Bi_2Te_3$  lattice and act as n-type dopant in  $Bi_2Te_3$  based semiconductors. A maximal figure of merit ZT  $\approx$  0.22 has been obtained for a sample of Ce–  $Bi_2Te_3$  at about 450 K.

Zhong Wang, et al. (2010) were Synthesis and characterization of  $Bi_2Te_3$ nanotubes by a hydrothermal method.  $Bi_2Te_3$  nanotubes were synthesized via an ultrasonic–assisted hydrothermal method at 180° C for 48 h. The products were characterized by XRD, SEM, EDS, TEM, and HRTEM. It what found that size of nanotubes is about 500–1000 nm in length and 50–100 nm in diameter. The  $Bi_2Te_3$  nanotubes grow along the (0 0 1) direction, whose angle with the tube axis is about 20, spirally along the longitude. The probable formation model of  $Bi_2Te_3$  nanotubes is proposed based on the experimental results. This strategy may be extended to prepare other one–dimensional nanomaterials.



Manganese silicide



MnSi has a tetragonal crystal structure with lattice parameter of a=5.507 Å, b=5.507 Å and c=17.390 Å as show in figure 10. The MnSi shows the highest thermoelectric figure of merit, ZT at intermediate temperatures of up to 973 K. MnSi consists of a group of crystallographic structures with a chemical composition of MnSi<sub>1.72-1.75</sub> which includes the Mn<sub>4</sub>Si<sub>7</sub>, Mn<sub>11</sub>Si<sub>19</sub>, Mn<sub>15</sub>Si<sub>26</sub> and Mn<sub>27</sub>Si<sub>47</sub> compounds. In the past few years enhanced efforts were devoted to increase the ZT values of MnSi compounds.

Itoh & Yamada (2009) were synthesized MnSi<sub>1.73</sub> by mechanical alloying and pulse discharge sintering. The sample mechanically alloyed at 400 rpm for the best thermoelectric performance. The maximum dimensionless figure of merit ZT of 0.47 was achieved at 873 K. Shin, et al. (2013) were synthesized MnSi by mechanical alloying and consolidated by hot pressing. The optimum condition of mechanical alloying was ball milling at 400 rpm for 6 h, and sound sintered compacts could be obtained by hot pressing at temperature higher than 1073 K. MnSi behaved as degenerate semiconductors in that the absolute values of the Seebeck coefficient increased and the electrical conductivity slightly decreased with increasing temperature. MnSi<sub>1.73</sub> showed the highest figure of merit of 0.28 at 823 K.

Schönecker, et al. (2015) were reported the progress in manufacturing higher manganese silicide material by the ribbon–growth–on–substrate (RGS). The maximum ZT values was found above 0.5 at 873 K.

Truong, et al. (2015) synthesized undoped Higher Manganese Silicides, involving ball milling under soft conditions to obtain homogeneous mixtures of constituting elements, and subsequent spark plasma sintering for a direct solid state reaction. The maximum thermoelectric figure of merit obtained is 0.55 at 850 K, a high value for undoped ZT.

Sadia, et al. (2016) synthesized MnSi by arc-melting followed by hot pressing. The maximum thermoelectric figure of merit obtained is 0.47 at 450 K, leading to ~10% ZT enhancement in parallel to the pressing direction compared to the transverse direction. This shows that more carful considerations are required while assuming isotropic behavior in non-cubic polycrystalline thermoelectric materials.

Magnesium Silicide



Figure 14 Crystal structure of Mg<sub>2</sub>Si (https://materialsproject.org/materials/mp=1367/)

Magnesium silicide (Mg<sub>2</sub>Si), is an inorganic compound consisting of magnesium and silicon. As–grown Mg<sub>2</sub>Si usually forms black crystals; they are semiconductors with n–type conductivity and have potential applications in thermoelectric generators its non–toxic, low production cost, and low weight (Hirayama, Naomi (2019) Mg<sub>2</sub>Si has a face–centered cubic CaF2 type of structure with a=b=c of lattice parameter as shown in figure 11, Si centers occupy the corners and face–centered positions of the unit cell and Mg centers occupy eight tetrahedral sites in the interior of the unit cell. The coordination numbers of Si and Mg are eight and four, respectively. The Mg<sub>2</sub>Si–based alloys are promising candidates for thermoelectric energy conversion for the middle–high range of temperature (Nazia S. Nazer, 2017). They could also result in thermoelectric generator weight reduction (a key feature for the automotive application field). The high value of thermal conductivity of the silicide–based materials could be reduced by increasing the phonon scattering in the presence of nanosized crystalline grains without heavily interfering with the electrical conductivity of the thermoelectric material (Fiameni, et al, 2012).

Fiameni, et al (Fiameni, et al, 2012, pp. 142–146) were reported the ZT value of  $Mg_2Si:Bi=1:x$  for x=0.01,0.02 and 0.04 M ratio preparing by ball milling, thermal treatment and spark plasma sintering processes.. The maximum ZT valueof 0.39 at 873 K was reached for the sample with x=0.02 Bi doped with the addition of Single Wall Carbon Nanohorns.

Berthebaud et al. (2013) were reported the ZT value of  $Mg_2Si$  preparing by microwave heating. The doping effect of several elements such as silver, tin, antimony, cobalt and bismuth has been studied. n–Type and p–type  $Mg_2Si$  based materials have been successfully synthesized, with maximum ZT value up to 0.7 and 0.35 at 770 K for a n–type and a p–type sample, respectively.

Khan et al. (2014) were reported the ZT value of Bi–doped  $Mg_2Si_{1-x-}$ <sub>y</sub>Sn<sub>x</sub>Ge<sub>y</sub> (x = 0.4 and y = 0.05) preparing by solid state synthesis and sintering via hot pressing. The material with x = 0.02 presents the maximum value of 1.4 at 800 K. Arai, et al. (2015) were reported the ZT value of  $Mg_2Si$  by Sb-doping and Ge-doping preparing by spark plasma sintering. The Ge-doped samples had a higher ZT value than the ZT value of the Sb-doped sample of the same concentration without Ge because the thermal conductivity of the former was lower. The maximum ZT value of Sb0.23 at %-doped  $Mg_2(Si_{0.995}Ge_{0.05})$  was 0.74 at 756 K.

Du, et al. (2015) were reported the ZT value of  $Mg_{2(1+x)}Si_{0.2}Ge_{0.1}Sn_{0.7}$ ( $0.06 \le x \le 0.12$ )  $B_2O_3$  flux method combined with spark plasma sintering technique. The electron effective mass enhancement for  $x \ge 0.08$  suggests the conduction band convergence of  $Mg_2Si_{0.2}Ge_{0.1}Sn_{0.7}$ .  $Mg_{2.16}(Si_{0.2}Ge_{0.1}Sn_{0.7})_{0.99}Sb_{0.01}$  with a maximum ZT of 0.94 at 780 K stand out as one of the best materials for intermediate temperature applications, providing a good nontoxic alternative to PbTe.

Gwansik Kim, et al. (2017) studied Up–scaled solid–state reaction for the synthesis of doped Mg2Si. The reported a synthesis technique based on the up– scaled solid–state reaction for AI and Bi co–doped Mg2Si polycrystalline bulks and investigated their thermoelectric transport properties. were synthesized for mass production by using the solid–state reaction, and the polycrystalline bulks were consolidated using hot pressing and spark plasma sintering techniques. Both 2 methods showed good reproducibility and positional uniformity of the thermoelectric properties.

Jianghua, Li et al. (2018) was prepared  $Mg_2Si_{1-x}Sb_x$  compounds by using high-pressure synthesis followed by spark plasma sintering. The structural and compositional characterizations indicated highly densified High pressure synthesized samples showed greatly enhanced thermoelectric performance compared with ambient-pressure synthesized ones. As a result, the highest ZT of 0.94 was achieved at 873 $\Box$ K.

Pawel, N. et al. (2019) studied the influence of Mg excess on the physicochemical properties with particular emphasis on thermoelectric properties of synthesized Mg<sub>2</sub>Si. Samples with 0-10 wt% of excessive Mg were prepared using the Spark Plasma Sintering (SPS) method. The experiments performed, allow

concluding that Mg excess which is in the liquid phase during the sintering process gathers mostly at the grain boundaries, enhancing the sintering process and decreasing the total porosity of the samples. Moreover, higher Mg content increases the electrical and thermal conductivity of Mg2<sub>s</sub>i, which causes a simultaneous decrease of the Seebeck coefficient.





Figure 15 Schematic illustrations of layered cobalt–based oxide structures  $CoO_2$  layers consisting of edge–shared  $CoO_6$  octahedral exist  $Ca_3Co_4O_9$  (Ohta, H., Sugiura, K., & Koumoto, K., 2008).

 $Ca_3Co_4O_9$  has a misfit-layered structure with a  $Cdl_2$ -type hexagonal  $CoO_2$  subsystem and a rock salt-type  $Ca_2CoO_3$  subsystem that are alternately stacked along the c-axis with identical a, c and parameters but different and incommensurate b parameters. Therefore, this misfit-layered oxide can be described as  $[Ca_2CoO_3]$   $[CoO_2]_{(b1/b2)}$  with a b1 to b2 ratio of approximately 1.62, where b1 to b2 are two lattice parameters for the rock salt and  $CoO_2$  subsystems respectively (Masset et al., 2000; Miyazaki et al., 2002). Shikano et al. have reported a p-type single-crystalline  $Ca_3Co_4O_9$  with a ZT value of 0.83 at 800 (Shikano & Funahashi, 2003). The methods

to produce polycrystalline  $Ca_3Co_4O_9$  are versatile and are commonly implemented due to the difficulty in single-crystalline sample preparation. Different  $Ca_3Co_4O_9$  syntheses and consolidation processes result in the inferences on the consequent texturing and densification, further affecting the TE properties.

Van Nong, et al. (2011) were studied that particle size is another factor that affects texturing; with the same consolidation process, highly textured  $Ca_3Co_4O_9$ can be obtained by smaller  $Ca_3Co_4O_9$  particles prepared through wet chemical reactions. Other than the TE properties, the consolidation process also exerts influence on the mechanic properties.

Wu et al. (2014) reported that highly dense polycrystalline  $Ca_3Co_4O_9$  can be obtained via a spark plasma sintering (SPS) processing with proper SPS conditions, the electrical conductivity may be enhanced. Due to the layered nature of the crystal structure, it is important to take into account the inherent anisotropy due to texturing when characterizing the TE properties of polycrystalline samples. Improving the texturing leads to the increase in "in–plane" electrical conductivity and larger power factor, however, the thermal conductivity increases simultaneously since the loss of structural disorder.

Tian et al. (2014) prepared co-doping Bi and Fe Ca<sub>3-x</sub>Bi<sub>x</sub>Co<sub>4-y</sub>Fe<sub>y</sub>O<sub>9+</sub>  $\delta$ (x =0, y =0; x = 0.3, y =0; x = 0.3, y = 0.1) by SSR and followed by a spark plasma sintering (SPS) method. They reported that Bi substitution leads up to 40% reduction in the thermal conductivity, which is mainly associated with doping-induced point defect phonon scattering. In addition, the power factor was found to be increased by  $\approx$ 33% by the co-doping of Fe and Bi. In present study, the thermoelectric figure of merit achieves  $\approx$ 0.4 at 973 K by the co-doped sample Ca<sub>2.7</sub>Bi<sub>0.3</sub>Co<sub>3.9</sub>Fe<sub>0.1</sub>O<sub>9+</sub>  $\delta$ .

Cho et al. (2015) prepared  $Ca_{3-x}Bi_xCo_4O_9$  (x =0, 0.025, 0.05, 0.1, 0.15, 0.2) by SSR method. They reported that the Seebeck coefficient increased with increasing Bi content due to the decrease in the hole carrier concentration after Bi doping. As the amount of Bi was increased, the electrical resistivity initially decreased but then increased with further addition of Bi.

Lin et al. (2016) prepared  $Ca_3Co_4O_9$  small amounts of silver nanoparticles (AgNPs) by SSR and followed by a spark plasma sintering (SPS) method. They reported that achieve a lower thermal conductivity due to the increased phonon scattering, decreasing from 3.1 Wm<sup>-1</sup>K<sup>-1</sup>(Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>) to 1.6 Wm<sup>-1</sup>K<sup>-1</sup> (AgNPs/ Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>) at 700 K. Besides, the nano–sized AgNPs effectively strengthen the p–type Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> grain orientation (from 0.5 to 0.7), leading to a significant enhancement of the electrical conductivity. As a result, the Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> sample containing 2.0 vol% AgNPs exhibits an exceedingly enhanced ZT value ≈0.1 at 700 K, which is about 5 times higher than that of pure bulk Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>.

Ohtaki, et al (2017) reported with Lu and Ag substitutions for Ca atom and the existence of Ag as nanoparticle, the electrical conductivity and Seebeck coefficient can be elevated significantly; together with the decreased thermal conductivity, the highest ZT value of 0.6 at about 900 K for polycrystalline  $Ca_3Co_4O_9$  to date has been achieve. Besides, along with the demonstration of the thermal stability, heavily doped  $Ca_3Co_4O_9$  with metallic nanoinclusions has presented the potential for high temperature TE applications. The methods to produce polycrystalline  $Ca_3Co_4O_9$  are versatile and are commonly implemented due to the difficulty in single–crystalline sample preparation. Different  $Ca_3Co_4O_9$  syntheses and consolidation processes result in the inferences on the consequent texturing and densification, further affecting the TE properties.  $Zn_{0.98}AI_{0.02}O$ 



Figure 16 Crystal structure of  $Zn_{0.98}Al_{0.02}O$  Red ball =0 and purple ball = Z (https://materialsproject.org/materials/mp-2133/)

Zn<sub>0.98</sub>Al<sub>0.02</sub>O thermoelectric material has shown a high Seebeck coefficient and low thermal conductivity. Nevertheless, the dimensionless figure of merit (ZT) value is quite low because of its high resistivity. ZnO there are 3 types of crystal structures namely cubic rock salt, cubic zinc blende lattice parameter a=b=c, and hexagonal wurtzite lattice parameters a=b and c (P. J. P. Espitia, et al. 2012). ZnO is a wide-bandgap semiconductor of the II-VI semiconductor group. The native doping of the semiconductor due to oxygen vacancies or zinc interstitials is n-type (Özgür Ü, et al 2005) other favorable properties include good transparency, high electron mobility, wide bandgap, and strong room-temperature luminescence. ZnO system is shown ntype and p-type depends on added material dopants such as aluminum, indium, and gallium for n-type (M. Yuichi, et al. 2017). While material doping for the p-type ZnO includes copper, lithium, and co-doping between magnesium with nitrogen (K. Kobayashi, et al. 2012). Zn<sub>0.98</sub>Al<sub>0.02</sub>O thermoelectric material shows a high electrical performance that can be sufficiently competitive to conventional materials such as PbTe, BiTe. However, the overall performance of the oxide has been only about 30 percent of the practical requirement (M. Ohtaki, et al., 2011).

CHRISTIAN, D. et al (2016) reported the Effect of Carbon Nanotubes on Thermoelectric Properties in  $Zn_{0.98}Al_{0.02}O$ . The preparation of the MW–CNT–added AZO was done using an ultrasonic mixing of the starting materials followed by a spark plasma sintering process under vacuum. The Seebeck coefficient S, thermal conductivity k, and electrical conductivity r were determined in the temperature range between 300 K and 900 K. It was observed that the thermal conductivity is significantly reduced by the incorporation of the MW–CNT. At the same time, the electrical conductivity is increased by a factor of 21 from 8700 S/m to 190,000 S/m.

Joshua, H. et al. (2016) reported the microstructure and thermoelectric properties of MnAl co-doped ZnO ceramics have been analyzed and clear trends related to Mn doping were observed. Al-doping leads to a microstructure with fine spinel precipitates (ZnAl<sub>2</sub>O<sub>4</sub>). Thermoelectric properties reveal a trend of increasing resistivity for increasing Mn doping. A transition from a metallic conductivity behavior for the Al-doped sample to an increasingly semiconducting behavior with increasing Mn doping was observed. The Seebeck coefficient increased in absolute value only at significant (10 at%) Mn dopant levels, caused by a high volume of spinel precipitates or increased low energy carrier scattering at high potential barrier grain boundaries. Overall, the power factor and ZT of ZnO were reduced with increasing Mn doping due to the increase in resistivity.

S. Jantrasee et al., (2016) Have prepared Thermoelectric properties of Al–doped ZnO: experiment and simulation. In this work, the effects of Al–doping in a ZnO system on the electronic structure and thermoelectric properties are presented, by experiment and calculation. Nanosized powders of Zn1<sub>x</sub>Al<sub>x</sub>O (x D 0; 0:01; 0:02; 0:03 and 0.06) were synthesized by hydrothermal method. The enhanced thermoelectric properties of Zn1<sub>x</sub>Al<sub>x</sub>O (x D 0.0, 0.01, 0.02, 0.03 and 0.06) were investi–gated from the nanoparticles of the wurtzite structure synthe–sized by hydrothermal method. The resultant ZT ~0.28 of 3% Al–doped ZnO expected at 400 °C is two orders of magnitude higher than pure ZnO at the same temperature.

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Hsuan-Ta Wu, et al. (2019) reported the thermoelectric properties of the Al-doped ZnO (AZO)/silicon-rich oxide (SRO) superlattices. The thermoelectric figure of merit (ZT) as functions of the grain size, thickness of the superlattices, the number of SRO layers, and conductance were studied. The use of the SRO layers markedly improved the thermoelectric ZT. Moreover, the replacement of ZnO by AZO further increased the ZT. The ZT value of the AZO/SRO superlattices was as high as 0.44 when the total thickness was 45 nm and three SRO interlayers were inserted. The improvement of ZT was contributed by the reduction of the grain size, formation of the Si nanocrystals, and the increase in the electrical conductance caused by using SRO interlayers and Al doping.

### THERMOELECTRIC MODULE

Thermoelectric generators (TEGs) are devices that convert temperature differences into electrical energy, which work on the thermoelectric phenomena known as the Seebeck effect. The thermoelectric phenomena have widely been used for heating and cooling applications, however electric power generation has only been limited to niche applications e.g., thermoelectric power generators for space missions. TEG provides one of the cleanest energy conversion methods, which is noise–free, virtually maintenance–free, and can continuously produce power for several years under ambient conditions. In recent years, energy generation through thermoelectric harvesting has witnessed an increased interest for various applications, including tapping waste heat from the exhaust of vehicles, from industries, etc. The development of an efficient TEG requires the fulfillment of several factors, which includes the availability of n–and p–type thermoelectric materials with high figure–of–merit (ZT), preparation of ohmic contacts between thermoelements and metallic interconnects, and management of maximum heat transfer through the device (Aswal, Basu, Singh, 2016).

Emina, et al. (2015) reported the results of the experimental investigation of n-type semiconductors based on  $Bi_2Te_3$  alloy were presented. This material is used in the manufacture of thermoelectric coolers and electrical power generation devices.  $Bi_2Te_{2.88}Se_{0.12}$  solid solution single crystal has been grown using the Czochralski method. The Vickers microhardness values are in the range between HV 187 and HV 39.02 and decrease with load increasing. It is shown that a very complex process of infrared thermography can be applied for the characterization of thermoelectric elements and modules.



Figure 17 Thermoelectric module by  $Bi_2Te_3$  and  $Bi_2Te_{2.88}Se_{0.12}$  materials

Skomedal, et al. (2016) were reported power generation of thermoelectric module fabricating from p-MnSi<sub>1.75</sub>Ge<sub>0.01</sub> and n-Mg<sub>2</sub>(Si<sub>0.4</sub>Sn<sub>0.6</sub>)<sub>0.99</sub>Sb<sub>0.01</sub>. The construction of the module is shown in figure 18. The initial resistance of module at room temperature was above 8  $\Omega$  but decreased rapidly as it was heated up to higher hot side temperatures. The decrease corresponds to the formation of a diffusion bond between the hot side electrode and the *n*-and *p*-type elements. As can be seen, resistance was reduced to a minimum value of 0.1  $\Omega$  at around 873 K. The hot side temperature was further ramped up to 1008 K were a maximum power of 3.24 W was measured under load-matching conditions and used the modeling tool COMSOL to estimate efficiencies at 1008 K and obtained values of 5.3%.



Figure 18 Sketch of unicouple with metallization and contact layers

Karina, et al. (2015) were fabricated TE module using n-type Mg<sub>2</sub>(Si,Sn) and p-type MnSi. TE samples were coated with nickel (1  $\mu$ m) by sputtering. Legs for TE modules were cut from the PECS wafers, with a length of 3 mm and cross section of 5 mm × 5 mm. Modules were assembled by connecting these TE legs to an Al<sub>2</sub>O<sub>3</sub> substrate with nickel-plated copper electrodes. The legs, brazing material, and substrate were arranged and then rapidly heated at 550 °C for one hour in an inert atmosphere using a homemade brazing setup. A TE module consisting of 31 pairs of TE legs is depicted in figure 19.



Figure 19 TE module with 31 pairs of thermoelectric legs and a base area of  $50 \times 50$  mm.

Choi et al. (2011) fabricated thermoelectric module 44 pairs composed of ptype Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and n-type (ZnO)<sub>7</sub>In<sub>2</sub>O<sub>3</sub> legs were constructed using Ag paste. The maximum power obtained was 423 mW, under the thermal condition of a hot-side temperature of 1100 K and a temperature difference  $\Delta T = 673$  K. The thermoelectric figure of merit values of the p-type and n-type legs at 1100 K were 0.55 x 10<sup>-4</sup>K<sup>-1</sup> and 1.35 x 10<sup>-4</sup> K<sup>-1</sup>, respectively.



Figure 20 Photograph of the oxide thermoelectric module for power generation measurements with eight p–n couples, taken after several power generation measurements

Park and Lee, (2013) fabricated thermoelectric modules of  $\prod$ -shaped 1-, 2-, and 4-pairs composed of p-type Ca<sub>2.76</sub>Cu<sub>0.24</sub>Co<sub>4</sub>O<sub>9</sub> and n-type Ca<sub>0.8</sub>Dy<sub>0.2</sub>MnO<sub>3</sub> oxide materials were constructed using Ag paste. The output powers of -, 2-, and 4-pairs increase with an increase in temperature difference  $\Delta$ T between the hot- and cold-side temperatures of the modules show in Figure 18 (right).



Figure 21 Photographs of four-pair ∏-shaped thermoelectric modules with Ag electrode (left) and maximum output powers of 1-, 2-, and 4-pair modules as a function of hotside temperature (right)

Paolo Mele, et al. (2014) reported the development of a Thermoelectric Module Based on Dense Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and Zn<sub>0.98</sub>Al<sub>0.02</sub>O Legs. The materials were prepared by conventional sintering (CS) and Spark Plasma sintering (SPS). The results are the output power of a module based on SPS Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and CS Zn<sub>0.98</sub>Al<sub>0.02</sub>O legs were 2.26 MW (with T = 500 °C,  $\Delta$ T = 248 °C).



Figure 22 (a) Picture of the module constituted by 6 couples of  $Zn_{0.98}Al_{0.02}O/Ca_3Co_4O_9$ (b) schematic representation of the arrangement for the experimental check.

Gunstein, S. et al. (2017) were tested oxide unicouple thermoelectric modules. they have assembled several thermoelectric modules made by pyrolyzed and spark plasma sintered n-type Ca $MnO_3$  and p-type Ca $_3Co_4O_9$  and then tested under different conditions mimicking end-user applications. A maximum specific power output of 56 mW/cm<sup>2</sup> with a temperature difference of 760°C was obtained. Cycling tests between 400 to 800°C during a period of 1 week showed a reduction in power output of more than 50% mainly due to crack-formation and oxidation near the nickel/oxide interface.



Figure 23 (a) Picture of test set-up with connections and insulating plate covering the module above the water-cooled Cu-block. (b) Sketch of module cross-section and test assembly with temperature measurement points  $(T_{H,n}, T_{H,p}, TC)$
## APPLIDATION OF THERMOELECTRIC GENERATORS

Thermoelectric generators can help to reduce the adverse effects of global warming by generating the electricity by harvesting waste heat which is a by-product of industries, automobile engines and solar power. These freely available sources of waste heat are the main driving force behind the development of commercial TEGs for electricity generation. Several leading automobile manufacturers are developing TEG (having electrical power of 1 kW) for waste heat recovery to improve the fuel economy of their automobiles (Elsheikh et al., 2014). Despite of low TEG efficiency, diligent harvesting of waste heat from resources such as automobile exhausts via judicious design and fabrication methods render TEGs as a worthwhile technology for the automobile manufacturers. A TEG with an efficiency of  $\approx 10\%$  could be used to harvest 35–40% of the energy from the exhaust pipe (having average temperature of  $\approx$ 523 K) to generate useable power that would contribute directly to the operation of the equipped vehicle, which could increase fuel efficiency by up to 16% (Yu., & Chau, 2009). In a recent study, 1 kW TEG system (based on n- and p-type half Heuslers) is experimentally demonstrated by recovering the exhaust waste heat from an automotive diesel engine. The TEG exhibited an efficiency of  $\approx 2.1\%$  with  $\Delta T$  of 340 K and exhaust temperature (T<sub>h</sub>) 823 K (Zhang et al., 2015). In oxide thermoelectric module application was used 140 pairs of oxide legs. Generating power up to 0.15 W was succeeded. This module shows excellent resistance to repeated heating and cooling in air because of using Ag paste incorporated the oxide powder. A lithium-ion battery in a portable phone can be charged using this module at  $T_{\rm h}$  higher than 723 K. Power generating modules fabricated using oxide thermoelectric materials could facilitate a revolution in small power sources for mobile devices or automobiles and, moreover, enable recovery of waste heat in the form of electrical energy from sources such as factories and incinerators (Funahashi et al., 2006).

Goudarzi et al., (2013) constructed thermoelectric generator system by using commercial 21 module size of 56 mm x 56 mm for produce electricity from wood stove. The maximum output power 14.7 W at  $\Delta$ T 452 K (T<sub>h</sub>= 773 K) to fulfill the basic needs of domestic electricity, hot water, and essential heat for warming the room and cooking.



Figure 24 Water cooling system and integration thermoelectric module on wood stove

O'Shaughnessy et al., (2013) developed a prototype electrical generator for portable stoves commonly in use in the developing world. They reported that a single thermoelectric module is utilized to convert a small portion of heat from the stove to electricity. The electricity produced is used to charge a single 3.3 V lithium– iron phosphate battery and drive a low power fan, as well as some other auxiliary features. A maximum TEG power output of 5.9 W has been obtained. On average, 3 W h of energy was stored in a battery during a typical 1 h long burn. Three 1 h long burns produced sufficient energy to fully charge the battery.



Figure 25 The prototype stoves(left) and power generation depend temperature(right)

S. MahmoudiNezhad, et al. (2020) were reported the performance of Bi<sub>2</sub>Te<sub>3</sub> and Zn<sub>4</sub>Sb<sub>3</sub> solar thermoelectric generators (STEGs) are studied under transient conditions using both experimental and numerical approaches. Variation of the temperatures of the hot and cold sides of the TEGs, open-circuit voltage, short circuit current, and maximum power generation to the fluctuation of the solar radiation, simulating semi-cloudy weather, are obtained and discussed. The results show that the hot and cold side temperatures of the STEGs and the electrical output power are affected by the sharp fluctuations of solar radiation. It is found that, by applying an identical solar radiation pattern, the graphite layer increases the power generation and the efficiency of the STEGs by 2.5 times.



Figure 26 (a) Schematic of the experimental setup (b) solar simulator used in this study.

# CHAPTER 3

# MATERIALS AND METHODOLOGY

This chapter presents the detail of the synthesis of all samples which were synthesized by the Hot–pressing method, crystal structure analysis, microstructure analysis, thermoelectric properties measurement, thermoelectric device fabrication, thermoelectric power generation for low temperature, medium temperature, and high temperature shown in Figure 27.



Figure 27 Diagram of methodology.

# SYNTHESIS AND PREPARATION THERMOELECTRIC MATERIALS

# Synthesis $Sb_2Te_3$ and $Bi_2Te_3$ thermoelectric materials for low temperature

The  $Sb_2Te_3$  and  $Bi_2Te_3$  materials were synthesized by planetary ball mill and hot-pressing method. Which chemicals powder and equipment used in this process are shown in Table 1 and Table 2, respectively.

Table 1 List of chemicals used for synthesized by planetary ball mill and hot–pressing method their symbol, supplier, and purity of low temperature

Chemical	Symbol	Supplier	Purity
Antimony	Sb	Sigma–Aldrich	99.5%
Bismuth	Bi	Sigma–Aldrich	99%
Tellurium	Те	Sigma–Aldrich	99.8%

Table 2 List of equipment used for synthesis of powder, preparation of bulk,

characterization and measurement of thermoelectric properties together with their model and area of application.

Equipment	Model	Application
planetary ball mill	planetary ball mill PM400	Mixing and milling of
	RETSCH	powders
Ultra-sonic cleaner	BAKU BK-3350	Cleaning of materials
Hot plate & stirrer	Vision vs–130SH	Drying of wet powders
Weight scale	METTLER TOLEDO	Weighing compound
Hot press	OTF-1200	Pressing and sintering of
		pellets
Saw low speed	BUEHLER Isomet	Cutting of materials
Grinder-Polisher	BUEHLER Metaseve 3000	Grinding–Polishing of
		materials
XRD	SHIMADZU-6100	Study phases composition
FE-SEM	JSM-7610FPlus (JEOL)	Study microstructure and
		phases composition
Density kit	METTLER TOLEDO MS204	Measure density of
		materials
ZEM-3	ZEM-3(M10)	Measure Seebeck coefficient
		and electrical resistivity of
		materials
Laser Flash Apparatus	LFA 457 MicroFlash®	Measure Thermal Diffusivity
		and Thermal Conductivity
		Method, Techniques and
		Applications

# $Sb_2Te_3$

The Sb<sub>2</sub>Te<sub>3</sub> precursors were prepared from bismuth powder (Sb; 99.5%, Sigma–Aldrich) and tellurium powder (Te; 99.8%, Sigma–Aldrich) then the powders were weighed in proper stoichiometric amounts. The precursor powder was mixed by planetary ball mill (planetary ball mill PM400 RETSCH) in agate grinding jar sizes 500 ml with using 5 mm diameter agate balls with the ball– per–powder 18 balls for 10 g at 350 rpm for 10 h next to step Sb<sub>2</sub>Te<sub>3</sub> powder was pellets under a uniaxial hot pressing at 723 K and 60 MPa for 2 h in Ar atmosphere on an alumina cup by using heat rate 5 K/min as shown in Figure 28, and schematic of a heating program for hot pressing as shown in Figure 29.



Figure 28 The step detail of Sb<sub>2</sub>Te<sub>3</sub> material synthesis



Figure 29 Schematic of heating program for hot pressing of  $Sb_2Te_3$  dense bodies used for all samples in Ar gas 0.08 MPa

Sb<sub>2</sub>Te<sub>3</sub> crystal structure was characterized by X-ray diffraction technique from 10° to 80° step 0.02° in 1 s, and 20 angle with CuK $\alpha$ -1 ( $\lambda$  = 1.541 Å) at 40 kV and 30 mA, radiation utilizing a Shimadzu diffractometer, XRD-6100 at room temperature. The microstructure was obtained from scanning electron microscopy, JSM-7610FPlus (JEOL). The bulk Sb<sub>2</sub>Te<sub>3</sub> with size 3 × 3 × 15 mm<sup>3</sup> was cut for measurement of the Seebeck coefficient and electrical resistivity by ZEM-3(M10) was gauged at room temperature to 523 K. The sample size diameter 9.5 mm thickness 1 mm for measurement thermal diffusivity measured by the laser flash method using a Netzsch LFA-457 apparatus use was gauged at room temperature to 523 K.

# $Bi_2Te_3$

The Bi<sub>2</sub>Te<sub>3</sub> precursors were prepared from bismuth powder (Bi; 99%, Sigma–Aldrich) and tellurium powder (Te; 99.8%, Sigma–Aldrich) then the powders were weighed in proper stoichiometric amounts. The precursor powder was mixed by planetary ball mill (planetary ball mill PM400 RETSCH) in agate grinding jar sizes 500 ml with using 5 mm diameter agate balls with the ball– per–powder 18 balls for 10 g at 350 rpm for 10 h next to step  $Bi_2Te_3$  powder was pellets under a uniaxial hot pressing at 723 K and 60 MPa for 2 h in Ar atmosphere on an alumina cup by using heat rate 5 K/min as shown in Figure 30, and schematic of a heating program for hot pressing as shown in Figure 31.



Figure 30 The step detail of Bi<sub>2</sub>Te<sub>3</sub> material synthesis



Figure 31 Schematic of heating program for hot pressing of  $Bi_2Te_3$  dense bodies used for all samples in Ar gas 0.08 MPa

Bi<sub>2</sub>Te<sub>3</sub> crystal structure was characterized by X–ray diffraction technique from 20° to 70° step 0.02° in 1 s, and 2 $\theta$  angle with CuK $\alpha$ –1 ( $\lambda$  = 1.541 Å) at 40 kV and 30 mA, radiation utilizing a Shimadzu diffractometer, XRD–6100 at room temperature. The microstructure was obtained from scanning electron microscopy, JSM–7610FPlus (JEOL). The bulk Bi<sub>2</sub>Te<sub>3</sub> with size 3 × 3 × 15 mm<sup>3</sup> was cut for measurement of the Seebeck coefficient and electrical resistivity by ZEM–3(M10) was gauged at room temperature to 523 K. The sample size diameter 9.5 mm thickness 1 mm for measurement thermal diffusivity measured by the laser flash method using a Netzsch LFA–457, apparatus use was gauged at room temperature to 523 K.

# Synthesis MnSi<sub>1.75</sub> and Mg<sub>2</sub>Si thermoelectric materials for medium temperature

The  $MnSi_{1.75}$  and  $Mg_2Si$  materials were synthesized by planetary ball mill and hot-pressing method which chemicals powder and equipment for used in this process are shown in Table 3 and Table 2, respectively.

Table 3 chemicals used for synthesized by planetary ball mill and hot-pressing method their symbol, supplier, and purity of medium temperature.

Chemical	Symbol	Supplier	Purity
Manganese	Mn	Sigma–Aldrich	99%
Magnesium	Mg	Sigma–Aldrich	99%
Silicon	Si	Sigma–Aldrich	99%

## $MnSi_{1.75}$

The MnSi<sub>1.75</sub> precursors were prepared from Manganese powder (Mn; 99%, Sigma–Aldrich) and Silicon powder (Si; 99%, Sigma–Aldrich) then the powders were weighed in proper stoichiometric amounts. The precursor powder was mixed by planetary ball mill (planetary ball mill PM400 RETSCH) in agate grinding jar sizes 500 ml with using 5 mm diameter agate balls with the ball– per–powder 18 balls for 10 g at 350 rpm for 12 h next to step MnSi<sub>1.75</sub> powder was pellets under a uniaxial hot pressing at 1173 K and 60 MPa for 1 h in an Ar atmosphere on an alumina cup by using heat rate 5 K/min as shown in Figure 32, and schematic of a heating program for hot pressing as shown in Figure 33.



Figure 32 The step detail of  $\text{MnSi}_{1.75}$  material synthesis



Figure 33 Schematic of heating program for hot pressing of  $MnSi_{1.75}$  dense bodies used for all samples in Ar gas 0.08 MPa

MnSi<sub>1.75</sub> crystal structure was characterized by X–ray diffraction technique from 20° to 60° step 0.02° in 1 s, and 2 $\theta$  angle with CuK $\alpha$ –1 ( $\lambda$  = 1.541 Å) at 40 kV and 30 mA, radiation utilizing a Shimadzu diffractometer, XRD–6100 at room temperature. The microstructure was obtained from scanning electron microscopy, JSM–7610FPlus (JEOL). The bulk MnSi<sub>1.75</sub> with size 3 × 3 × 15 mm<sup>3</sup> was cut for measurement of the Seebeck coefficient and electrical resistivity by ZEM–3(M10) was gauged at room temperature to 773 K. The sample size diameter 10 mm thickness 1 mm for measurement thermal diffusivity measured by the laser flash method using a Netzsch LFA–457 apparatus use was gauged at room temperature to 773 K.

#### $Mg_2Si$

The Mg<sub>2</sub>Si precursors were prepared from Magnesium powder (Mg; 99%, Sigma–Aldrich) and Silicon powder (Si; 99%, Sigma–Aldrich) then the powders were weighed in proper stoichiometric amounts. The precursor powder was mixed by planetary ball mill (planetary ball mill PM400 RETSCH) in agate grinding jar sizes 500 ml with using 5 mm diameter agate balls with the ball– per–powder 18 balls for 10 g at 350 rpm for 12 h next to step Mg<sub>2</sub>Si powder was pellets under a uniaxial hot pressing at 1023 K and 60 MPa for 1 h in an Ar atmosphere on an alumina cup by using heat rate 5 K/min as shown in Figure 34, and schematic of a heating program for hot pressing as shown in Figure 35.



Figure 34 The step detail of  $Mg_2Si$  material synthesis



Figure 35 Schematic of heating program for hot pressing of  $Mg_2Si$  dense bodies used for all samples in Ar gas 0.08 MPa

Mg<sub>2</sub>Si crystal structure was characterized by X–ray diffraction technique from 20° to 60° step 0.02° in 1 s, and 20 angle with CuK $\alpha$ –1 ( $\lambda$  = 1.541 Å) at 40 kV and 30 mA, radiation utilizing a Shimadzu diffractometer, XRD–6100 at room temperature. The microstructure was obtained from scanning electron microscopy, JSM–7610FPlus (JEOL). The bulk Mg<sub>2</sub>Si with size 3 × 3× 15 mm<sup>3</sup> was cut for measurement of the Seebeck coefficient and electrical resistivity by ZEM–3(M10) was gauged at room temperature to 773 K. The sample size diameter 10 mm thickness 1 mm for measurement thermal diffusivity measured by the laser flash method using a Netzsch LFA–457 apparatus use was gauged at room temperature to 773 K.

# Synthesis $Ca_3Co_4O_9$ and $Zn_{0.98}Al_{0.02}O$ thermoelectric materials for high temperature

The  $Ca_3Co_4O_9$  and  $Zn_{0.98}Al_{0.02}O$  materials were synthesized by planetary ball mill and hot-pressing method which chemicals powder and equipment for used in this process are shown in Table 4 and Table 2, respectively.

Table 4 chemicals used for synthesized by planetary ball mill and hot-pressing method their symbol, supplier, and purity of high temperature.

Chemical	Symbol	Supplier	Purity
Calcium carbonate	CaCO <sub>3</sub>	Sigma–Aldrich	99%
Cobalt oxide	$Co_3O_4$	Sigma–Aldrich	99.5%
Zinc oxide	ZnO	QRëC™.	95%
Aluminium oxide	$AI_2O_3$	Ajax Finechem	95%
		Pty Ltd.	

# Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>

The  $Ca_3Co_4O_9$  precursors were prepared from Calcium carbonate powder (CaCO<sub>3</sub>; 99%, Sigma–Aldrich) and Cobalt oxide powder (Co<sub>3</sub>O<sub>4</sub>; 99.5%, Sigma– Aldrich) then the powders were weighed in proper stoichiometric amounts. The precursor powder was mixed by planetary ball mill (planetary ball mill PM400 RETSCH) in agate grinding jar sizes 500 ml with using 5 mm diameter agate balls with the ball-per-powder 18 balls for 10 g at 350 rpm for 5 h next to step  $Ca_3Co_4O_9$  powder was calcined at 1073 K 10 h in air, then pellets under a uniaxial hot pressing at 1123 K and 60 MPa for 1 h in an Ar atmosphere on an alumina cup by using heat rate 5 K/min, after that as-deposited  $Ca_3Co_4O_9$  bulk sample was annealed at 1023 K/5 h in air as shown in Figure 36, and schematic of a heating program for hot pressing as shown in Figure 37.



Figure 36 The step detail of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> material synthesis



Figure 37 Schematic of heating program for hot pressing of  $Ca_3Co_4O_9$  dense bodies used for all samples in Ar gas 0.08 MPa

Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> crystal structure was characterized by X–ray diffraction technique from 10° to 80° step 0.02° in 1 s, and 2 $\theta$  angle with CuK $\alpha$ –1 ( $\lambda$  = 1.541 Å) at 40 kV and 30 mA, radiation utilizing a Shimadzu diffractometer, XRD–6100 at room temperature. The microstructure was obtained from scanning electron microscopy, JSM–7610FPlus (JEOL). The bulk Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> with size 3 × 3× 15 mm<sup>3</sup> was cut for measurement of the Seebeck coefficient and electrical resistivity by ZEM–3(M10) was gauged at room temperature to 1023 K. The sample size diameter 9.5 mm thickness 1 mm for measurement thermal diffusivity measured by the laser flash method using a Netzsch LFA–457 apparatus use was gauged at room temperature to 1023 K.

# $Zn_{0.98}AI_{0.02}O$

The  $Zn_{0.98}Al_{0.02}O$  precursors were prepared from Zinc oxide powder (ZnO; 95%, QRëC <sup>TM</sup>.) and Aluminium oxide powder (Al<sub>2</sub>O<sub>3</sub>; 95%, Ajax Finechem Pty Ltd) then the powders were weighed in proper stoichiometric amounts. The precursor powder was mixed by planetary ball mill (planetary ball mill PM400 RETSCH) in agate grinding jar sizes 500 ml with using 5 mm diameter agate balls with the ball–per–powder 18 balls for 10 g at 350 rpm for 24 h next to step  $Zn_{0.98}Al_{0.02}O$  powder was calcined at 773 K 5 h in air, then  $Zn_{0.98}Al_{0.02}O$  powder was pellets under a uniaxial hot pressing at 1173 K and 60 MPa for 1 h in an Ar atmosphere on an alumina cup by using heat rate 5 K/min, after that as–deposited  $Zn_{0.98}Al_{0.02}O$  bulk sample was annealed at 923 K / 5 h in air as shown in Figure 38, and schematic of a heating program for hot pressing as shown in Figure 39.



Figure 38 The step detail of Zn<sub>0.98</sub>Al<sub>0.02</sub>O material synthesis



Figure 39 Schematic of heating program for hot pressing of  $Zn_{0.98}AI_{0.02}O$  dense bodies used for all samples in Ar gas 0.08 MPa

Zn<sub>0.98</sub>Al<sub>0.02</sub>O crystal structure was characterized by X–ray diffraction technique from 30° to 80° step 0.02° in 1 s, and 2 $\theta$  angle with CuK $\alpha$ –1 ( $\lambda$  = 1.541 Å) at 40 kV and 30 mA, radiation utilizing a Shimadzu diffractometer, XRD–6100 at room temperature. The microstructure was obtained from scanning electron microscopy, JSM–7610FPlus (JEOL). The bulk Zn<sub>0.98</sub>Al<sub>0.02</sub>O with size 3 × 3× 15 mm<sup>3</sup> was cut for measurement of the Seebeck coefficient and electrical resistivity by ZEM–3(M10) was gauged at room temperature to 1023 K. The sample size diameter 10 mm thickness 1 mm for measurement thermal diffusivity measured by the laser flash method using a Netzsch LFA–457 apparatus use was gauged at room temperature to 1023 K.

#### Hot pressing (HP) method

Hot pressing sintering (HP) is expected to be used increasingly to prepare high density and decreased micro-cracking of materials. The schematic view of the HP machine and the main unit is shown in Figure 40. The system of HP OTF-1200 included a furnace for the heating unit outside and a chamber quartz tube for the control the atmosphere. The graphite punches up from hydraulic on the bottom plate when graphite rods on top of the mold is pulled up and pressed with rods graphite top, it will cause the pressure within the mold to compound powder. The calcined powder of samples was compressed in a graphite die diameter 20 mm to pellet



Figure 40 Schematic view of hot press machine and working chamber

In the present study, the HP process was carried out using an OTF-1200x-VHP-4 high-temperature vacuum hot press. The powder was filled in cylindrical graphite die with 20 mm inner diameter and pressed by using two graphite punches at 60 MPa. Before filling powder into the die, a mica was placed at the bottom of the die, and filled with powder using mica for the top powder. The high temperature was used for sintering powder. Then the graphite die with press powder was placed into a graphite punch and installed into the vacuum chamber.

## CHARACTORIZATION TECHNIQUES

### X-ray diffraction

X-ray diffraction (XRD) analysis was used to establish phase identification for crystalline material and can provide information on crystal structure such a at unit cell. XRD used scattering and diffraction technique from x-ray are generated by a cathode ray tube then the x-ray is filtered before toward to sample. The diffraction pattern from XRD based on Bragg's law shown in Figure 41 (a).

$$2d\sin\theta = n\lambda \tag{3.1}$$

Where d is the lattice spacing in the crystal sample,  $\theta$  is the angle between the incident beam and the atomic plane,  $\lambda$  is the wavelength of electromagnetic radiation from source, *n* is an integer corresponding to the order of diffraction. The radiation from sample was detected and counted. Due to the random orientation of the sample materials, all possible diffraction directions of the lattice should be attained by scanning the sample through a range of  $2\theta$  angle shown in Figure 41 (b). Since most materials have unique diffraction patterns, compounds can be identified by using a database of diffraction patterns. All images presented in this thesis were taken with SHIMADZU XRD-6100.



Figure 41 (a) X-ray diffraction and (b) construction of an X-ray diffractometer

The X-ray diffraction (XRD, Shimadzu, XRD-6100) measurements was performed on Center of Excellence on Alternative Energy at Sakon Nakhon Rajabhat University, Thailand as shown in Figure 42. The crystal structure was analyzed by Xray diffractometer by using Cu-K $\alpha$ 1 radiation at room temperature ( $\lambda$ = 1.5406 Å) in scan range 20–80 degree of 2 $\theta$  for 2 deg/min of scan speed with 0.02 of sampling pitch.



Figure 42 X–ray diffractometer of Center of Excellence on Alternative Energy at Sakon Nakhon Rajabhat University

#### Microstructure analysis

The microstructure of bulk samples was analyzed by scanning electron microscope JSM-7610FPlus (JEOL) shown in Figure 43(a) and the sample preparation is shown in Figure 43(b). Scanning electron microscopy (SEM) was used to investigate the three dimensions of microstructure and sample composition. During analysis, the electron source is excited by high voltage, and the resulting electron beam is focused on an electron scan at or near the surface of the sample and produces an image. This produces several different signals and the ones that were used for analysis. Firstly, secondary electrons (SE) - result in the excitation and replacement of outside shell electrons by the primary electrons enabling use to view the microstructure of the sample. Secondly, backscatter electrons (BSE) – inelastically scattered primary electrons. The energy loss is dependent on the weight of surface atoms electrons are interacting with giving an image of phase segregation. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). The SEM is also the characteristic xrays used in energy dispersive spectroscopy (EDS or EDX) – produced from excitation by the primary electron beam and enable users to see the phase composition by determining its chemical composition.



Figure 43 (a) scanning electron microscope JSM-7610FPlus (JEOL) (b) the sample preparation

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#### Extensibility: Energy Dispersive X-ray Spectrometer (EDS)

The High–Power Optics make it possible to effectively take advantage of the features of the EDS (SDD: Silicon Drift Detector) detector that is difficult to saturate even with large probe currents. By using a low accelerating voltage and a large probe current, good quality mappings can be obtained in a very short period of time. The EDS analysis here was performed on a Field Emission Scanning Electron Microscopy JSM–7610FPlus, JEOL (FE–SEM).

#### Archimedes density measurement

Bulk density was determined by Archimedes method via distilled water using the following Equations:

$$\rho = \frac{A}{A-B}(\rho_0 - \rho_L) + \rho_L \tag{3.2}$$

$$v = \alpha \, \frac{A - B}{\rho_0 - \rho_L} \qquad (3.3)$$

where,

ρ

is Density of the sample

- A is Weight of the sample in air
- B is Weight of the sample in the auxiliary liquid (distilled water)
- v is Volume of the sample
- $ho_{\circ}$  is Density of the auxiliary liquid (distilled water)
- $\rho_{\rm c}$  is Density of air (0.0012 g/cm<sup>3</sup>)
- α is Weight correction factor (0.99985), to take the
  atmospheric buoyancy of the adjustment weight into
  account.

The theoretical densities of the samples were calculated using the

following formula:

$$d_{th} = \frac{4 \times Molecularweight}{N_A V}$$
(3.4)

where, v is cell volume obtained from XRD data.

$$N_A$$
 is Avogadro number =  $6.02 \times 10^{23}$  (1/mol)

4 is the number of unite cell in a cell volume

# THERMOELECTRIC PREOPERTIES MEASURMENTS

### Seebeck coefficient and electrical resistivity measurements

The ZEM–3 unit is the measuring instrument be accepted worldwide standard for thermoelectric material measurements at temperatures from –130 °C to 1,000 °C. Easy to use and operation with great accuracy & repeatability is why the ZEM–3 becomes the be accepted instrument in many labs across the globe. The Seebeck Coefficient / Electric Resistance Measurement System is shown in Figure 44.



Figure 44 The Seebeck Coefficient / Electric Resistance Measurement System, ZEM-3

The Seebeck coefficient (s) and electrical resistivity ( $\rho$ ) measurements were performed with a ZEM–3(M10) (Advane riko, Inc) in vacuum with the step detail as follow by Figure 45.



Figure 45 Schematic diagram of the step detail for Seebeck coefficient and electrical resistivity measurement

A prism sample is set in a vertical position between the upper and lower blocks in the heating furnace. While the sample is heated, and held, at a specified temperature, it is heated by the heater in the lower block to provide a temperature gradient. Seebeck coefficient is measured by measuring the upper and lower temperatures  $T_1$  and  $T_2$  with the thermocouples pressed against the side of the sample, followed by measurement of thermal electromotive force dE between the same wires on one side of the thermocouple. Electrical resistivity is measured by the dc four-terminal method, in which a constant current I is applied to both ends of the sample to measure and determine voltage drop dV between the same wires of the thermocouple by subtracting the thermo-electromotive force between leads as show in Figure 46.



Figure 46 The schematic diagram of Seebeck coefficient and electrical resistivity measurement

The Seebeck coefficient and electrical resistivity is found by using the following Eq. 3.5 and 3.6, respectively.

Seebeck coefficient (S) 
$$S = \frac{\Delta V}{Temp1 - Temp2}$$
 (3.5)

where  $\Delta V$  is Voltage, Temp1 is lower probe temperature and Temp2 is upper probe temperature.

electrical resistivity (
$$\rho$$
)  $\rho = \frac{RA}{l}$  (3.6)

where R is resistance value (R=V/I), A is cross section area of sample and l is distance between probes.

#### Thermal conductivity measurement

The schematic diagram of the Laser Flash Netzsch LFA-457 apparatus is shown in Figure 47. The Laser Flash (LFA) technique is a fast, non-destructive and non-contact method for determining thermal diffusivity and specific heat. The front surface of the plane-parallel sample is heated by a short energy light pulse. From the resulting temperature excursion of the rear face, measured with an infrared (IR) detector, thermal diffusivity and, if a reference specimen is used, specific heat of both is determined shown in Figure 48. Combining these thermophysical properties with the density value allows for the calculation of the thermal conductivity as follows:

 $\lambda(T) = \alpha(T) \cdot C_{p}(T) \cdot \rho(T) \qquad (3.7)$ 

where	λ	=thermal conductivity [W/(m•K)]
	α	= thermal diffusivity [mm²/s]
	Cp	= specific heat [J/(g•K)]
	ρ	= bulk density $[g/cm^3]$

This set of thermophysical properties can be the base of development for new materials, process optimization and numerical simulations. The data yielded by LFA analysis thus allows values for the following properties to be obtained either directly or calculated:

> Thermal diffusivity ( $\alpha$ ) Specific heat capacity ( $C_p$ ) Thermal conductivity ( $\lambda$ ) – via calculation Thermal effusivity (b) – via calculation · k–value – via calculation



Figure 47 The schematic diagram of Laser Flash Netzsch LFA-457 apparatus



Figure 48 The schematic diagram of Flash Technique Measurement

### THERMOELECTRIC SUBSTRATE

The thermoelectric materials were used at 3 temperature ranges, low temperature, medium temperature, and high temperature, so the substrate must be stable in high temperatures and low oxidation. With respect to the required high thermal cycling stability, ceramic substrates made of alumina with a low thermal expansion and high thermal conductivity are good choices. The active metal brazing (AMB) was used for the fabrication of TE substrate because this method is rapid and made a lot.

#### Preparation thermoelectric substrate

Generally, the substrate of thermoelectric materials used was alumina (Al<sub>2</sub>O<sub>3</sub>) metalized with the copper fabrication of thermoelectric module. However, copper used in high temperatures has a big problem with oxidation on the surface to increase ohmic contract and module resistance. The manufacturing process most widely in metalized metal to alumina was using direct copper bonding (DCB) (Fu, et al., 2015) and active metal brazing (AMB) which is a different process for fabrication (Sri Harini Rajendran, et al., 2021). The DCB was using the eutectic technique to connect metal with interlayer and alumina which is made in an eutectic temperature and control atmosphere. However, the DCB had been difficult to control the atmosphere and samples were poor so the AMB process was used for the prepared substrate. The AMB was fabricated from alumina plate size 50x50x1 mm<sup>3</sup>, metal brazing, and silver plate, thin 0.05 mm which was easily fabricated in the air because silver was low oxidation, good conduction, and use for fabricate thermoelectric module in 3 temperature ranges as decent.

In this process preparation, the substrate is shown a flowchart illustrating thermoelectric substrate prepared by AMB process Shown in Figure 49. The surface of the alumina was cleaned with ultrasonic acetone for 30 minutes. The thermoelectric substrate was designed by a solid works program. The design of the substrate size of  $50 \times 50 \times 1 \text{ mm}^3$  for 16 pairs. Thermoelectric materials were used in

the sizes of  $4 \times 4 \times 7 \text{ mm}^3$  and Ag electrode bottom sizes of  $10 \times 10 \times 0.5 \text{ mm}^3$  for 14 electrodes, and sizes of  $10 \times 20 \times 0.5 \text{ mm}^3$  for 3 electrodes. Then sticker-cover on substrate and silver paste was screened to alumina and dried at 423 K for 15 minutes 2 times on a hot plate. After that, stick a silver plate attached on top for electrode p and n legs to  $\Pi$ -shape drying at 423 K for 15 minutes and firings at 953 K for 15 minutes in the air using a heating rate of 5 K/min according to the thermal inertia of the furnace. Figure 50 shows the preparation of substrate the real thing that follows a flowchart illustrating substrate prepared by the AMB process.



Figure 49 Flowchart illustrating thermoelectric substrate prepared by AMB process



Substrate for fabrication module stick a silver plate attached on top for junction p and n legs to  $\Pi$ -shape.

Figure 50 Preparation of thermoelectric substrate

## PREPARATION OF THERMOELECTRIC MATERIALS

#### Preparation of thermoelectric materials for low temperature

Figure 51 shows the flowchart of preparation thermoelectric materials for low temperatures. The bulk of thermoelectric materials were cut and polished into  $4x4x7 \text{ mm}^3$  rectangular legs; p– Sb<sub>2</sub>Te<sub>3</sub> and n– Bi<sub>2</sub>Te<sub>3</sub> and the TE materials were cleaned with acetone on an ultrasonic cleaner 50 W for 30 min and dried at 373 K for 30 minutes on a hot plate. The TE materials were soldered with lead on top and bottom and materials that fabricate the module.



Figure 51 Flowchart of preparation thermoelectric materials for low temperature

#### Preparation of thermoelectric materials for medium temperature

Figure 52 shows the flowchart of preparation thermoelectric materials for medium temperatures. The bulk of thermoelectric materials were cut into size  $4\times4\times7$  mm<sup>3</sup> rectangular legs; p–MnSi<sub>1.75</sub> and n–Mg<sub>2</sub>Si. After that, cleaned TE materials with acetone on ultrasonic cleaner 50 W for 30 min and dried at 373 K for 30 minutes on a hot plate. The TE materials were painted with silver paste on top and bottom and dried at 423 K for 15 minutes on a hot plate, then firings in an HP machine at 823 K for 1 h in Ar atmosphere by using a heat rate of 5 K/min.



Figure 52 Flowchart of preparation thermoelectric materials for medium temperature

#### Preparation of thermoelectric materials for high temperature

Figure 53 shows the flowchart of preparation thermoelectric materials for high temperatures. The bulk of thermoelectric materials were cut into size  $4\times4\times7$  mm<sup>3</sup> rectangular legs; p–Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and n–Zn<sub>0.98</sub>Al<sub>0.02</sub>O. After that, cleaned TE materials with acetone on ultrasonic cleaner 50 W for 30 min and drying at 373 K for 30 minutes on a hot plate. The TE materials were painted with silver paste on top and bottom and drying at 423 K for 15 minutes on a hot plate, then firings in a furnace at 953 K for 15 minutes in the air using a heating rate of 5 K/min according to the thermal inertia of the furnace.



Figure 53 Flowchart of preparation thermoelectric materials for high temperature
# FABRICATION OF THERMOELECTRIC MODULES

Fabrication of the thermoelectric modules for the 3-temperatures ranges was according used at each temperature range so the fabrication process required stability at various temperatures. For the TE module, construction silver metalized ceramic substrates were made by brazing silver plates. In addition, within the electric contract between the substrate and thermoelectric materials silver paste metalized brazing can be used as well.

## Thermoelectric module design

Thermoelectric modules were designed by Solidworks program. The design of the thermoelectric module was stated by assigning the substrate size of  $50\times50\times1$  mm<sup>3</sup> for 16 pairs. Thermoelectric materials were used in the sizes of  $4\times4\times7$  mm<sup>3</sup> and Ag electrode on top sizes of  $10\times5\times0.5$  mm<sup>3</sup> as shown in Figure 54.



Figure 54 Model design of thermoelectric configuration

### Fabrication of the thermoelectric module for low temperature

The TE module of low temperature with legs size  $4\times 4\times 7 \text{ mm}^3$  was assembled using 2 types of Sb<sub>2</sub>Te<sub>3</sub> and Bi<sub>2</sub>Te<sub>3</sub> thermoelectric legs. The thermoelectric materials 16 pairs are electrically connected in double series by a thin silver plate of 0.05 mm using lead solder as a bonding agent. The first pellet was started at the left side of the thermoelectric device by p-type material and connected by switching n and p continuously on the silver paste electrode by lead solder. The top of materials between n-type and p-type was also connected with lead solder electrode to completed 16 pairs as shown in Figure 55.



Figure 55 Flowchart illustrating fabrication of thermoelectric module for low temperature

#### Fabrication of the thermoelectric module of medium temperature

The TE module of medium temperature with leg size  $4x4x7 \text{ mm}^3$  were assembled using of MnSi<sub>1.75</sub> and n–Mg<sub>2</sub>Si thermoelectric legs. The thermoelectric materials 16 pairs are electrically connected in a double series by a silver plate of  $10\times5\times0.5 \text{ mm}^3$  using a silver paste as a bonding agent. The first pellet was started on the left side of the thermoelectric device by p–type material and connected by switching n and p continuously by silver paste. The top of materials between n–type and p–type was also connected electrode silver plate of  $10\times5\times0.5 \text{ mm}^3$  by silver paste, then drying at 423 K for 15 minutes/side with a hot plate both above and below. The last step was firings in a hot press machine at 823 K for 1 h in Ar atmosphere by using a heat rate of 5 K/min, the module completed 16 pairs as shown in Figure 56.



Figure 56 Flowchart illustrating fabrication of thermoelectric module for medium temperature

### Fabrication of the thermoelectric module of high temperature

The TE module of high temperature with leg size  $4x4x7 \text{ mm}^3$  were assembled using of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and Zn<sub>0.98</sub>Al<sub>0.02</sub>O thermoelectric legs. The thermoelectric materials 16 pairs are electrically connected in a double series by a silver plate of  $10\times5\times0.5 \text{ mm}^3$  using silver paste as a bonding agent. The first pellet was started on the left side of the thermoelectric device by p-type material and connected by switching n and p continuously by silver paste. The top of materials between n-type and p-type was also connected electrode silver plate of  $10\times5\times0.5 \text{ mm}^3$  by silver paste, then drying at 423 K for 15 minutes/side with a hot plate both above and below. The last step was firings in a furnace at 953 K for 15 minutes in air using a heating rate of 5 K/min according to the thermal inertia of the furnace, the module completed 16 pairs as shown in Figure 57.



Figure 57 Flowchart illustrating fabrication of thermoelectric module for high temperature

# POWER GENERATION MEASUREMENT OF THOERMOELECTRIC MODULE

The power generation of the Thermogenerator described above were installed over a heater, and water cooling was placed over the module. To measure the temperatures of hot and cold side temperatures, the two K-type thermocouples were attached on the thin mica plate of high temperature and low temperature sides using an alumina substrate, respectively. A photograph of output power measurement of thermoelectric module is shown in Figure 58. The output power (W) was calculated by the output voltage (V) and current (I) caused by changing a resistor. Figure 59 shows the setting up of a power measurement system in a thermoelectric laboratory.



Figure 58 Power generation measurement of Thermogenerator



Figure 59 The setting up power measurement system

# Fabrication thermoelectric generator

The figure 60 shown thermoelectric generator module (TEG) was fabricated by using (a) 6 thermoelectric modules (b) no. SP1845 27145 SA per 1 TEG. Thermoelectric modules were connected series and stick with (c) aluminum plate for hot side and aluminum water cooling for cool side by heat conducting silicone. The figure 61 thermoelectric generator 4 sets were installed on the concentrate bar of the parabola for creating a hot side on the surface of the aluminum plate and cooling with water from ice melted.



Figure 60 The fabrication of thermoelectric generator module by using aluminum plate and water cooling.



Figure 61 the installation of thermoelectric generator module with concentrator bar of parabola.

#### Fabrication solar concentrator parabola

The fabrication of solar concentrator parabola was used for creation hot side for thermoelectric generators. The solar concentrator parabola was designed by using SolidWorks software for 3D sketching in figure 62. All part of solar concentrator parabola fabricated from galvanized steel for rust protection and longtime operation in outdoor in after that glossy stainless steel was used for reflection plate to creation hot side in figure 63. The solar concentrate parabola for thermoelectric generators consists of 4 modules of thermoelectric generators, cooling tube, water pump, solar cell for pumping, and 2 LED lamps in figure 64(a). A testing of solar concentrator parabola for thermoelectric generators system in KORNDECH–ICE was used cool water temperature about 285 K and a hot side from concentrator parabola about 360 K can generating electricity maximum power 3 W (5.87 V 0.512 A) at 13.00 O'clock in figure 64(b).



Figure 62 The 3D design of concentrator parabola by using SolidWorks software.



Figure 63 the fabrication of concentrator parabola by using galvanized steel and glossy stainless steel.



Figure 64 (a) the solar concentrate parabola for thermoelectric generators and (b) open circuit voltage from thermoelectric generator module.

# CHAPTER 4

# **RESULTS AND DISCUSSION**

This chapter represents thermoelectric materials synthesis, crystal structure analysis, microstructure analysis, thermoelectric properties, power generation of the generator of thermoelectric materials in 3 temperature ranges: low temperature, medium temperature, and high temperature.

# CRYSTAL STRUCTURE



Crystal Structure of Sb<sub>2</sub>Te<sub>3</sub>



Figure 65 XRD patterns of  $Sb_2Te_3$  powder from the processing of hot pressing at 723 K for 2 h in Ar atmosphere.

The X-ray diffraction pattern of  $Sb_2Te_3$  powder from HP at 723 K for 2 h in an Ar atmosphere at room temperature is shown in Figure 65. For the  $Sb_2Te_3$ powder, the diffraction angles at 28.22°, 38.22°, and 42.22° correspond to the (0 1 5), (1 0 10), and (1 1 0) crystalline phases, respectively. The diffraction pattern of the powder was shown binary-phase and shows high-intensity peaks associated with the (0 1 5) and shows that the diffraction peaks corresponding to the (0 1 5), (1 0 10), and (1 1 0) crystalline phases were obvious (Lin, J. M., et al. 2015). The XRD pattern corresponding with a pure Sb<sub>2</sub>Te<sub>3</sub> phase indicates a rhombohedral structure  $R\overline{3}m$  in space group (166) compared to ICDD PDF Card 00-015-0874 (a = 4.260 Å, and c = 30.422 Å). All diffraction peaks of the Sb<sub>2</sub>Te<sub>3</sub> powder coincided with those of JCPDS data, that is, the main phase is  $p-type Sb_2Te_3$  (Rajput, I., et al. 2015). The XRD patterns of the Sb<sub>2</sub>Te<sub>3</sub> materials, indicating that pure Sb<sub>2</sub>Te<sub>3</sub> crystalline phases were obtained without any impurities. Meanwhile it was found that the diffraction angles at 27.6° show the Te element, the likelihood that insufficient HP time. The lattice parameter was calculated from XRD data meanwhile. The calculated volume of unit cell from Eq.  $\left(V = a^3 \sqrt{1 + 3 - \cos^2 + 2\cos^3 \alpha}\right)$  (Tannous, C., 2019). The theoretical density for compared with bulk density to get the relative density of the sample as shown in Table 5.

	Lattic	ce parameters (Å)		Unit cell	density	Relative
Sample	а	b	С	Volume (Å <sup>3</sup> )	(g/cm <sup>3</sup> )	density (%)
Sb <sub>2</sub> Te <sub>3</sub>	4.260	_	30.4221	175.861	6.447	92.34
Wu, F., et al.,						
2017	4.262	_	30.435	178.442	6.35	91.45

Table 5 Lattice parameters, densities of  $Sb_2Te_3$  sample compared with the reference.

### Crystal Structure of Bi<sub>2</sub>Te<sub>3</sub>



Figure 66 XRD patterns of  $Bi_2Te_3$  powder from the processing of hot pressing at 723 K for 2 h in Ar atmosphere.

The X-ray diffraction pattern of  $B_{i2}Te_3$  powder from HP at 723 K for 2 h in an Ar atmosphere at room temperature is shown in Figure 66. The diffraction pattern of the powder was shown single–phase corresponding with a pure  $Bi_2Te_3$ phase indicating a hexagonal structure in  $R\overline{3}m$  space group (166) compared ICDD PDF Card 00–015–0863 (a = b = 4.321 Å and c = 30.4377 Å) (Yaprintsev, M., et al, 2018). For the  $Bi_2Te_3$  it shows that diffraction angles of 27.78°, 37.94°, and 41.26° correspond to (0 1 5), (1 0 <u>10</u>), and (1 1 0) diffraction planes appeared. The peak intensity of (0 1 5) orientation was highest (Lin, J. M., et al. 2013). The XRD patterns of the  $Bi_2Te_3$  materials, indicating that pure  $Bi_2Te_3$  crystalline phases were obtained without any impurities. This XRD data is good for thermoelectric materials. The lattice parameter was calculated from XRD data meanwhile. The calculated volume of unit cell from the Eq.  $V = \frac{\sqrt{3}a^2c}{2}$ . The theoretical density for compared with bulk density to get the relative density of the sample as shown in Table 6.

Table 6 Lattice parameter	s, densities of Bi <sub>2</sub> Te <sub>3</sub>	3 sample compared	with the reference.
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Samplo	Lattice parameters (Å)			Unit cell	density	Relative
Sumple	а	a b c		Volume (Å <sup>3</sup> )	/olume ( $Å^3$ ) (g/cm <sup>3</sup> )	
Bi <sub>2</sub> Te <sub>3</sub>	4.321	4.321	30.4377	177.842	7.62	92.02
Zheng, J.,	4.385	4.385	30.475	178.124	7.64	92.81
et al., 2017						

Crystal Structure of medium temperature

Crystal Structure of MnSi<sub>1.75</sub>



Figure 67 XRD patterns of  $MnSi_{1.75}$  powder from the processing of hot pressing at 1023 K for 1 h in Ar atmosphere.

The X-ray diffraction pattern of MnSi<sub>1.75</sub> powder from HP at 1023 K for 1 h in Ar atmosphere was analyzed at room temperature is shown in Figure 67 analyzed by X-ray diffraction technique in scan range 20–80 degree of 20 for 2 deg/min of scan speed with 0.02 of sampling pitch. The XRD pattern of the sample shows a mixed-phase between MnSi<sub>1.75</sub> for the main phase and MnSi for the second phase. This mixed phase was also observed in the samples containing a large amount of MnSi prepared by mechanical alloying followed by hot-pressing (Chen, X., et al. 2015, Shin, D. K., et al., 2013). The main phase is shown as a tetragonal structure with P4c2 (118) of space group. The calculated lattice parameters are in good agreement with the ICDD PDF Card 00–026–1251 (a = b = 5.526 Å and c = 117.67 Å) (Singsoog, K., et al. 2019). The peak intensity of (2 1 2 7) orientation was the highest at diffraction angle of 41.9°. This complex structure will result in low thermal conductivity. The calculated volume of unit cell from the Eq.  $V = a^2c$ . The theoretical density for compared with bulk density to get the relative density of the sample as shown in Table 7.

	Lattice parameters (Å)		Unit cell	density	Relative	
Sample	a	b c		Volume (Å <sup>3</sup> )	(g/cm <sup>3</sup> )	density (%)
MnSi <sub>1.75</sub>	5.526	5.526	117.67	3.5832	4.574	91.5
Le Tonquesse,						
et al., 2020	5.53	5.53	117.9	3.5989	4.662	92.65

Table 7 Lattice parameters, densities (	f MnSi <sub>1.75</sub>	compared with	the reference.
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Figure 68 XRD patterns of  $Mg_2Si$  powder from the processing of hot pressing at 1023 K for 1 h in Ar atmosphere.

The X-ray diffraction pattern of Mg<sub>2</sub>Si powder from HP at 1023 K for 1 h in Ar atmosphere was analyzed at room temperature is shown in Figure 68 analyzed by X-ray diffraction technique in scan range 20–80 degrees of 20 for 2 deg/min of scan speed with 0.02 of sampling pitch. The XRD pattern of Mg<sub>2</sub>Si of the powder was shown single–phase. For the Mg<sub>2</sub>Si it shows that all diffraction angles of 24.26°, 28.08°, 40.1°, 47.4°, 49.68°, 58°, 63.8°, 65.66°, 72.86°, and 78.1° correspond to (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (3 3 1), (4 2 0), (4 2 2), and (5 1 1) diffraction planes appeared. The peak intensity of (2 2 0) orientation was highest show cubic structure space group *Fm–3m* and corresponded with ICDD PDF Card 00–035–0773 (Zhang, Q., et al., 2016), the calculated lattice parameters are a = b = c = 6.351 Å (Chen, S et al., 2015). The calculated volume of unit cell from the Eq.  $V = a^3$ . The theoretical density for compared with bulk density to get the relative density of the sample as shown in Table 8.

Cample	Lattice parameters (Å)			Unit cell	density	Relative
Sumple	а	b c		Volume (Å <sup>3</sup> )	(g/cm <sup>3</sup> )	density (%)
Mg <sub>2</sub> Si	6.342	6.342	6.342	255.081	1.923	94.2
Nozariasbmarz,						
A. et al., 2016	6.351	6.351	6.351	259.82	1.856	93.65

Table 8 Lattice parameters, densities of  $Mg_2Si$  sample compared with the reference.

# Crystal Structure of high temperature

Crystal Structure of  $Ca_3Co_4O_9$ 



Figure 69 XRD patterns of  $Ca_3Co_4O_9$  powder calcine 1073 K for 10 h in air, hot pressing at 1123 K for 1 h in Ar, and annealed 1023 K for 5 h in air.

The X-ray diffraction pattern of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> powder calcine 1073 K for 10 h, hot pressing at 1123 K for 1 h in Ar, and annealed 1023 K for 5 h in air. The crystal structure of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> was analyzed at room temperature shown in Figure 69 analyzed by X-ray diffraction technique in scan range 10–65 degrees of 20 for 2 deg/min of scan speed with 0.02 of sampling pitch (Prasoetsopha, N., et al., 2014). The phase of annealed Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> shows single phase and compared ICDD PDF Card 00–058–0661 (Sedmidubský, D., et al., 2012). The two high intensity peaks of all samples associate with (0 0 2) and (0 0 4) planes and an orientation at diffraction angle of 16.52°, and 33.4° respectively. (Puri, N., et al., 2018). The crystal structure of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> evaluated by lattice parameters of a = 4.8564 Å, b = 4.4546 Å, c = 10.8273 Å indicated that monoclinic structure, space group 8 Cm (C1 m1). The calculated volume of unit cell of monoclinic structure is  $V = abc \sin \theta$ . The theoretical density for compared with bulk density to get the relative density of the sample as shown in Table 9.

Table 9 Lattice parameters	, densities of Ca <sub>3</sub>	<sub>3</sub> Co <sub>4</sub> O <sub>9</sub> sample	compared with	n the reference.
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Lattice parameters (Å)					Unit cell	density	Relative
Sumple	$a  b  c  \beta$		Volume(Å <sup>3</sup> )	(g/cm <sup>3</sup> )	density(%)		
Ca <sub>3</sub> Co <sub>4</sub> O <sub>9</sub>	4.8564	4.4546	10.827	98.72	234.12	4.48	92.6
Porokhin, S.,							
et al., 2016	4.8676	4.5686	10.857	98.11	273.45	4.33	91.7

#### Crystal Structure of Zn<sub>0.98</sub>Al<sub>0.02</sub>O



Figure 70 XRD patterns of  $Zn_{0.98}Al_{0.02}O$  powders hot pressing at 1723 K for 1 h in Ar, and annealed 923 K for 5 h in air.

The X-ray diffraction pattern of Zn<sub>0.98</sub>Al<sub>0.02</sub>O powders hot pressing at 1723 K for 1 h in an Ar atmosphere, and annealed 923 K for 5 h in the air analyzed at room temperature is shown in Figure 70. The powders were analyzed by X-ray diffraction technique in scan range 30–80 degrees of 2 $\theta$  for 2 deg/min of scan speed with 0.02 of sampling pitch. All observed XRD peaks can be assigned to those of pure ZnO phase. The phase of annealed Zn<sub>0.98</sub>Al<sub>0.02</sub>O shows single–phase and high– intensity peaks associate with the (1 0 1) (Han, L. 2014) an orientation at diffraction angle of 36.35° plane which compared ICDD PDF Card 00–036–1451 (Jantrasee, S., et al., 2016). The crystal structure of Zn<sub>0.98</sub>Al<sub>0.02</sub>O evaluated by lattice parameters of a =b= 3.248 Å, and c = 5.2075 Å indicated that hexagonal structure, space group P6<sub>3</sub>mc (186) (Permukaan, K. G. B., 2016). The unit cell volume of hexagonal

(wurtzite) structure calculated from the equation  $V = \frac{\sqrt{3}a^2c}{2}$ . The theoretical density for compared with bulk density to get the relative density of the sample as shown in Table 10.

Sample	L	attice parar	meters (Å)	Unit cell	donsity	Relative	
	а	b	С	β	Volume (Å <sup>3</sup> )	(g/cm <sup>3</sup> )	density (%)
Zn <sub>0.98</sub> Al <sub>0.02</sub> O	3.24982	3.24982	5.20661	90	47.6216	5.427	91.4
Arias-Serrano,							
B., et al., 2021	3.250	3.250	5.212	90	48.719	5.406	90.6

Table 10 Lattice parameters, densities of  $Zn_{0.98}AI_{0.02}O$  sample compared with the reference.

# MICROSTRUCTURES ANALYSIS

Microstructure analysis for low temperature

Microstructure analysis of  $Sb_2Te_3$ 



Figure 71 FE–SEM micrographs of thermoelectric material bulk sample of  $Sb_2Te_3$ (a) high–magnification 10k and (b) high–magnification 20k.

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The microstructure analysis of Sb<sub>2</sub>Te<sub>3</sub> bulk is shown in Figure 71. The sample was investigated and analysed by Field Emission Scanning Electron Microscope–FESEM (JSM–761FPlus). The microstructure details, including the morphology, size, and crystallinity of the fabricated, have shown the morphology of the Sb<sub>2</sub>Te<sub>3</sub> plate a high–magnification. Figure 71(a) shows the FESEM images of the surfaces from the HP method high–magnification 10k, in which a dense morphology with typical fine cleavage step patterns is observed. Interestingly, The Sb<sub>2</sub>Te<sub>3</sub> shows composed of Sb and Te elements. Clusters of fine grains are observed among coarse grains the sample is found to have some randomly spaced pores (Yue–Zhen Jiang, et al., 2019). It is clearly seen that the fine grains have the size of grains larger than 1 µm but not more than 5 µm which the growth of grains occurred during the HP process. Figure 71(b) shows the FESEM images of the surfaces high–magnification 20k, it can be seen the plate–like grains are more pronounced and quite dense and show a relatively good orientation.



Figure 72 EDS micrographs of thermoelectric material bulk sample of  $Sb_2Te_3$ (a) EDS analyzed, (b) Sb element, (c) Te element, (d) C element, and (e) O element.

The energy-dispersive X-ray spectroscopy (EDS) of  $Sb_2Te_3$  bulk are shown in Figure 72 was analyzed and shows the results agree with the composition shown in figure 72(a). Figure 72(b) show the Sb element has a weight of 28.90% and Figure 72(c) the Te element has a weight of 66.38%, Figure 72(d) show the C element has a weight of 2.04%, and Figure 72(e) show the O element has a weight of 2.68% total is 100%.

### Microstructure analysis of Bi<sub>2</sub>Te<sub>3</sub>



Figure 73 FE–SEM micrographs of thermoelectric material bulk sample of  $Bi_2Te_3$ (a) high–magnification 10k and (b) high–magnification 20k.

The microstructure of thermoelectric material bulk sample  $Bi_2Te_3$  is shown in Figure 73. The sample was investigated and analyzed by Field Emission Scanning Electron Microscope–FESEM (JSM–761FPlus). The microstructure details, including the morphology, size, and crystallinity of the fabricated. Figure 73(a) shown the morphology of the  $Bi_2Te_3$  plate a high–magnification 10K found that a large number of plate–like structures are randomly dispersed on the surface (Fu, J., Song., et al., 2012) clear crystalline grained structures with a mean grain size of ~1 µm. Figure 73(b) shows the FESEM images of the surfaces high–magnification 20k, it can be seen the sample is found to have some randomly spaced pores.



Figure 74 EDS micrographs of thermoelectric material bulk sample of  $Bi_2Te_3$ (a) EDS analyzed, (b) Bi element, (c) Te element, (d) O element, and (e) C element.

The energy-dispersive X-ray spectroscopy (EDS) of thermoelectric material bulk sample  $Bi_2Te_3$  was analyzed, and show the results agree with the composition of the initial atomic ratio as shown in figure 74(a). Figure 74(b) show the Bi element has a weight of 43.69%, Figure 74(c) show the Te element has a weight of 43.82%, Figure 74(d) show the O element has a weight of 8.47%, and Figure 74(e) show the C element has a weight of 4.02% total is 100%.

## Microstructure analysis for medium temperature

Microstructure analysis of MnSi<sub>1.75</sub>



Figure 75 FE–SEM micrographs of thermoelectric material bulk sample of MnSi<sub>1.75</sub> (a) high–magnification 1k and (b) high–magnification 3k.

The microstructure of thermoelectric material bulk sample MnSi<sub>1.75</sub> was analyzed by Field Emission Scanning Electron Microscope–FESEM (JSM–761FPlus) as shown in Figure 75. The microstructure details, including the morphology, size, and crystallinity of the fabricated, have shown the morphology of the MnSi<sub>1.75</sub> plate Figure 66 yielded results consistent with the XRD analysis, the average grain size was several hundred nanometres. As shown in Fig. 75(a), shows the grain size of the sample at high–magnification 1K. It was found that the sample of some small particles with tetragonal shapes was found among the large particles as the grain size reached about 20 µm (Chen, X., et al., 2012). Figure 75(b) shows the FE–SEM images of the surfaces high–magnification 3k, found that the plate–like grains are more pronounced and quite dense which shows a relatively good orientation.



Figure 76 EDS micrographs of thermoelectric material bulk sample of MnSi<sub>1.75</sub>
(a) EDS analyzed, (b) Mn element, (c) Si element, (d) C element, and (e) O element.

The energy–dispersive X–ray spectroscopy (EDS) was analyzed, show the results agree with the composition of the initial atomic ratio as shown in figure 76(a). Figure 76(b) shows the Mn element has a weight of 30.59% and Figure 76(C) the Si element has a weight of 53.19%, Figure 76(d) show the C element has a weight of 4.02%, and Figure 76(e) show the O element has a weight of 8.47% total is 100%.

## Microstructure analysis of Mg<sub>2</sub>Si



Figure 77 FE–SEM micrographs of thermoelectric material bulk sample of  $Mg_2Si$ (a) high–magnification 5k and (b) high–magnification 20k.

The microstructure of the Mg<sub>2</sub>Si bulk sample is shown in Figure 76. The microstructure details, including the morphology, size, and crystallinity of the fabricated, have shown the morphology of the Mg<sub>2</sub>Si plate a high–magnification 5K in Figure 77(a) presents typical secondary electron images of primary Mg<sub>2</sub>Si in the base alloy. The primary Mg<sub>2</sub>Si particles may display different morphologies, including octahedral, "hopper–like," cubic, truncated octahedral, and massive dendrite forms its average size  $3-5 \ \mu m$  (Tebib, M., et al., 2014). Figure 77(b) shows the FESEM images of the surfaces high–magnification 20k, found that the clearly octahedral, "hopper–like," cubic, shapes which are more noticeable but have a lot of randomly spaced pores.



Figure 78 EDS micrographs of thermoelectric material bulk sample of  $Mg_2Si$ (a) EDS analyzed, (b) Mg element, (c) Si element, (d) C element, and (e) O element.

The energy–dispersive X–ray spectroscopy (EDS) was analyzed, showing the results agree with the composition of the initial atomic ratio as shown in figure 78(a). Figure 78(b) shows the Mg element has a weight of 55.38% and Figure 78(c) the Si element has a weight of 25.38%, Figure 78(d) show the C element has a weight of 8.69%, and Figure 78(e) show the O element has a weight of 10.24% total is 100%.

# Microstructure analysis for high temperature Microstructure analysis of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>



Figure 79 FE–SEM and EDS micrographs of thermoelectric material bulk sample of  $Ca_3Co_4O_9$  (a) high–magnification 20k and (b) high–magnification 10k.

The microstructure of the Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> bulk sample is shown in Figure 78. The microstructure details, including the morphology, size, and crystallinity of the fabricated, have shown the morphology of the Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> plate a high-magnification 10K in Figure 79(a). The surface area of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> exhibited the morphology of plate-like particles stacked in many layers. The average particle size of all samples was  $\sim$ 3 µm. The grains are showing the orientation of large platelets compactly stacked up along the applied pressure axis (Noudem, J. G., & Xing, Y., 2021 and Prasoetsopha, N., et al., 2016). Figure 79(b) shows the FESEM images of the surfaces high-magnification 10k, found that the clearly plate-like grains show a relatively good orientation and superposition in many layers.



Figure 80 EDS micrographs of thermoelectric material bulk sample of  $Ca_3Co_4O_9$ (a) EDS analyzed, (b) Ca element, (c) O element, (d) Co element, and (e) C element.

The energy–dispersive X–ray spectroscopy (EDS) was analyzed, show the results agree with the composition of the initial atomic ratio as shown in figure 80(a). Figure 80(b) shows the Ca element has a weight of 22.25% and Figure 80(c) the O element has a weight of 27.24%, Figure 80(d) show the Co element has a weight of 46.14%, and Figure 80(e) show the C element has a weight of 4.36% total is 100%.

## Microstructure analysis of $Zn_{0.98}AI_{0.02}O$



Figure 81 FE–SEM and EDS micrographs of thermoelectric material bulk sample of  $Zn_{0.98}AI_{0.02}O$  (a) high–magnification 10k and (b) high–magnification 20k.

The microstructure of the Zn<sub>0.98</sub>Al<sub>0.02</sub>O bulk sample as shown in Figure 80. The microstructure details, including the morphology, size, and crystallinity of the fabricated, have shown the surface morphology of the Zn<sub>0.98</sub>Al<sub>0.02</sub>O plate a high– magnification 10K in Figure 81(a). It can be seen that Zn<sub>0.98</sub>Al<sub>0.02</sub>O possess uniform grains and are almost homogeneously distributed and hexagonal like grains and do not observe any phase aggregation other. The average particles size is estimated at ~1 µm and has randomly spaced pores obviously a lot. Figure 81(b) shows the FE–SEM images of the surfaces high–magnification 20k, found that clearly the grains are almost homogeneously distributed and hexagonal like grains.



Figure 82 EDS micrographs of thermoelectric material bulk sample of  $Zn_{0.98}Al_{0.02}O$ (a) EDS analyzed, (b) Zn element, (c) Al element, (d) O element, and (e) C element.

The energy-dispersive X-ray spectroscopy (EDS) was analyzed, show the results agree with the composition of the initial atomic ratio as shown in figure 82(a). Figure 82(b) shows the Zn element has a weight of 76.66% and Figure 82(c) the Al element has a weight of 0.10%, Figure 82(d) show the O element has a weight of 17.97%, and Figure 82(e) show the C element has a weight of 5.27% total is 100%.

## THERMOELECTRIC PROPERTIES

Thermoelectric Properties of materials for low temperature

Seebeck coefficient



Figure 83 Seebeck coefficient dependence on temperature of  $p-Sb_2Te_3$  and  $n-Bi_2Te_3$ bulk samples by hot-press method compared to references.

Figure 83 shows the temperature dependence of of Seebeck coefficient  $p-Sb_2Te_3$  and  $n-Bi_2Te_3$  bulk samples by hot-press method, measured by ZEM-3 technique in the range 273 – 523 K. The red line shows the sign of the Seebeck coefficient of  $Sb_2Te_3$  indicating p-type behavior. The magnitude of S value increases with increasing temperature from is 117 ( $\mu$ V/K) at 303 K to 147 (( $\mu$ V/K)) at 523 K and increases with increasing temperature compared with the literature. The S in the  $Sb_2Te_3$  single-crystal of this work is substantially higher than that in the single-crystal of literature. It is documented that the Seebeck coefficient of a degenerate semiconductor is determined by the scattering factor g and the reduced Fermi energy.

The black line shows the sign of the Seebeck coefficient of  $Bi_2Te_3$  material. Since the majority of charge carriers in these compounds are electrons, the Seebeck coefficient has a negative sign indicating n-type (Han, M. K., et al., 2017). Hence, the highest Seebeck coefficient of  $Bi_2Te_3$  is -163 ( $\mu$ V/K) at 323 K. The magnitude of Seebeck coefficient value decreases with the increase in temperature. The decrease of the Seebeck coefficient value at high temperatures is due to the start of intrinsic excitation and two-band conduction from both electrons and holes (Tang, G., et al. 2016). The Seebeck Coefficient of this work composites has the highest value as compared to other references prepared with the ditto HP.



**Electrical resistivity** 

Figure 84 Electrical resistivity dependence on temperature of  $p-Sb_2Te_3$  and  $n-Bi_2Te_3$ bulk samples by hot-press method compared to references.

Figure 84 shows the temperature dependence of electrical resistivity p-Sb<sub>2</sub>Te<sub>3</sub> and n-Bi<sub>2</sub>Te<sub>3</sub> bulk samples by hot-press method, measured by ZEM-3 technique in the range 273 – 523 K. The electrical resistivity red line value of  $p-Sb_2Te_3$  bulk is shown similarly to literature data, The measured electrical resistivity shows the resistivity appears to increase with the increase in temperature representing positive temperature coefficient behavior the studied bulk Sb<sub>2</sub>Te<sub>3</sub> single crystal exhibits a metallic nature. The electrical resistivity of Sb<sub>2</sub>Te<sub>3</sub> single-phase increases from  $1.23 \times 10^{-5} \,\Omega$  cm at 303 K and this tendency is still continuously remained increases is 2.29 imes 10<sup>-5</sup>  $\Omega$  cm at 523 K. The black line shows the electrical resistivity value of  $n-Bi_2Te_3$  bulk is showing the same direction as literature data. The  $Bi_2Te_3$  composite shows higher electrical resistivity throughout the temperature range but decreases in the last temperature measurement, indicating a semiconducting conduction behavior at a temperature of 523 K which has a value is 5.48 imes 10<sup>-5</sup>  $\Omega$  cm. The black line at the temperature range 303-473 K indicates a metallic conduction behavior. The electrical resistivity value of Bi<sub>2</sub>Te<sub>3</sub> shows 5.11  $\times$  10<sup>-5</sup>  $\Omega$  cm gradually up to 5.61  $\times$  $10^{-5}\,\Omega$  cm at 303 K and 473 K respectively. This likely originated from carrier scattering notice from the FESEM because the grains in the sample HP at 723 K are relatively small (Rong, Z., et al. 2015). From the data, it is observed that the scattering of the charge carriers is the increased temperature (Soni, A., et al., 2012). The single-phase is also documented by XRD analysis and considering the narrow bandgap is pure  $Bi_2Te_3$  (0.15 eV) where donor and acceptor levels lie extremely close to the conduction and valence band edges (Yang, F., et al., 2015). the present HP have a Relative density of  $\sim$ 92%, which means that there exists a large number of grain boundaries in the composites. The grain boundaries also the charge carriers and thus better the carrier mobility resulting in lower electrical resistivity when comparing which literature data.





Figure 85 power factor dependence on temperature of  $p-Sb_2Te_3$  and  $n-Bi_2Te_3$  bul samples by hot-press method compared to references.

The temperature dependence on power factor of p–Sb<sub>2</sub>Te<sub>3</sub> and n–Bi<sub>2</sub>Te<sub>3</sub> bulk samples by hot–press method, the calculated value is shown in Figure 85. The red line shows the power factor values as calculated from the electrical resistivity values and the Seebeck coefficients of Sb<sub>2</sub>Te<sub>3</sub> characteristics with the values decreased with increasing temperature corresponding with literature data. The maximum calculated PF value of the Sb<sub>2</sub>Te<sub>3</sub> sample is 2.12 × 10<sup>-4</sup> W/mK<sup>2</sup> at 303 K and gradually decrease to 1.95 × 10<sup>-4</sup> W/mK<sup>2</sup> at 523 K, this value is higher than literature data synthesized by the HP method. The black line shows the power factor values as calculated from the electrical resistivity values and the Seebeck coefficients of Bi<sub>2</sub>Te<sub>3</sub> material. The values increased with increasing temperature from 0.32 × 10<sup>-4</sup> W/mK<sup>2</sup> at 303 K up to the maximum value is 0.43 × 10<sup>-4</sup> W/mK<sup>2</sup> at 523 K. This the value is higher than literature data synthesized by the HP method.

#### Thermal conductivity



Figure 86 Temperature dependence of thermal conductivity of  $p-Sb_2Te_3$  and  $n-Bi_2Te_3$ bulk samples by hot-pressing method compared to references.

Figure 86 shows the temperature dependence of thermal conductivity of  $p-Sb_2Te_3$  and  $n-Bi_2Te_3$  bulk samples by hot-press method, measured by the laser flash method (Netzsch LFA-457) in the range 273 -523 K. The red line shows thermal conductivity of  $Sb_2Te_3$  characteristics with the values decreased with increasing temperature corresponding with literature data. The value of  $Sb_2Te_3$  was exhibited lower thermal conductivities over the whole temperature range that decreases when temperature increases from 2.12 (W/m K) at temperature 303 K to 1.54 (W/m K) at 523 K. It is evident that the lower thermal conductivity values were caused by the  $Sb_2Te_3$  sample that was synthesized from the HP identical. It was found that the highly densified when corresponding with literature data (Wu, F., et al., 2017). This result shows that a similarly significant reduction of the total thermal conductivity in the Sb<sub>2</sub>Te<sub>3</sub> regardless that phonon anharmonicity significantly influences the thermal
property. Hence, the reduction in the thermal conductivity may have originated from the lattice phonon and carrier scattering (Das, D., et al., 2018). The black line shows the thermal conductivity of Bi2Te3 it can be seen that the thermal conductivity is much lower than all literature data. The value of Bi2Te3 was exhibited lower thermal conductivity over the whole temperature range when the temperature increases and the value of thermal conductivity gradually increase from 0.39 (W/m K) to 0.45 (W/m K) at temperature 303 K up to 523 K are respectively. While it is observed that the temperature range 303 – 373 K The value of thermal conductivity decreases from 0.39 (W/m K) to 0.38 W/mK and gradually increases to 0.45 (W/m K) at 523 K. The single crystal of Bi<sub>2</sub>Te<sub>3</sub> is a clear indication of the benefits of stronger phonon scattering resulting from the smaller grains. The thermal conductivity does not increase too much quickly. Therefore, then the ball-milled and HP method of  $Bi_2Te_3$  creates more interfaces, defects, and increases the density of grain boundaries. The thermal conductivity of the Bi<sub>2</sub>Te<sub>3</sub> composites decreases due to phonon scattering from the grain boundaries (Shi, W., ET AL., 2014). This indicates that the lattice thermal conductivity has been efficiently restrained by using ball milling and HP method, which enhances phonon-grain boundary scattering and results in a remarkable decrease in thermal conductivity (Pundir, S. K., et al., 2016).

## Dimensionless figure of merit



Figure 87 Temperature dependence of Dimensionless figure merit of  $p-Sb_2Te_3$  and  $n-Bi_2Te_3$  bulk samples by hot-pressing method compared to references.

Figure 87 presents the calculation of the ZT values of the bulk samples of  $p-Sb_2Te_3$  and  $n-Bi_2Te_3$  samples by hot-press method, the calculated value between 298 K to 523 K. The red line shows ZT of  $Sb_2Te_3$  characteristics with the values increased with increasing temperature corresponding with literature data. Because of the simultaneous optimization in electrical and thermal transport properties. The figure of merit increases with increasing temperature and up to ~0.51 at 473 K but will decrease slightly at 523 K without significant significance. The black line shows the ZT value on the above of  $Bi_2Te_3$  characteristics with the values increased with increasing temperature data. The ZT was increased with increasing temperature due to the high electrical conductivity and low thermal conductivity. The maximum ZT value is around 0.54 at 473 K when compared with the same methods from literature data (Min, Y., et al., 2013).

Observed that the synthesis of  $p-Sb_2Te_3$  and  $n-type Bi_2Te_3$  materials and utilize them to demonstrate high-performance TEG modules for waste heat recovery application (Nozariasbmarz, A., et al., 2020). Both p- and n-type alloys with high average and peak ZT were synthesized by ball milling and Hot-pressing method. The enhancement in ZT resulted from the large reduction of thermal conductivity and the enhanced power factor by a carrier filtering effect. The ZT have a similar value in alloy-based modules were achieved.





Figure 88 Temperature dependence of Seebeck coefficient of p–MnSi<sub>1.75</sub> and n–Mg<sub>2</sub>Si bulk samples by hot–pressing method compared to references.

Figure 88 shows the Temperature dependence of Seebeck coefficient  $p-MnSi_{1.75}$  and  $n-Mg_2Si$  bulk samples by hot-press method, measured by ZEM-3 technique in the range 273 – 773 K. The red line shows the temperature dependence of the value of the Seebeck coefficient of  $MnSi_{1.75}$  characteristics corresponding with literature data. The Seebeck coefficient steadily increases with temperature

compatibility of p-type material in the measured temperature range, then gradually decreases above 623 K. The value of MnSi1.75 gradually increases from 78.2 ( $\mu$ V/K) at 298 K up to the maximum value is 129 ( $\mu$ V/K) at 623K and then gradually decrease is 123 ( $\mu$ V/K) at 773 K which indicate that is a group of semiconductors. The black line shows the sign of the Seebeck coefficient of Mg<sub>2</sub>Si material. Since the majority of charge carriers in these compounds are electrons, the Seebeck coefficient has a negative sign indicating n-type. The Mg<sub>2</sub>Si sample shows an early onset of intrinsic conduction occurring around 623 K due to its low carrier concentration (Zhang, Q., et al., 2016). The Seebeck coefficient of samples shows a rough curvature dependence on temperature, the typical behavior of semiconductors is expressed as Eq.  $\alpha = -\frac{k}{e} \left( \frac{5}{2} + r - \frac{E_c - E_F}{kT} \right) = -\frac{k}{e} \left( \frac{5}{2} + r \ln \frac{N_c}{n} \right) \Box \gamma - \ln n$ , where k is the Boltzmann constant, r is the exponent of the power function in the energy-dependent relaxation time expression,  $E_C$  is the bottom of the conduction band,  $E_F$  is the Fermi energy, T is the absolute temperature and  $N_c$  are the effective density-of-states in the conduction band, n is the charge-carrier concentration and  $\gamma$  are the scattering factor (You, S. W et al., 2011). The highest Seebeck coefficient of Mg<sub>2</sub>Si is -435.5 $(\mu V/K)$  at 623 K. The Seebeck coefficient is the competition result between carrier scattering and the carrier concentration.

## Electrical resistivity



Figure 89 Temperature dependence of electrical resistivity of  $p-MnSi_{1.75}$  and  $n-Mg_2Si$  bulk samples by hot-pressing method compared to references.

Figure 89 shows the Temperature dependence of of Seebeck coefficient  $p-MnSi_{1.75}$  and  $n-Mg_2Si$  bulk samples by hot-press method, measured by ZEM-3 technique in the range 273 – 773 K. The red line shows the sign of the electrical resistivity of MnSi\_{1.75} material this work has a higher value as compared to references prepared with the ditto HP. Electrical resistivity showed very similar values to the analog studies (Itoh, T., & Yamada, M. 2009) and increased with increasing temperature, representing a degenerating semiconductor behavior (Lee, Y. G., et al., 2012). The electrical resistivity of the MnSi\_{1.75} material increases with the temperature gradually due to the lattice scattering (He, Y. J., et al., 2011). The lowest electrical resistivity achieved of the MnSi\_{1.75} is around 12 × 10<sup>-4</sup>  $\Omega$  cm at 298K, then gradually increases up to the maximum value is around 24× 10<sup>-4</sup>  $\Omega$  cm at 773K. The black line shows the sign of the electrical resistivity of Mg<sub>2</sub>Si material this work has the highest

value as compared to other references prepared with the ditto HP. The resistivity decreases with an increasing temperature significantly due to increasing electron concentration. The resistivity of all materials prepared is semiconductor–like and thus decreases with increasing temperature and exhibiting a shoulder around 298–573 K (Cederkrantz, D., et al., 2012). The lowest electrical resistivity achieved of the Mg<sub>2</sub>Si is  $1.89 \times 10^{-4}\Omega$  cm at 773K, which has a similar value obviously in the temperature range 573–773 K. the electrical resistivity would presumably have increased instead due to increased grain boundary scattering caused.



Power factor

Figure 90 Temperature dependence of power factor of  $p-MnSi_{1.75}$  and  $n-Mg_2Si$  bulk samples by hot-pressing method compared to references.

Figure 90 presents the temperature dependence of the calculated value Power factor of  $p-MnSi_{1.75}$  and  $n-Mg_2Si$  bulk samples by the hot-press method. The red line shows the sign of the Power factor of  $p-MnSi_{1.75}$  is similar to the Seebeck coefficient because the PF has a tradeoff relationship between the electrical resistivity and the Seebeck coefficient, as shown in Eq.  $PF = \frac{S^2}{\rho}$ , a positive temperature dependence appears, and then a peak value appears at a certain temperature has value is 2.2257 × 10<sup>-4</sup> W m<sup>-1</sup>K<sup>-2</sup> at 673K. This is the result of the degenerate behavior of the electrical resistivity and the intrinsic transition effect on the Seebeck coefficient. The black line shows the sign of the Power factor of n–Mg<sub>2</sub>Si is higher when characteristics correspond with literature data. The sample of MgSi mainly related to large differences has a tradeoff relationship between the electrical resistivity and the Seebeck coefficient (Nieroda, P., et al., 2019). PF for Mg<sub>2</sub>Si is relatively small and will increase rapidly has a peak value of 1.63 × 10<sup>-4</sup> W m<sup>-1</sup>K<sup>-2</sup> at 573 K. Then the Power factor of Mg<sub>2</sub>Si will gradually be decreased to 0.86 × 10<sup>-4</sup> W m<sup>-1</sup>K<sup>-2</sup> at

## Thermal conductivity



Figure 91 Temperature dependence of thermal conductivity of  $p-MnSi_{1.75}$  and  $n-Mg_2Si$  bulk samples by hot-pressing method compared to references.

Figure 91 show the temperature dependence of thermal conductivity of p-MnSi<sub>1.75</sub> and n-Mg<sub>2</sub>Si bulk samples by hot-press method, measured by the laser flash method (NetzschLFA-457) in the range 273 – 773 K. The red line shows the thermal conductivity value of MnSi<sub>1.75</sub> characteristics corresponding with literature data. The thermal conductivity of the MnSi<sub>1.75</sub> sample displays a metallic behavior of the increased thermal conductivity with temperature. The thermal conductivity of the MnSi<sub>1.75</sub> sample gradually decreases at 673 K and gradually increases when the temperature up to 773 K which has a value is 2.84 (W/m K) up to 2.92 (W/m K) respectively (Shi, X., et al., 2012). The value of MnSi<sub>1.75</sub> increases only slowly increase with temperature at T>673 K which is attributed to the ambipolar thermal diffusion. For this reason, lowered thermal conductivity in this process might be attributed to the induced phonon scattering by grain refinement which is typically in the MA process. The grain boundaries scatter electrons, which are thermally excited, more than holes due to the electrons' smaller energy (Lee, Y. G., et al., 2012). black line shows the thermal conductivity value of Mg<sub>2</sub>Si characteristics corresponding with literature data, but as seen in the graph all materials of Mg<sub>2</sub>Si show quite apart values. The thermal conductivity of Mg<sub>2</sub>Si decreases from 5.19 (W/m K) at room temperature which is reduced to a minimum of around 1.94 (W/m K) at 773 K due to the 3-phonon scattering dominates and the thermal conductivity starting the thermal conductivity decreased with increasing temperature (Nozariasbmarz, A., et al., 2020). For the  $Mg_2Si$  and reference materials, the general trend of the thermal conductivity agrees with that of a semiconductor with increased conductivity at high temperatures where the intrinsic transition has occurred (Cederkrantz, D., et al., 2012).

## Dimensionless figure of merit



Figure 92 Temperature dependence of Dimensionless figure merit of  $p-MnSi_{1.75}$  and  $n-Mg_2Si$  bulk samples by hot-pressing method compared to references.

The calculation of the Dimensionless figure of merit (ZT) of p–MnSi<sub>1.75</sub> and n–Mg<sub>2</sub>Si samples by hot–press method, the calculated value between 293 K to 773 K is shown in Figure 92. The red line shows ZT of MnSi<sub>1.75</sub> characteristics with the values increased with increasing temperature corresponding with literature data, but the value less than literature data. Because of the simultaneous optimization in electrical and thermal transport properties. The figure of merit increases with increasing temperature and up to around 0.44 at 773 K. has the value of a decrease  $\sim$ 2.89 %. The black line shows the ZT value on the above of Mg<sub>2</sub>Si characteristics with the values increased with increasing temperature corresponding with literature data. The ZT was increased with increasing temperature due to the high electrical conductivity and low thermal conductivity. The maximum ZT value is around 0.73 at 773 K when compared with the same methods from literature data has the value an increase  $\sim$ 10 %. Observed that the synthesis of p–MnSi<sub>1.75</sub> and n–Mg<sub>2</sub>Si materials and utilize them to demonstrate high–performance TEG modules for waste heat recovery application. Both p–type and n–type alloys with high average and peak ZT were synthesized by ball milling and Hot–pressing method. The enhancement in ZT resulted from the large reduction of thermal conductivity and the enhanced power factor by a carrier filtering effect. The ZT have a similar value in alloy–based modules were achieved. The p–MnSi<sub>1.75</sub> shows a high ZT value of about 0.44 at 773 K and n–Mg<sub>2</sub>Si shows a maximum ZT value, about0.73 at 773 K, hence the ZT value of Mg<sub>2</sub>Si is approximately 29 times higher than that of MnSi<sub>1.75</sub> (Singsoog, K., & Seetawan, T. (2019). Both of these materials are attractive, the high ZT value because is a base material that does not contain other doped.

Thermoelectric Properties of materials for high temperature Seebeck coefficient



Figure 93 Temperature dependence of Seebeck coefficient of  $p-Ca_3Co_4O_9$  and  $n-Zn_{0.98}AI_{0.02}O$  bulk samples by hot-pressing method compared to references.

Figure 93 shows the temperature dependence of of Seebeck coefficient  $p-Ca_3Co_4O_9$  and  $n-Zn_{0.98}Al_{0.02}O$  bulk samples by hot-press method, measured by ZEM-3 technique in the range 273 – 1023 K. The Seebeck coefficient red line is the Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> samples were similarly behavior corresponding with metal to semiconducting and indicates the p-type behavior in good agreement with the literature from 303 K to 1073 K. The magnitude of S value increases with increasing temperature from is 140.07 ( $\mu$ V/K) at 623 K to 186.65 ( $\mu$ V/K) at 923 K and increases with increasing temperature. Observed from SEM images the morphology of plate-like particles platelike grains show a relatively good orientation, grain has made high mobility and low phonon transport properties make a high Seebeck coefficient. In addition,  $Ca_3Co_4O_9$ sample sintering by hot-pressing has high S values more than another sample when compared with the literature, because this method is the capability to compact the powder into a dense bulk within the same times the grain size increasing the influence on the S values of the scattering effect will be increased. The Seebeck coefficient black line is the  $Zn_{0.98}Al_{0.02}O$  sample the negative sign indicated n-type conductivity shows the relation to the carrier concentration in semiconductors. The maximum of S is about  $-408 (\mu V/K)$  at 1073 K, this is due to the increase in more electrons (i.e. Charge carriers) being promoted above the Fermi level into the conduction band because of the increase in temperature and hence more electrons moving from the hot junction to the cold junction. An increase in temperature suggests that after carrier saturation there is no significant scattering to lattice vibrations. The magnitude of S apparently would decrease with increasing carrier concentration provided that the scattering parameter remains unchanged. When S of Zn<sub>0.98</sub>Al<sub>0.02</sub>O was compared with references found that the S of our work at high temperature has a high value compared with references.

## **Electrical resistivity**



Figure 94 Temperature dependence of electrical resistivity of  $p-Ca_3Co_4O_9$  and  $n-Zn_{0.98}Al_{0.02}O$  bulk samples by hot-pressing method compared to references.

Figure 94 shows the temperature dependence of electrical resistivity p– Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and n–Zn<sub>0.98</sub>Al<sub>0.02</sub>O bulk samples by hot–press method, measured by ZEM– 3 technique in the range 273 – 1023 K. The electrical resistivity red line values of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> bulk are shown similarly to literature data, The values were increased with increasing temperature has a value is 15.9 m $\Omega$  cm at 1023 K. The monoclinic structure of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> is comprised of two misfits layered was composed of rock–salt– type Ca<sub>2</sub>CoO<sub>3</sub> layer serve as phonon scattering regions resulting in low thermal conductivity. and the conducting CoO<sub>2</sub> layer a strongly correlated electron system serves as electronic transport layers. The magnitude of electrical resistivity apparently would decrease with increasing carrier concentration provided that the scattering parameter remains unchanged. In addition, the activated type of conduction in resistivity is not reconciled with the metal–like temperature dependence of electrical resistivity. The electrical resistivity variation with a metallic–like behavior over the whole measured temperature range, such a phenomenon may begin from the increase of the grain boundary potential barrier scattering as the carrier mobility increases, which leads to the increase of conductivity. The electrical resistivity black line values of  $Zn_{0.98}AI_{0.02}O$  bulk are shown similarly to literature data, The electrical resistivity of  $Zn_{0.98}AI_{0.02}O$  is lower than that of the homologous phase in the whole temperature range with increasing Al concentration the resistivity increases. The measured electrical resistivity shows the resistivity of  $Zn_{0.98}AI_{0.02}O$  decreases from 116 m $\Omega$  cm at 303 K and this tendency is still continuously remained increases is 51.2 m $\Omega$  cm at 1073 K. For  $Zn_{0.98}AI_{0.02}O$  the temperature dependence of the resistivity changes to show behavior characteristic of a semiconductor with activated electrical conductivity and there is a gradual shift of resistivity behavior from metallic to semiconducting with increasing Al concentration.



Power factor



The temperature dependence of power factor of p–Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and n–Zn<sub>0.98</sub>Al<sub>0.02</sub>O bulk samples by hot–press method, the calculated value is shown in Figure 95. The red line PF value of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> characteristics with the values increased with increasing temperature corresponding with literature data. The maximum calculated PF value of the Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> sample is 1.99 × 10<sup>-4</sup> W/mK<sup>2</sup> at 973 K this value is higher than literature data synthesized by the HP method. The black line PF value of Zn<sub>0.98</sub>Al<sub>0.02</sub>O characteristics with the values increased with increasing temperature corresponding with literature data. The maximum calculate is higher than literature data synthesized by the HP method. The black line PF value of Zn<sub>0.98</sub>Al<sub>0.02</sub>O characteristics with the values increased with increasing temperature corresponding with literature data. The maximum PF is 78.52 × 10<sup>-4</sup> W/mK<sup>2</sup> at 1073 K this value is higher than literature data synthesized by the HP method.



Thermal conductivity

Figure 96 Temperature dependence of thermal conductivity of  $p-Ca_3Co_4O_9$  and  $n-Zn_{0.98}Al_{0.02}O$  bulk samples by hot-pressing method compared to references.

Figure 96 shows the temperature dependence of thermal conductivity of  $p-Ca_3Co_4O_9$  and  $n-Zn_{0.98}Al_{0.02}O$  bulk samples by hot-press method, measured by the laser flash method (NetzschLFA-457) in the range 273 - 1023 K. The red line shows the thermal conductivity of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> was exhibited lower thermal conductivities over the whole temperature range that decreases when temperature increases from 2.49 (W/m K) at temperature 273 K were which became 1.38 (W/m K) at 973 K, characteristics with the values increased with increasing temperature corresponding with literature data. It is evident that the lower thermal conductivity values were caused by the Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> sample that was synthesized from the HP method and annealing was highly densified. The  $Ca_3Co_4O_9$  was expected from the random disorder and boundary phonon scattering influencing to create porosity on thermal transport properties. Therefore, it is evident that the lower K values were caused by the enhancement of phonon scattering due to the fine microstructure. The thermal conductivity is dominated by phonon vibrations when the semiconductor material has a low carrier concentration. The black line shows the thermal conductivity value of Zn<sub>0.98</sub>Al<sub>0.02</sub>O characteristics with the values decreased with increasing temperature corresponding with literature data. The thermal conductivity considerably decreases with Al. The value of  $Zn_{0.98}AI_{0.02}O$  was exhibited lower thermal conductivities over the whole temperature range that decreases when temperature increases from 6.26 (W/m K) at temperature 273 K to 1.79 (W/m K) at 973 K. The thermal conductivity K is dominated by the lattice thermal conductivity KI because of the relatively low electrical conductivity of the materials. This result indicates a possibility to further improve the thermoelectric performance of Al-doped ZnO might cause more free electrons and induce the electronic thermal conductivity rather than lattice thermal conductivity. In addition, the reduction in Al doping samples was expected from the random disorder and boundary phonon scattering influencing to created porosity on  $K_{\rm att}$  thermal transport properties.

#### Dimensionless figure of merit



Figure 97 Temperature dependence of Dimensionless figure of merit of  $p-Ca_3Co_4O_9$ and  $n-Zn_{0.98}Al_{0.02}O$  bulk samples by hot-pressing method compared to references.

The temperature dependence of Dimensionless figure of merit of p– Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and n–Zn<sub>0.98</sub>Al<sub>0.02</sub>O bulk samples by hot–press method, the calculated value is shown in Figure 97. The red line shows ZT of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> characteristics with the values increased with increasing temperature corresponding with literature data. The figure of merit increases with increasing temperature and reaches 0.108 at 973 K. The black line ZT value of Zn<sub>0.98</sub>Al<sub>0.02</sub>O characteristics with the values increased with increasing temperature corresponding with literature data. The ZT was increased with increasing temperature due to the high electrical conductivity and low thermal conductivity. The maximum ZT value of Zn<sub>0.98</sub>Al<sub>0.02</sub>O is 0.28 at 1073 K when compared with other methods from literature data. It Observed be noted that the Hot-pressing method can report for effectively increasing electrical conductivity and reduction of thermal conductivity. The thermoelectric efficiency of this system is effectively improved by HP method and annealing after HP. The results show, the enhanced ZT was increased with increasing temperature due to the lower electrical resistivity and significantly lower thermal conductivity in our sample due to the method for synthesizing.

## FABRICATION OF THERMOELECTRIC MODULES

Thermoelectric modules 16 pairs for 3 temperature ranges are low temperature, medium temperature, and high temperature was designed by the Solidworks program as shown in Figure 98. The thermoelectric module was fabricated following the design using Bi<sub>2</sub>Te<sub>3</sub> for P-type and Sb<sub>2</sub>Te<sub>3</sub> for n-type at low temperature as shown in Figure 99(a), using MnSi<sub>1.75</sub> for P-type and mg<sub>2</sub>Si for n-type at medium temperature as shown in Figure 99(b) and using Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> for P-type and Zn<sub>0.98</sub>Al<sub>0.02</sub>O for n-type at high temperature as shown in Figure 99(c) exhibit resistance about 1.7  $\Omega$ , 570  $\Omega$  and 35 M $\Omega$ , respectively.



Figure 98 Model design by the Solidworks program of thermoelectric configuration



Figure 99 Thermoelectric modules by my self–assembled of (a) low temperature, (b) medium temperature, and (c) high temperature.

## POWER GENERATION MEASUREMENT OF THERMOELECTRIC MODULES



Thermoelectric modules of low temperature ( $R_{module}$ =1.7  $\Omega$ )

Figure 100 (a) the open circuit voltages, (b) the I–V characteristics and the output power measurement with load resistance R<sub>matching load</sub> = 8  $\Omega$ 

Figure 100(a) open-circuit voltages, and (b) the I–V characteristics and the output power measurement with load resistance for low thermoelectric modules. The heat source for hot side was used heater wire into TE module and water cooling used for could side. The TE module 16 pairs had been generating open circuit voltage, electrical power, 0.658 V at  $\Delta$ T=100 K (hot side:423 K; cold side 323 K). Moreover, the I–V curve results of power curve measurements with an applied load resistance for low-temperature TEG with  $\Delta$ T=100 K are shown in Figure 99(b). The open circuit voltage, V<sub>oc</sub> and the maximum output power, P<sub>MAX</sub> for low temperature TEG were about 0.5 V and 8.75 mW (0.25V, 0.035 A). The matching load for TE module was nearly internal resistant of module so to decrease the internal resistant was important for improve performance of TE module.



Figure 101 (a) the open circuit voltages, and (b) the I–V characteristics and the output power measurement with load resistance for a medium thermoelectric module  $R_{matching \ load} = 600 \ \Omega$ 

The (a) open circuit voltages, and (b) the I–V characteristics and the output power measurement with load resistance for medium thermoelectric modules were shown in Figure 101. The heat source for hot side was used heater wire into TE module and water cooling used for could side. The TE module 16 pairs had been generating open circuit voltage 0.447 V and at  $\Delta$ T=100 K (hot side:523 K; cold side 423 K), the I–V curve results of power curve measurements with an applied load resistance for low-temperature TEG with  $\Delta$ T=100 K are shown in Figure 100(b). The open circuit voltage, V<sub>oc</sub> and the maximum output power, P<sub>MAX</sub> for low temperature TEG were about 0.39 V and 6.4 mW (0.2V, 0.032 A) The matching load for TE module was nearly internal resistant of module so to decrease the internal resistant was important for improve performance of TE module.



Thermoelectric modules of high temperature ( $R_{module}$ = 35 M $\Omega$ )

Figure 102 (a) the open circuit voltages, and (b) the I–V characteristics and the output power measurement with load resistance for a high thermoelectric module  $R_{matching \ load} = 700 \ K\Omega$ 

The open circuit voltages, and the I–V characteristics and the output power measurement with load resistance for low thermoelectric modules were shown in Figure 102 (a) and (b), respectively. The heat source for hot side was used heater wire into TE module and water cooling used for could side. The TE module 16 pairs had been generating open circuit voltage, electrical power, 0.658 V and 0.672 W at  $\Delta$ T=100 K (hot side:573 K; cold side 473 K), respectively. Moreover, the I–V curve results of power curve measurements with an applied load resistance for low–temperature TEG with  $\Delta$ T=100 K are shown in Figure 101(b). The open circuit voltage, V<sub>oc</sub> and the maximum output power, P<sub>MAX</sub> for low temperature TEG were about 0.1418 V and 0.61 mW (0.06V, 0.0105 A) The matching load for TE module was nearly internal resistant of module so to decrease the internal resistant was important for improve performance of TE module.

# SOLAR CONCENTRATOR PARABOLA FOR THERMOELECTRIC GENERATOR

The ice production industry has a large supply of cold water from the melting of ice chips throughout the day's production this is a potential cooling source for cooling thermoelectric power generation systems. Therefore, the researcher designed a thermoelectric power generation system by using parabola concentrate sunlight and cooling water to generate electricity shown in Figure 103 (a) and (b) respectively. The charging the electric power to the battery inside the LED lamp. The 12 thermoelectric modules series generate electricity similar to the solar panel from a set of lamps, the voltage starts about 4 volts, current 0.2 amperes. So that the 25 Watt LED lamp can charge with parabola thermoelectric generator 2 lamps for use in 3 hours. However, the main problem of this prototype is solar tracking for the concentration solar line in the center of the thermoelectric module at hot side temperature during daylight.



Figure 103 the Solar concentrate parabola for thermoelectric generator (a) 3D designed with Solid Work program (b) the prototype installed at KORNDECH–ICE Part., Ltd. at Sakon Nakhon province



Figure 104 The daylight solar radiation and the corresponding temperature for parabola during the experimental test



Figure 105 The temperature different of thermoelectric generator module for parabola with water cooling

Figure 103 shows the relationship between daylight solar radiation and the corresponding temperature for parabola during the experimental test can created hot side temperature in aluminum plate during cold side in water cooling plate and ambient temperature. The solar radiation at the start of daylight was approximately  $200 \text{ Wm}^{-2}$  at 7.00 O'clock, which induced a temperature difference of 3 K, and increased to a maximum of approximately 1,200 W m<sup>-2</sup> about 11.30 – 15.00 O'clock for a temperature difference of approximately 30 K. the clouds moved about after 15.00 O'clock, thereby decreasing the radiation intensity: the temperature was decreased. The temperature from solar radiation was calculated by using the Stefan-Boltzmann law for a diffuse black body system following,

$$T = \left(\frac{\text{Solar radiation (W m-2)}}{\sigma_{_{SB}}}\right)^{1/4}$$
(3.8)

where T and  $\sigma_{sB}$  are the calculated temperature from solar radiation and Stefan–Boltzmann constant = 5.670367×10<sup>-8</sup> W m<sup>-2</sup> K<sup>4</sup>

When assuming that all the incoming radiation was absorbed and reemitted, which agrees with results reported by Bjørk, R., & Nielsen, K. K. (2018). The hot-side temperature of non-concentrate at solar radiation at 1,200 W m<sup>-2</sup>  $\approx$  381 K. Moreover, the reflection index of glossy stainless steel about 85 % (Gallego Len, A. J., 2018) so that the hot side temperature from reflection was calculated should be 324.2 K. However, the concentration model on this work was measured hot side temperature on aluminum plat about 360 K so that the parabola was concentrate solar radiation increased. the temperature difference was not only directly dependent on the solar radiation but also on the wind speed and ambient air, which produced a small variation of approximately 5% in the induced temperature difference during the field tests.

## THE POWER GENERATION OF SOLAR CONCENTRATOR PARABOLA

The power generation of the parallel 2 thermoelectric generator module was generated under the condition of the sunny days shown in Figure 106. The power generation related with solar radiation and water cooling which nearly solar cell set for solar lamp start charging about 4 V 0.2 A to maximum 5.87 V 0.512 A at 13.00 O'clock. The solar concentrate parabola consists of 4 pieces of thermoelectric generator modules shown in Figure 107 and cooling by cool water about 285 K can charged 2 lamp solar LED power 25 watt shown in Figure 108(a). However, the power generation of electricity to charging LED lamps used time about 5 hours but can turn on for using LED lamps only about 2.30 hours shown in Figure 108(b).

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Figure 106 The power generation from 2 thermoelectric generator module were generated under the condition of a sunny day



Figure 107 The 4 thermoelectric generator modules were generated electricity for charging 2 LED lamp



Figure 108 (a) Infar red image during testing parabola TEG (b) Testing LED lamp in KORNDECH–ICE Part., Ltd. at Sakon Nakhon province

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## CHAPTER 5

## CONCLUSION

This thesis is focused on the conclusion of the synthesis of thermoelectric materials, processes for fabrication of the thermoelectric module generators in 3 temperature ranges are low temperature, medium temperature, and high temperature. Application at the low-temperature heat source in KORNDECH-ICE Part., Ltd., and Conclusions and suggestions based on the finding of this thesis are as follow:

## THRTMOELECTRIC MATERAILS

## Thermoelectric materials of low temperature

## $Sb_2Te$

The Sb<sub>2</sub>Te<sub>3</sub> material synthesis by planetary ball milling and HP method. The crystal structure of the sample shows a binary–phase rhombohedral structure. All diffraction peaks show the main phase is p–type Sb<sub>2</sub>Te<sub>3</sub>. The FE–SEM images of the surfaces at the high–magnification clusters of fine grains are observed among coarse grains the sample has some randomly spaced pores and the plate–like grains are more pronounced and quite dense which shows a relatively good orientation. The EDS shows the results agree with the composition of all is a Sb<sub>2</sub>Te<sub>3</sub> and composition of all total is 100%. The maximum value Seebeck coefficient is 147  $\mu$ V/K at 523 K and which increases with increasing temperature. The electrical resistivity of p–Sb<sub>2</sub>Te<sub>3</sub> shows the resultive appears to increase with the increase in temperature representing positive temperature coefficient behavior the studied bulk Sb<sub>2</sub>Te<sub>3</sub> single crystal exhibits a metallic nature. The value increases and this tendency is still continuously remained increase is 2.29 × 10<sup>-5</sup>  $\Omega$  cm at 523 K. The PF of Sb<sub>2</sub>Te<sub>3</sub> characteristics with the values decreased with increasing temperature. The thermal conductivity of Sb<sub>2</sub>Te<sub>3</sub> characteristics with the values decreased with increasing temperature from 2.12 (W/m K) at temperature 303 K to 1.54 W/m K at 523 K. It is evident that the lower thermal conductivity values were caused by the Sb<sub>2</sub>Te<sub>3</sub> sample that was synthesized from the HP identical. The ZT of Sb<sub>2</sub>Te<sub>3</sub> shows characteristics with the values increased with increasing temperature, because of the simultaneous optimization in electrical and thermal transport properties. The figure of merit increases with increasing temperature and up to ~0.51 at 473 K.

## $Bi_2Te_3$

The  $Bi_2Te_3$  material synthesis by planetary ball milling and HP method. The crystal structure shows a single-phase corresponding with a pure  $Bi_2Te_3$  phase indicating a hexagonal structure. All diffraction peaks show the main phase is n-type Bi<sub>2</sub>Te<sub>3</sub>. The FE–SEM images of the bulk sample show plate a high–magnification found that reveals a large number of plate-like structures are randomly dispersed on the surface and have randomly spaced pores. The EDS shows the results agree with the composition of all is a  $Bi_2Te_3$  and composition of all total is 100%. The Seebeck coefficient has a negative sign indicating n-type the maximum value Seebeck coefficient is  $-163 \ \mu\text{V/K}$  at 323 K and which the value decreases with the increase in temperature. The electrical resistivity of Bi<sub>2</sub>Te<sub>3</sub> shows higher electrical resistivity throughout the temperature range but decreases in the last temperature measurement, indicating a semiconducting conduction behavior and in the temperature range, 303–473 K indicates a metallic conduction behavior. The PF of Bi<sub>2</sub>Te<sub>3</sub> characteristics with the values increased with increasing temperature. The value of Bi<sub>2</sub>Te<sub>3</sub> was exhibited lower thermal conductivity over the whole temperature range when the temperature increases are 0.45 W/m K at temperature 523 K. the ZT value on the above of Bi<sub>2</sub>Te<sub>3</sub> characteristics with the values increased with increasing temperature. The ZT was increased with increasing temperature due to the high electrical conductivity and low thermal conductivity. The maximum ZT value is around 0.54 at 473 K.

# Thermoelectric materials of medium temperature

## MnSi<sub>1.75</sub>

The MnSi<sub>1.75</sub> material synthesis by planetary ball milling and HP method. The crystal structure shows a mixed-phase between MnSi<sub>1.75</sub> for the main phase and MnSi for the second phase. The main phase is shown as a tetragonal structure and shows the main phase is n-type. The FE-SEM images of the bulk sample show plate a high-magnification found that the sample of some small particles with tetragonal shapes was found among the large particles as the grain size reached about 20  $\mu$ m and plate-like grains are more pronounced and guite dense which show a relatively good orientation. The EDS shows the results agree with the composition of all is a MnSi<sub>1.75</sub> and composition of all total is 100%. The Seebeck coefficient has a positive sign indicating p-type the maximum value Seebeck coefficient is  $129 \ \mu\text{V/K}$  at 623 Kwhich indicates that is a group of semiconductors. Electrical resistivity showed very similar values to the analog studies and increased with increasing temperature, The lowest electrical resistivity achieved of the MnSi\_{\rm 1.75} is around 12  $\times$  10^{-4}  $\Omega$  cm at 298 K. the Power factor of MnSi<sub>1.75</sub> is similar to the Seebeck coefficient because the PF has a tradeoff relationship between the electrical resistivity and the Seebeck coefficient which has a value is 2.2257  $\times$  10<sup>-4</sup> W m<sup>-1</sup>K<sup>-2</sup> at 673K. The thermal conductivity of the MnSi<sub>1.75</sub> sample displays a metallic behavior of the increased thermal conductivity with temperature. The thermal conductivity of the MnSi<sub>1.75</sub> gradually decreases at 673 K and gradually increases when the temperature up to 773 K which has a value is 2.84 W/m K. The ZT of MnSi<sub>1.75</sub> increases with increasing temperature and up to around 0.44 at 773 K.

#### Mg<sub>2</sub>Si

The  $Mg_2Si$  material synthesis by planetary ball milling and HP method. The crystal structure shows a cubic structure and shows a single phase. The FE–SEM images of the sample show the primary  $Mg_2Si$  may display different morphologies, including octahedral, "hopper–like," cubic, truncated octahedral, and massive dendrite forms its average size 3–5  $\mu$ m and clearly octahedral, "hopper–like," cubic, but have randomly spaced pores obviously a lot. The EDS shows the results agree with the composition of all is a Mg<sub>2</sub>Si and composition of all total is 100%. the Seebeck coefficient of Mg<sub>2</sub>Si material has a negative sign indicating n-type. The highest Seebeck coefficient of Mg<sub>2</sub>Si is -435.5  $\mu$ V/K at 623 K increased with increasing temperature due to electron-phonon scattering. The electrical resistivity of Mg<sub>2</sub>Si prepared is semiconductor-like and thus decreases with increasing temperature and exhibiting a shoulder around 298–573 K. The lowest electrical resistivity achieved of the Mg<sub>2</sub>Si is 1.89 × 10<sup>-4</sup> $\Omega$  at 773K. The PF for Mg<sub>2</sub>Si is relatively small and will increase rapidly has a peak value of 1.63 × 10<sup>-4</sup> W m<sup>-1</sup>K<sup>-2</sup> at 573 K. The Power factor of Mg<sub>2</sub>Si will gradually be decreased to 0.86 × 10<sup>-4</sup> W m<sup>-1</sup>K<sup>-2</sup> at 573 K. The thermal conductivity of Mg<sub>2</sub>Si decreases from 5.19 W/m K at room temperature which is reduced to a minimum of around 1.94 W/m K at 773 K. The ZT was increased with increasing temperature due to the high electrical conductivity and low thermal conductivity. The maximum ZT value is around 0.73 at 773 K.

## Thermoelectric materials of high temperature

## $Ca_3Co_4O_9$

The Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> material synthesis by planetary ball milling, HP method, and last step annealed. The crystal structure shows a monoclinic structure and shows a single-phase. The FE-SEM images of the sample the morphology of the Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> plate a high-magnification. The surface area exhibited the morphology of plate-like particles stacked in many layers has of all samples was ~3 µm, and clearly of platelike grains show a relatively good orientation and superposition in many layers. The EDS shows the results agree with the composition of all is a Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and composition of all total is 100%. The Seebeck coefficient of the sample was similarly behavior corresponding with metal to semiconducting and indicates the p-type behavior. The maximum value is 186.65  $\mu$ V/K at 923 K which increases with increasing temperature. The electrical resistivity has values were increased with increasing temperature has a value is 15.9 m $\Omega$  cm at 1023 K. The maximum calculated PF value of the Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> sample is 1.99 x 10<sup>-4</sup> W/mK<sup>2</sup> at 973 K. the thermal conductivity of  $Ca_3Co_4O_9$  was exhibited lower thermal conductivities over the whole temperature range that decreases when temperature increases from 2.49 W/m K at temperature 273 K were which became 1.38 (W/m K) at 973 K. The ZT of  $Ca_3Co_4O_9$  characteristics with the values increased with the increasing temperature and increases with increasing temperature and reaches 0.108 at 973 K.

## Zn<sub>0.98</sub>Al<sub>0.02</sub>O

The Zn<sub>0.98</sub>Al<sub>0.02</sub>O material synthesis by planetary ball milling, HP method, and last step annealed. The crystal structure shows a hexagonal structure and shows a single-phase. All observed XRD peaks can be assigned to those of the pure ZnO phase. The microstructure of the Zn<sub>0.98</sub>Al<sub>0.02</sub>O from FE-SEM shows the surface morphology of the  $Zn_{0.98}AI_{0.02}O$  plate a high-magnification. possess uniform grains and are almost homogeneously distributed and hexagonal like grains and do not observe any phase aggregation other. The average particles size is estimated at  $\sim 1$ µm and has randomly spaced pores obviously a lot and clearly, the grains are almost homogeneously distributed and hexagonal like grains. The EDS shows the results agree with the composition of all is a  $Zn_{0.98}AI_{0.02}O$  and composition of all total is 100%. The Seebeck coefficient of the  $Zn_{0.98}Al_{0.02}O$  shows the negative sign indicating n-type conductivity shows the relation to the carrier concentration in semiconductors. The maximum of S is about  $-408 \mu$ V/K at 1073 K. The electrical resistivity values of  $Zn_{0.98}Al_{0.02}O$  are very high. The electrical resistivity of  $Zn_{0.98}Al_{0.02}O$  decreases from 116 m $\Omega$  cm at 303 K and this tendency is still continuously remained increases is 51.2 m $\Omega$  cm at 1073 K. The maximum PF is 78.52 x 10<sup>-4</sup> W/mK<sup>2</sup> at 1073 K this value is higher than literature data synthesized by the HP method. The thermal conductivity value of  $Zn_{0.98}AI_{0.02}O$  was exhibited lower thermal conductivities over the whole temperature range that decreases when temperature increases from 6.26 (W/m K) at temperature 273 K to 1.79 W/m K at 973 K. The ZT of Zn<sub>0.98</sub>Al<sub>0.02</sub>O was increased with increasing temperature due to the high electrical conductivity and low thermal conductivity. The maximum ZT value of  $Zn_{0.98}Al_{0.02}O$  is 0.28 at 1073 K.

## FABRICATION OF THERMOELECTRIC MODULES

## Thermoelectric module of low temperature

The thermoelectric module of low temperature was fabricated by using soldering method for connecting TE materials with Ag electrode. The TE module 16 pairs had been generating open circuit voltage, electrical power, 0.658 V at  $\Delta$ T=100 K (hot side:423 K; cold side 323 K) and the I–V curve results of open circuit voltage, V<sub>oc</sub> and the maximum output power, P<sub>MAX</sub> for low temperature TEG were about 0.5 V and 8.75 mW (0.25V, 0.035 A).

## Thermoelectric module of medium temperature

The thermoelectric module of medium temperature was fabricated by using silver brazing in hot press under inert gas method for connecting TE materials with Ag electrode. The TE module 16 pairs had been generating open circuit voltage, electrical power, 0.4237 V at  $\Delta$ T=100 K (hot side:523 K; cold side 423 K) and the I–V curve results of open circuit voltage, V<sub>oc</sub> and the maximum output power, P<sub>MAX</sub> for medium temperature TEG were about 0.39 V and 6.4 mW (0.2V, 0.032 A)

## Thermoelectric module of high temperature

The thermoelectric module of high temperature was fabricated by using silver brazing in air method for connecting TE materials with Ag electrode. The TE module 16 pairs had been generating open circuit voltage, electrical power, 0.1418 V at  $\Delta$ T=100 K (hot side:573 K; cold side 473 K) and the I–V curve results of open circuit voltage, V<sub>oc</sub> and the maximum output power, P<sub>MAX</sub> for high temperature TEG were about 0.13 V and 0.61 mW (0.06V, 0.0105 A).

## Solar concentrator parabola for thermoelectric generator

The ice production industry has a large supply of cold water from the melting of ice chips throughout the day's production this is a potential cooling source for cooling thermoelectric power generation systems. Therefore, the researcher designed a thermoelectric power generation system by using parabola concentrate sunlight and cooling water to generate electricity by charging the electric power to battery inside LED lamp. The 12 thermoelectric modules series generate electricity similar with the solar panel from a set of lamps, the voltage start about 4 volts, current 0.2 amperes to maximum 5.87 V 0.512 A at 13.00 O'clock. So that the 25–Watt LED lamp can charge with parabola thermoelectric generator 2 lamps for using in 2.30 hours. However, the main problem of this prototype is solar tracking for concentration solar line in the center of thermo electric module at hot side temperature during a day light.

## SUGGESTIONS

#### Thermoelectric materials

The Sb<sub>2</sub>Te<sub>3</sub> and MnSi1.75 materials XRD pattern of the samples shows a mixed phase, not yet form a single-phase. Should increase the time and temperature of hot pressing to increase for Sb2Te3 and MnSi 1.75 which will the result shows a single-phase.

## Thermoelectric module

The fabrication thermoelectric module should be chosen specific brazing or soldering materials for any kind of materials for good contact, between materials and electrode. The good contact between materials and electrode was decreasing ohmic contact for module resistant decreased.

## Solar concentrate parabola for thermoelectric generator

The main problem of this prototype is solar tracking for concentration solar line in the center of thermoelectric module at hot side temperature during daylight. However, the suggestion of this problem was changing the aluminum plate to evacuate tube in hot side for harvesting solar radiation in all time stability.
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APPENDICE

APPENDICE A

## TABLE OF ROW MATERIALS AND WEIGH AT AN ATOMIC RATIO AND MATERIALS BALANCE

formula for calculation	Materials	Balance (10 g)		
2Sb + 3Te →	Sb <sub>2</sub> Te <sub>3</sub>	Sb = 3.8881 Te = 6.1119		
2Bi + 3Te →	Bi <sub>2</sub> Te <sub>3</sub>	Bi = 5.2195 Te = 4.7805		
Mn + 1.75Si →	MnSi <sub>1.75</sub>	Mn = 5.2781 Si = 4.7219		
2Mg + Si →	Mg <sub>2</sub> Si	Mg = 6.3381 Si = 3.6619		
$\begin{array}{c} CaCO_3 + Co_3O_4 \\ = 3Ca + 4Co + 09 \end{array} \longrightarrow$	Ca <sub>3</sub> Co <sub>4</sub> O <sub>9</sub>	$CaCO_3 = 6.0057$ $Co_3O_4 = 6.6325$ $Co_2 = 2.6408$		
0.98ZnO + 0.02Al <sub>2</sub> O <sub>3</sub> =0.98Zn + 0.02Al + 10 →	Zn <sub>0.98</sub> Al <sub>0.02</sub> O	ZnO = 9.8738 $Al_2O_3 = 0.1262$ O = 0.0198		

Table 11 Raw materials and weigh at an atomic and ratio materials balance

APPENDICE B

TABLE OF CALCULATION LATTICE PARAMETER OF  $Sb_2Te_3$ (RHOMBOHEDRAL STRUCTURE)

Table 12 Calculation lattice parameterr of  ${\rm Sb_2Te_3}$ 

(Rhombohedral structure) a = 4.260 Å and c = 30.422 Å, and

Flow constant =  $1.30 \times 10^{-2}$ 

Peak	2 ( )	L	L.	1	2 $ heta$	$\theta$	$\sim 20$
No.	<b>Λ</b> (nm)	n	n ĸ	I	(degree)	(radian)	Sin <sup>2</sup>
1	0.15406	0	0	6	17.400	0.152	0.022878648
2	0.15406	0	0	9	26.400	0.230	0.052141412
3	0.15406	0	1	5	28.220	0.246	0.05942769
4	0.15406	0	1	8	33.840	0.295	0.084697652
5	0.15406	0	1	10	38.220	0.334	0.107173944
6	0.15406	0	1	11	40.160	0.350	0.117870651
7	0.15406	1	1	0	42.280	0.369	0.130060258
8	0.15406	0	0	15	44.520	0.389	0.143489677
9	0.15406	0	0	13	45.700	0.399	0.150784527
10	0.15406	2	0	5	51.520	0.450	0.188869484
11	0.15406	0	2	10	58.360	0.509	0.237697459
12	0.15406	1	0	19	63.100	0.551	0.273768429
13	0.15406	1	2	5	68.820	0.601	0.319333864
14	0.15406	0	1	26	71.220	0.622	0.339014779
15	0.15406	0	2	10	74.780	0.653	0.368717844

APPENDICE C

TABLE OF CALCULATION LATTICE PARAMETER OF  $Bi_2Te_3$ (HEXAGONAL STRUCTURE)

Table 13 Calculation lattice parameter of  ${\rm Bi}_2{\rm Te}_3$ 

(Hexagonal structure) a, b = 4.321 Å and c = 30.4377 Å, Flow constant =  $1.95 \times 10^{-4}$ 

Peak	2 ( )		-			2 $ heta$	θ	c: 2 <b>0</b>
No.	ん (nm)	n	ĸ		(degree)	(radian)	Sin <sup>2</sup> Ø	
1	0.15406	1	0	1	23.700	0.207	0.042098717	
2	0.15406	0	1	5	27.780	0.242	0.057532496	
3	0.15406	0	1	8	33.480	0.292	0.082823096	
4	0.15406	1	0	10	37.940	0.331	0.10567248	
5	0.15406	0	1	11	40.420	0.353	0.119343988	
6	0.15406	1	1	0	41.260	0.360	0.124137641	
7	0.15406	0	0	15	44.640	0.390	0.144232161	
8	0.15406	1	1	6	45.120	0.394	0.147187865	
9	0.15406	1	0	13	45.540	0.397	0.149794425	
10	0.15406	2	0	5	50.440	0.440	0.181557043	
11	0.15406	1	0	16	53.900	0.470	0.205401821	
12	0.15406	0	2	10	57.220	0.499	0.229292618	
13	0.15406	1	1	15	62.340	0.544	0.267888094	
14	0.15406	0	1	20	66.180	0.578	0.298067674	
15	0.15406	1	2	5	67.020	0.585	0.304795106	

APPENDICE D

TABLE OF CALCULATION LATTICE PARAMETER OF MnSi<sub>1.75</sub> (TETRAGONAL STRUCTURE)

Table 14 Calculation lattice parameter of  $Mg_2Si$ 

(Tetragonal structure) a, b = 5.526 Å, c = 117.67 Å, and Flow constant = –  $3.67 \times 10^{-4}$ 

Peak	2	h	Ŀ		2 $ heta$	$\theta$	$(c; \Omega)^2$
No.	<b>Λ</b> (nm)	n	ĸ	1	(degree)	(radian)	$(Sin \boldsymbol{\sigma})^2$
1	0.15406	1	0	27	25.900	0.226	0.050218503
2	0.15406	2	0	4	32.300	0.282	0.077365066
3	0.15406	1	1	42	39.420	0.344	0.113738112
4	0.15406	2	1	27	41.900	0.366	0.127837588
5	0.15406	1	1	47	42.620	0.372	0.132062758
6	0.15406	2	2	2	46.380	0.405	0.155055805
7	0.15406	2	2	13	47.620	0.416	0.162969249
8	0.15406	3	0	27	53.920	0.471	0.205532187
9	0.15406	1	0	27	25.900	0.226	0.050218503
10	0.15406	2	0	4	32.300	0.282	0.077365066

## APPENDICE E

## TABLE OF CALCULATION LATTICE PARAMETER OF $Mg_2Si$ (CUBIC STRUCTURE)

Table 15 Calculation lattice parameter of  $Mg_2Si$ 

(Cubic structure) a = b = c = 6.351 Å, and Flow constant =  $-1.89 \times 10^{-5}$ 

Peak	2 ( )	L	L.		2 heta	θ	$(c; \Omega)^2$
No.	<b>Λ</b> (nm)	n	к	I	(degree)	(radian)	$(Sin \boldsymbol{O})^2$
1	0.15406	1	1	1	24.260	0.212	0.044081545
2	0.15406	2	0	0	28.080	0.245	0.058756708
3	0.15406	2	2	0	40.100	0.350	0.1175393
4	0.15406	3	1	1	47.400	0.414	0.161562015
5	0.15406	2	2	2	49.680	0.434	0.176472019
6	0.15406	4	0	0	58.000	0.506	0.235040368
7	0.15406	3	3	1	63.800	0.557	0.279247074
8	0.15406	4	2	0	65.660	0.573	0.293924731
9	0.15406	4	2	2	72.860	0.636	0.352646239
10	0.15406	5	1	1	78.100	0.682	0.396897907

APPENDICE F

TABLE OF CALCULATION LATTICE PARAMETER OF  $Ca_3Co_4O_9$ (MONOCLINIC STRUCTURE)

Table 16 Calculation lattice parameter of  $Ca_3Co_4O_9$ 

(Monoclinic structure) a = 4.8564 Å, b = 4.4546 Å, c = 10.8273 Å,

eta = 98.72 deg., and Flow constant = 1.49×10^{-4}

Peak	2 ( )	L	L.	1	2 $ heta$	$\theta$	c:r <sup>2</sup> <i>O</i>
No.	<b>λ</b> (nm)	n	ĸ	I	(degree)	(radian)	SIT
1	0.15406	0	0	2	16.520	0.144	0.020639732
2	0.15406	0	0	3	24.900	0.217	0.046477993
3	0.15406	1	1	1	29.040	0.253	0.062859483
4	0.15406	1	1	2	30.400	0.265	0.068743165
5	0.15406	0	0	4	33.440	0.292	0.082768324
6	0.15406	1	1	3	37.380	0.326	0.102686707
7	0.15406	2	0	0	39.600	0.346	0.114743379
8	0.15406	0	0	5	42.100	0.367	0.12901208
9	0.15406	2	0	2	43.540	0.380	0.137553184
10	0.15406	2	0	3	48.660	0.425	0.169737006
11	0.15406	0	0	6	51.080	0.446	0.185882661
APPENDICE G

TABLE OF CALCULATION LATTICE PARAMETER OF  $Zn_{0.98}AI_{0.02}O$ (HEXAGONAL STRUCTURE)

Table 17 Calculation lattice parameter of  $Zn_{0.98}AI_{0.02}O$ 

(Hexagonal structure) a, b = 3.2498 Å and c = 5.2066 Å, Flow constant =  $2.80 \times 10^{-2}$ 

Peak	2 ( )	Ŀ			2 $ heta$	$\theta$	c: 2 <b>0</b>
No.	ん (nm)	n	к	I	(degree)	(radian)	Sin <sup>2</sup> O
1	0.15406	1	0	0	31.890	0.278	0.075342796
2	0.15406	0	0	2	34.530	0.301	0.087939055
3	0.15406	1	0	1	36.350	0.317	0.097132851
4	0.15406	1	0	2	47.650	0.416	0.163171146
5	0.15406	1	1	0	56.690	0.495	0.225415657
6	0.15406	1	0	3	62.950	0.549	0.272616062
7	0.15406	2	0	0	66.470	0.580	0.300385407
8	0.15406	1	1	2	68.050	0.594	0.313101335
9	0.15406	2	0	1	69.190	0.604	0.322364943
10	0.15406	2	0	4	72.690	0.634	0.351229247
11	0.15406	2	0	2	77.030	0.672	0.387779578

APPENDICE H

TABLE OF OPEN-CIRCUIT VOLTAGE OF LOW TEMPERATURE MODULE

Different	Open circuit	Different	Open circuit	Different	Open circuit
temperature	voltages	temperature	voltages	temperature	voltages
(K)	(∨)	(K)	(∨)	(K)	(V)
0.2	0.02549	5.4	0.03595	10.6	0.05391
0.4	0.02647	5.6	0.03616	10.8	0.0549
0.6	0.02646	5.8	0.03642	11	0.05591
0.8	0.02645	6	0.0377	11.2	0.05698
1	0.02743	6.2	0.03702	11.4	0.05801
1.2	0.02743	6.4	0.03837	11.6	0.0591
1.4	0.02741	6.6	0.03976	11.8	0.0602
1.6	0.02838	6.8	0.03902	12	0.06133
1.8	0.02836	7	0.04064	12.2	0.06246
2	0.02834	7.2	0.04112	12.4	0.06362
2.2	0.02833	7.4	0.04164	12.6	0.0648
2.4	0.02931	7.6	0.04221	12.8	0.06599
2.6	0.0293	7.8	0.04277	13	0.06725
2.8	0.03029	8	0.04338	13.2	0.06845
3	0.03028	8.2	0.04403	13.4	0.0697
3.2	0.03027	8.4	0.0447	13.6	0.07097
3.4	0.03226	8.6	0.0454	13.8	0.07226
3.6	0.03226	8.8	0.04613	14	0.07356
3.8	0.03226	9	0.04689	14.2	0.07488
4	0.03228	9.2	0.04769	14.4	0.07621
4.2	0.03531	9.4	0.04853	14.6	0.07756
4.4	0.03536	9.6	0.04936	14.8	0.07897
4.6	0.03543	9.8	0.05021	15	0.0803
4.8	0.03552	10	0.05109	15.2	0.0817
5	0.03563	10.2	0.052	15.4	0.08311
5.2	0.03577	10.4	0.05294	15.6	0.08453

Table 18 Open circuit voltages of low-temperature module

Table 18 (C	ontinued)
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	Different	Open circuit	Different	Open circuit	Different	Open circuit
	temperature	voltages	temperature	voltages	temperature	voltages
	(K)	(∨)	(K)	(∨)	(K)	(∨)
_	15.8	0.09334	21.2	0.12884	26.6	0.17673
	16	0.09485	21.4	0.1306	26.8	0.17857
	16.2	0.09638	21.6	0.13226	27	0.18038
	16.4	0.09791	21.8	0.13397	27.2	0.18221
	16.6	0.09945	22	0.1357	27.4	0.18404
	16.8	0.10101	22.2	0.13744	27.6	0.18588
	17	0.10257	22.4	0.13917	27.8	0.18777
	17.2	0.10415	22.6	0.14091	28	0.18955
	17.4	0.10578	22.8	0.14266	28.2	0.1914
	17.6	0.10733	23	0.14441	28.4	0.19324
	17.8	0.10894	23.2	0.14623	28.6	0.19509
	18	0.11055	23.4	0.14794	28.8	0.19693
	18.2	0.11218	23.6	0.1497	29	0.19877
	18.4	0.1138	23.8	0.15148	29.2	0.20062
	18.6	0.11545	24	0.15326	29.4	0.20247
	18.8	0.11709	24.2	0.15504	29.6	0.20438
	19	0.11875	24.4	0.15683	29.8	0.20614
	19.2	0.12067	24.6	0.15862	30	0.20798
	19.4	0.12211	24.8	0.16041	30.2	0.20981
	19.6	0.12376	25	0.16227	30.4	0.21165
	19.8	0.12545	25.2	0.16402	30.6	0.21348
	20	0.12714	25.4	0.16582	30.8	0.2153
	20.2	0.12884	25.6	0.16763	31	0.21712
	20.4	0.1306	25.8	0.16945	31.2	0.21895
	20.6	0.13226	26	0.17132	31.4	0.22081
	20.8	0.13397	26.2	0.17308	31.6	0.22261
	21	0.12714	26.4	0.17491	31.8	0.22442

Table 18 (Continued)

Different	Open circuit	Different	Open circuit	Different	Open circuit
temperature	voltages	temperature	voltages	temperature	voltages
(K)	(∨)	(K)	(∨)	(K)	(∨)
32	0.22622	37.4	0.27547	42.8	0.32413
32.2	0.22804	37.6	0.27731	43	0.3259
32.4	0.22984	37.8	0.27913	43.2	0.32765
32.6	0.23167	38	0.28096	43.4	0.3294
32.8	0.23349	38.2	0.28279	43.6	0.33115
33	0.23531	38.4	0.28462	43.8	0.33289
33.2	0.23718	38.6	0.28651	44	0.33468
33.4	0.23894	38.8	0.28829	44.2	0.33636
33.6	0.24076	39	0.29011	44.4	0.33809
33.8	0.24257	39.2	0.29194	44.6	0.33982
34	0.2444	39.4	0.29376	44.8	0.34154
34.2	0.24621	39.6	0.29557	45	0.34326
34.4	0.24804	39.8	0.29738	45.2	0.34497
34.6	0.24986	40	0.29919	45.4	0.34668
34.8	0.25169	40.2	0.30099	45.6	0.34838
35	0.25357	40.4	0.30285	45.8	0.35014
35.2	0.25533	40.6	0.30458	46	0.35179
35.4	0.25716	40.8	0.30637	46.2	0.3535
35.6	0.25898	41	0.30816	46.4	0.3552
35.8	0.26082	41.2	0.30995	46.6	0.3569
36	0.26265	41.4	0.31172	46.8	0.35861
36.2	0.26448	41.6	0.3135	47	0.36028
36.4	0.26631	41.8	0.31528	47.2	0.36196
36.6	0.26814	42	0.31705	47.4	0.36365
36.8	0.27002	42.2	0.31887	47.6	0.36534
37	0.27181	42.4	0.3206	47.8	0.36701
37.2	0.27364	42.6	0.32236	48	0.36868

Table 18	(Continued)
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Different	Open circuit	Different	Open circuit	Different	Open circuit
temperature	voltages	temperature	voltages	temperature	voltages
(K)	(∨)	(K)	(∨)	(K)	(∨)
48.2	0.37034	53.6	0.41341	59	0.45372
48.4	0.37201	53.8	0.41496	59.2	0.45516
48.6	0.37372	54	0.41655	59.4	0.45663
48.8	0.37533	54.2	0.41805	59.6	0.45802
49	0.37699	54.4	0.41959	59.8	0.45944
49.2	0.37862	54.6	0.42112	60	0.46086
49.4	0.38031	54.8	0.42265	60.2	0.46229
49.6	0.38196	55	0.42417	60.4	0.46371
49.8	0.38357	55.2	0.42569	60.6	0.46512
50	0.38517	55.4	0.4272	60.8	0.46654
50.2	0.38675	55.6	0.4287	61	0.46795
50.4	0.38838	55.8	0.43025	61.2	0.4694
50.6	0.38992	56	0.43171	61.4	0.47076
50.8	0.3915	56.2	0.4332	61.6	0.47215
51	0.39308	56.4	0.4347	61.8	0.47354
51.2	0.39466	56.6	0.43619	62	0.47494
51.4	0.39624	56.8	0.43767	62.2	0.47632
51.6	0.39781	57	0.43915	62.4	0.4777
51.8	0.39937	57.2	0.44063	62.6	0.47908
52	0.40094	57.4	0.4421	62.8	0.48045
52.2	0.40252	57.6	0.44358	63	0.48183
52.4	0.40407	57.8	0.44503	63.2	0.48319
52.6	0.40563	58	0.44648	63.4	0.48454
52.8	0.40719	58.2	0.44794	63.6	0.4859
53	0.40875	58.4	0.44939	63.8	0.48725
53.2	0.41031	58.6	0.45083	64	0.48859
53.4	0.41186	58.8	0.45228	64.2	0.48994

Table 18 (Continued)

Different	Open circuit	Different	Open circuit	Different	Open circuit
temperature	voltages	temperature	voltages	temperature	voltages
(K)	(V)	(K)	(∨)	(K)	(V)
64.4	0.49127	69.8	0.52388	75.2	0.5531
64.6	0.49261	70	0.52505	75.4	0.55411
64.8	0.49397	70.2	0.52625	75.6	0.55517
65	0.49525	70.4	0.52738	75.8	0.55618
65.2	0.49657	70.6	0.52854	76	0.55724
65.4	0.49789	70.8	0.5297	76.2	0.5583
65.6	0.4992	71	0.53086	76.4	0.55937
65.8	0.50045	71.2	0.53201	76.6	0.56043
66	0.50135	71.4	0.53316	76.8	0.56153
66.2	0.50253	71.6	0.53429	77	0.56267
66.4	0.50384	71.8	0.53542	77.2	0.56384
66.6	0.50514	72	0.53658	77.4	0.56499
66.8	0.50633	72.2	0.53765	77.6	0.56606
67	0.50756	72.4	0.53874	77.8	0.56722
67.2	0.50878	72.6	0.53982	78	0.56844
67.4	0.50998	72.8	0.54089	78.2	0.56957
67.6	0.51116	73	0.54194	78.4	0.57066
67.8	0.51233	73.2	0.54297	78.6	0.57173
68	0.51349	73.4	0.54398	78.8	0.57278
68.2	0.51462	73.6	0.54499	79	0.57383
68.4	0.51577	73.8	0.546	79.2	0.57488
68.6	0.51692	74	0.547	79.4	0.57592
68.8	0.51808	74.2	0.54802	79.6	0.57696
69	0.51924	74.4	0.54903	79.8	0.57804
69.2	0.5204	74.6	0.55005	80	0.57912
69.4	0.52156	74.8	0.55107	80.2	0.58017
69.6	0.52272	75	0.55208	80.4	0.58115

Table	18	(Continued)
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Differe	nt Open circu	it Different	Open circuit	Different	Open circuit
temperat	ure voltages	temperature	voltages	temperature	voltages
(K)	(V)	(K)	(∨)	(K)	(V)
80.6	0.58214	86	0.60438	91.4	0.62701
80.8	0.58315	86.2	0.60524	91.6	0.62778
81	0.58418	86.4	0.60616	91.8	0.62859
81.2	0.58512	86.6	0.60701	92	0.62936
81.4	0.58602	86.8	0.60788	92.2	0.63016
81.6	0.5869	87	0.60878	92.4	0.63095
81.8	0.58773	87.2	0.60967	92.6	0.63173
82	0.58852	87.4	0.61055	92.8	0.6325
82.2	0.58929	87.6	0.61145	93	0.63327
82.4	0.59008	87.8	0.61239	93.2	0.63403
82.6	0.59087	88	0.61331	93.4	0.6348
82.8	0.59164	88.2	0.61422	93.6	0.63558
83	0.59237	88.4	0.61504	93.8	0.63632
83.2	0.59313	88.6	0.61588	94	0.6371
83.4	0.5939	88.8	0.61674	94.2	0.63788
83.6	0.59467	89	0.61759	94.4	0.63867
83.8	0.59544	89.2	0.61837	94.6	0.63944
84	0.59622	89.4	0.61914	94.8	0.64021
84.2	0.59701	89.6	0.61994	95	0.64098
84.4	0.5978	89.8	0.62081	95.2	0.64175
84.6	0.5986	90	0.62163	95.4	0.64252
84.8	0.5994	90.2	0.62242	95.6	0.6433
85	0.60021	90.4	0.6232	95.8	0.64408
85.2	0.60103	90.6	0.62397	96	0.64486
85.4	0.60186	90.8	0.62473	96.2	0.64563
85.6	0.60269	91	0.62548	96.4	0.6464
85.8	0.60353	91.2	0.62624	96.6	0.64719

Table 18 (Continued)

Different	Open circuit	Different	Open circuit	Different	Open circuit
temperature	voltages	temperature	voltages	temperature	voltages
(K)	(V)	(K)	(∨)	(K)	(∨)
96.8	0.64798	102.2	0.66833	107.6	0.68557
97	0.64875	102.4	0.669	107.8	0.68619
97.2	0.64952	102.6	0.66969	108	0.68683
97.4	0.65025	102.8	0.67033	108.2	0.68742
97.6	0.651	103	0.67098	108.4	0.68803
97.8	0.65174	103.2	0.67162	108.6	0.68864
98	0.65248	103.4	0.67227	108.8	0.68925
98.2	0.65322	103.6	0.67291	109	0.68986
98.4	0.65398	103.8	0.67355	109.2	0.69047
98.6	0.65476	104	0.67419	109.4	0.69107
98.8	0.6556	104.2	0.67482	109.6	0.69167
99	0.65649	104.4	0.67548	109.8	0.69228
99.2	0.65729	104.6	0.67609	110	0.69285
99.4	0.65811	104.8	0.67672		
99.6	0.65891	105	0.67734		
99.8	0.6597	105.2	0.67798		
100	0.66047	105.4	0.67863		
100.2	0.66124	105.6	0.67928		
100.4	0.66199	105.8	0.67992		
100.6	0.66273	106	0.68055		
100.8	0.66347	106.2	0.68118		
101	0.66418	106.4	0.68181		
101.2	0.66489	106.6	0.68243		
101.4	0.66559	106.8	0.68306		
101.6	0.66628	107	0.68369		
101.8	0.66697	107.2	0.68432		

APPENDICE I

TABLE OF THE I-V CHARACTERISTICS AND THE OUTPUT POWER MEASUREMENT WITH LOAD RESISTANCE OF LOW TEMPERATURE

Current	Voltages	Output power	Current	Voltages	Output power
(mA)	(∨)	(mW)	(mA)	(∨)	(mW)
		0			0
		0			0
		0	0.06707		0
0.06757		0			0
		0			0
		0			0
		0			0
		0			0
		0			0
		0			0
		0			0
		0			0
		0			0
		0			0
		0			0
		0			0
		0			0
		0			0
		0			0
		0	0.06686	0.0069	0.04611
		0			0
		0			0
		0		0.06531	0
		0		0.06527	0
		0		0.06529	0

Table 19 The I–V characteristics and the output power measurement with load resistance low temperature

Current	Voltages	Output power	Current	Voltages	Output power
(mA)	(∨)	(mW)	(mA)	(∨)	(mW)
	0.0653	0		0.11159	0
	0.06527	0		0.11162	0
	0.06528	0		0.11166	0
	0.06527	0		0.11169	0
	0.06529	0		0.11172	0
	0.0653	0		0.11172	0
	0.06532	0		0.11174	0
	0.06534	0		0.11174	0
	0.06535	0		0.11176	0
	0.06537	0	0.05315	0.11173	0.59387
	0.06539	0	0.05316	0.11175	0.59413
	0.0654	0	0.05318	0.11176	0.59432
0.05909	0.06542	0.38659	0.05319	0.11178	0.59456
0.05911	0.06544	0.38683		0.11181	0
0.05913	0.06546	0.38708		0.11183	0
	0.06548	0		0.14924	0
0.05916	0.06549	0.38746		0.14925	0
	0.0655	0		0.14928	0
	0.11133	0		0.14931	0
	0.11135	0		0.14934	0
	0.11138	0		0.14937	0
	0.11141	0		0.1494	0
	0.11144	0		0.14943	0
	0.11147	0		0.14947	0
	0.1115	0		0.1495	0
	0.11153	0		0.14952	0
	0.11156	0		0.14956	0

Current	Voltages	Output power	Current	Voltages	Output power
(mA)	(∨)	(mW)	(mA)	(∨)	(mW)
	0.14959	0		0.17999	0
	0.14963	0		0.18001	0
	0.14967	0		0.18006	0
	0.14971	0		0.18011	0
	0.14975	0		0.18015	0
	0.14979	0		0.18019	0
	0.14983	0		0.18024	0
	0.14986	0		0.18023	0
0.04825	0.14979	0.72267		0.18015	0
	0.14951	0		0.18004	0
	0.14948	0		0.18008	0
	0.14943	0		0.18013	0
	0.14946	0	0.04401	0.18017	0.79294
	0.14921	0	0.04402	0.18022	0.79332
	0.14915	0		0.18028	0
	0.1491	0		0.20628	0
	0.14914	0		0.20632	0
	0.14919	0		0.20636	0
	0.17999	0		0.20639	0
	0.18002	0		0.20641	0
	0.18007	0		0.20644	0
	0.18012	0		0.20648	0
	0.18016	0		0.20651	0
	0.1802	0		0.20655	0
	0.18015	0		0.20658	0
	0.17997	0		0.20661	0
	0.17994	0		0.20664	0

Current	Voltages	Output power	Current	Voltages	Output power
(mA)	(∨)	(mW)	(mA)	(∨)	(mW)
	0.20667	0		0.22886	0
	0.2067	0	0.0376	0.22892	0.86082
	0.20673	0	0.03761	0.22897	0.8612
	0.20668	0	0.03762	0.22902	0.8616
0.0405	0.20636	0.83582		0.22907	0
	0.20638	Ο		0.22913	0
	0.22841	0		0.22919	0
	0.22844	Ο		0.22903	0
	0.22849	Ο		0.22885	0
	0.22854	Ο		0.24776	0
	0.22851	Ο		0.24782	0
	0.22829	Ο		0.24789	0
	0.22794	0		0.24795	0
	0.22795	0		0.24801	0
	0.22803	0		0.24806	0
	0.22811	0		0.24796	0
	0.22819	0		0.24794	0
	0.22826	0		0.24781	0
	0.22833	0	0.03495	0.2477	0.86577
	0.2284	0		0.24769	0
	0.22846	0		0.2477	0
	0.22852	0		0.24747	0
	0.22858	0		0.24746	0
	0.22864	0		0.24726	0
	0.22869	0		0.24719	0
	0.22875	0		0.24727	0
	0.22881	0		0.26374	0

Current	Voltages	Output power	Current	Voltages	Output power
(mA)	(∨)	(mW)	(mA)	(∨)	(mW)
	0.26381	0		0.27874	0
	0.26386	0		0.27879	0
	0.2639	0		0.27884	0
	0.26395	0		0.27889	0
	0.264	0	0.03072	0.27894	0.85695
	0.26406	0		0.27896	0
	0.26412	0		0.27896	0
	0.26417	0	0.03069	0.27859	0.85505
	0.26423	0		0.27867	0
0.03273	0.2643	0.86504		0.29187	0
	0.26436	0		0.29193	0
	0.26442	0		0.29157	0
	0.26449	0	0.02888	0.29162	0.84207
	0.26456	0	0.02888	0.29166	0.84242
	0.27928	0		0.29174	0
	0.27936	0	0.0289	0.29181	0.84326
	0.27942	0		0.29187	0
	0.27948	0		0.29188	0
	0.27928	0		0.29193	0
	0.27899	0		0.29199	0
	0.27877	0		0.29206	0
	0.27863	0		0.29212	0
	0.27866	0	0.02894	0.29219	0.84547
	0.27855	0		0.29225	0
	0.2786	0		0.29231	0
	0.27864	0		0.18114	0
	0.27869	0		0.1809	0

Current	Voltages	Output power	Current	Voltages	Output power
(mA)	(∨)	(mW)	(mA)	(∨)	(mW)
	0.00673	0		0.30518	0
	0.0661	0		0.30523	0
	0.30394	0		0.30529	0
	0.30407	0		0.30535	0
	0.30409	0		0.30541	0
	0.30417	0		0.30547	0
	0.30426	0		0.30503	0
0.02743	0.30434	0.83475		0.30492	0
0.02743	0.30443	0.83518		0.30488	0
	0.3045	0	0.02748	0.30492	0.83794
	0.30457	0	0.02749	0.30499	0.83836
	0.30466	0	0.02749	0.30507	0.8388
	0.30468	0		0.30515	0
0.02745	0.30461	0.83617	0.02749	0.3052	0.83901
	0.30466	0	0.02748	0.30507	0.83845
	0.3047	0	0.02743	0.30501	0.83655
	0.30476	0		0.30436	0
	0.30482	0		0.30435	0
	0.30487	0		0.3044	0
	0.30492	0		0.3043	0
	0.30497	0		0.30416	0
	0.30502	0		0.3042	0
	0.30507	0		0.30415	0
	0.3051	0		0.30422	0
	0.30514	0		0.3043	0
	0.3051	0		0.30439	0
	0.30514	0		0.30448	0

Current	Voltages	Output power	Current	Voltages	Output power
(mA)	(∨)	(mW)	(mA)	(∨)	(mW)
	0.30458	0		0.34178	0
	0.30467	0	0.02265	0.3417	0.77384
	0.3045	0		0.34169	0
	0.30427	Ο	0.02265	0.34175	0.77423
	0.30406	Ο		0.3418	0
	0.30418	0	0.0217	0.34892	0.75718
	0.30429	0	0.0217	0.34898	0.75739
	0.3044	Ο	0.02171	0.34902	0.75759
0.02745	0.30453	0.83591	0.02169	0.34907	0.75715
0.02746	0.30464	0.83646	0.02168	0.3488	0.75627
	0.30473	0	0.02169	0.34868	0.75613
	0.31518	0	0.0208	0.34873	0.7253
	0.31529	0	0.0208	0.35526	0.73889
	0.3154	0	0.0208	0.35525	0.73891
0.02607	0.31538	0.82215		0.35509	0
	0.31541	0	0.02074	0.35421	0.73477
0.02481	0.31551	0.78293	0.02076	0.35433	0.73543
	0.32491	0	0.02076	0.35446	0.73599
0.02483	0.32502	0.80696		0.36053	0
	0.32506	0	0.01996	0.3606	0.71985
	0.32504	0	0.01993	0.36072	0.71903
0.02368	0.33353	0.78993		0.3601	0
0.02369	0.33364	0.79045		0.35975	0
	0.33374	0	0.01988	0.35948	0.71467
	0.33384	0	0.01912	0.35918	0.68683
	0.33391	0		0.36473	0
0.02265102	0.33398	0.75655	0.01914	0.36489	0.69839

Current	Voltages	Output power	Current	Voltages	Output power
(mA)	(∨)	(mW)	(mA)	(∨)	(mW)
0.01915	0.36504	0.69894		0.37265	0
0.01843	0.36517	0.67304		0.37276	0
0.01844	0.3703	0.68272		0.37286	0
	0.3704	0			0.5089
	0.37051	0		0.40938	0
	0.37063	0		0.4095	0
	0.37074	0		0.40962	0
	0.36565	0		0.40975	0
	0.35425	0		0.4095	0
	0.35431	0		0.40944	0
	0.34086	0		0.40949	0
	0.30492	0		0.4082	0
	0.29344	0		0.40715	0
	0.30516	0	0.0135	0.40581	0.54775
	0.30525	0		0.40498	0
	0.30537	0		0.42545	0
	0.29386	0		0.42584	0
	0.29392	0		0.42613	0
	0.29402	0		0.42637	0
	0.29413	0		0.42655	0
	0.29422	0	0.01067	0.42669	0.45517
	0.2943	0		0.42682	0
	0.29439	0	0.01067	0.42693	0.45564
	0.37216	0		0.42703	0
	0.37228	0	0.01068	0.42713	0.45606
	0.37242	0	0.01068	0.42722	0.45624
	0.37254	0		0.42731	0

Table 19 (Continued)

Current	Voltages	Output power	Current	Voltages	Output power
(mA)	(∨)	(mW)	(mA)	(V)	(mW)
	0.44096	0	0.00576	0.46033	0.26498
0.00883	0.44106	0.38944	0.00576	0.4601	0.2649
0.00883	0.44116	0.38962	0.00517	0.46017	0.23777
0.00883	0.44126	0.3898	0.00517	0.46453	0.24008
	0.44136	0	0.00517	0.46463	0.24017
	0.44078	0	0.00517	0.4647	0.24023
	0.44079	0	0.00517	0.46478	0.24032
0.00751	0.45046	0.33846	0.00517	0.46485	0.24038
0.00752	0.4506	0.33865	0.00517	0.46491	0.24045
0.00752	0.45072	0.33881	0.00517	0.46498	0.24052
0.00752	0.45081	0.33895	0.00517	0.46505	0.24058
0.00749	0.4509	0.33774	0.00517	0.46509	0.24051
0.00748	0.44903	0.33605	0.00469	0.46838	0.21966
0.00748	0.4487	0.33561	0.00469	0.46832	0.21963
0.00747	0.44849	0.335	0.00469	0.46832	0.21963
0.00746	0.44787	0.33401	0.00469	0.4683	0.21961
0.00649	0.45407	0.2946	0.00469	0.46831	0.21963
	0.45387	0	0.00469	0.46832	0.21963
0.00649	0.45407	0.29484	0.00469	0.46832	0.21964
0.0065	0.45424	0.29506		0.46833	0
0.0065	0.45439	0.29524		0.45501	0
0.0065	0.45452	0.29541		0.43835	0
0.00576	0.45465	0.26173		0.43838	0
0.00576	0.46015	0.26496		0.43364	0
0.00576	0.46026	0.26508		0.42486	0
0.00576	0.46036	0.26512		0.35611	0
0.00576	0.4603	0.2651		0.00632	0

Current	Voltages	Output power	Current	Voltages	Output power
(mA)	(∨)	(mW)	(mA)	(∨)	(mW)
	0.00629	0	0.00396	0.4756	0.4756
	0.00628	0	0.00396	0.4757	0.4757
	0.00626	0	0.00396	0.47579	0.47579
	0.00626	0	0.00367	0.47587	0.47587
	0.00625	0	0.00367	0.47685	0.47685
	0.00625	0	0.00367	0.47689	0.47689
	0.00625	0	0.00367	0.477	0.477
	0.00624	0	0.00367	0.47709	0.47709
	0.00624	0	0.00367	0.47716	0.47716
	0.00624	0	0.00367	0.47722	0.47722
	0.00627	0	0.00342	0.47726	0.47726
	0.00626	0	0.00342	0.4791	0.4791
	0.00625	0	0.00342	0.47915	0.47915
	0.29115	0	0.00342	0.4792	0.4792
	0.00627	0	0.00342	0.47926	0.47926
0.00468	0.46868	0.21947	0.00342	0.47932	0.47932
0.00468	0.4689	0.21966	0.00321	0.47937	0.47937
0.00429	0.4691	0.20111	0.00321	0.48096	0.48096
0.00429	0.47215	0.20247	0.00321	0.481	0.481
0.00429	0.47228	0.20259	0.00321	0.48106	0.48106
0.00429	0.47242	0.2027	0.00321	0.48112	0.48112
0.00429	0.47254	0.2028	0.00321	0.48117	0.48117
0.00396	0.47265	0.18703	0.00321	0.48123	0.48123
0.00396	0.47519	0.18806	0.00321	0.48128	0.48128
0.00396	0.4753	0.18816	0.0032	0.48134	0.48134
0.00396	0.4754	0.18823	0.0032	0.48013	0.48013
0.00396	0.4755	0.18831	0.00301	0.4796	0.4796

Table 19 (Continued)

	Current	Voltages	Output power	Current	Voltages	Output power
	(mA)	(∨)	(mW)	(mA)	(V)	(mW)
-	0.00301	0.48112	0.14469	0.00243	0.48661	0.11847
	0.00301	0.48124	0.14477	0.00243	0.48666	0.11848
	0.00301	0.48136	0.14483	0.00321	0.4858	0.15578
	0.00301	0.48146	0.14488	0.00321	0.48104	0.15426
	0.00301	0.48154	0.14493	0.00321	0.48109	0.15431
	0.00301	0.4816	0.14496	0.00321	0.48114	0.15434
		0.48287	0		0.4812	0
		0.48288	0		0.47321	0
	0.00284	0.48293	0.1372		0.47327	0
	0.00284	0.48297	0.13722		0.47037	0
	0.00284	0.48301	0.13725	0.00243		0.11449
	0.00284	0.48306	0.13727	0.00243	0.48707	0.11857
		0.4831	0	0.00243	0.48713	0.1186
	0.00269	0.48419	0.13028	0.00243	0.48721	0.11862
	0.00269	0.48424	0.13029	0.00244	0.48726	0.11866
	0.00269	0.48428	0.13032	0.00244	0.48732	0.11868
	0.00269	0.48432	0.13034	0.00244	0.48737	0.11871
	0.00269	0.48437	0.13036	0.00244	0.48742	0.11873
	0.00256	0.4844	0.12378	0.00244	0.48747	0.11876
	0.00256	0.48541	0.12406	0.00244	0.48752	0.11878
	0.00256	0.48546	0.12408	0.00244	0.48756	0.11879
	0.00256	0.4855	0.12411	0.00244	0.48759	0.11882
	0.00245	0.48555	0.11904	0.00232	0.48765	0.11338
	0.00243	0.48646	0.11838	0.00233	0.4885	0.11359
	0.00243	0.48647	0.1184	0.00233	0.48852	0.11359
	0.00243	0.48652	0.11842	0.00233	0.48856	0.11361
-	0.00243	0.48657	0.11844	0.00233	0.48862	0.11364

Table 19 (Continued)

Current	Voltages	Output power	Current	Voltages	Output power
(mA)	(∨)	(mW)	(mA)	(∨)	(mW)
0.00233	0.48867	0.11366	0.00124	0.49715	0.06176
0.002	0.48872	0.0977	0.00124	0.49718	0.06177
0.00197	0.49137	0.09659	0.00127	0.49721	0.06332
0.00197	0.49141	0.09661	0.00142	0.49678	0.07033
0.00197	0.49148	0.09663	0.00111	0.49594	0.05485
0.00197	0.49153	0.09665	0.00111	0.49821	0.05512
0.00197	0.49158	0.09668	0.00111	0.49823	0.05512
0.00182	0.49164	0.08971		0.49826	0
0.00165	0.49265	0.08115	0.00111	0.49829	0.05514
0.00165	0.49396	0.08137	0.00111	0.49831	0.05514
0.00165	0.49402	0.08139	0.00111	0.49833	0.05514
0.00165	0.49407	0.08139	0.00111	0.49835	0.05515
0.00165	0.4941	0.08141	0.00104	0.49853	0.05177
0.00197	0.49413	0.09719		0.49878	0
0.00197	0.49175	0.09674		0.49902	0
0.00197	0.49177	0.09675		0.49909	0
0.00142	0.49179	0.0696		0.49912	0
0.00142	0.4958	0.07018	9.98E-04	0.49915	0.0498
0.00142	0.49581	0.07018		0.49918	0
0.00142	0.49584	0.07019	0.00106	0.49915	0.05292
0.00142	0.49585	0.07019		0.49859	0
0.00142	0.49587	0.0702		0.49838	0
0.00142	0.49589	0.07021	9.08E-04	0.49984	0.0454
0.00134	0.4959	0.06649	9.08E-04	0.49988	0.0454
0.00134	0.49642	0.06656	9.08E-04	0.49991	0.04541
0.00124	0.49643	0.06167	9.08E-04	0.49993	0.04542
0.00124	0.49711	0.06176	9.08E-04	0.49996	0.04541

Table 19 (Continued)

Current	Voltages	Output power	Current	Voltages	Output power
(mA)	(∨)	(mW)	(mA)	(∨)	(mW)
9.08E-04	0.49998	0.04542	7.14E-04	0.4999	0.03569
8.64E-04	0.5	0.04319	7.14E-04	0.49996	0.03568
8.33E-04	0.50027	0.04169	7.14E-04	0.50001	0.03569
8.34E-04	0.50039	0.04171	7.14E-04	0.50006	0.0357
8.34E-04	0.50048	0.04173	7.14E-04	0.50009	0.03571
8.34E-04	0.50053	0.04174	7.14E-04	0.50013	0.0357
8.34E-04	0.50057	0.04174	7.24E-04	0.50017	0.03623
8.34E-04	0.5006	0.04174	7.68E-04	0.50011	0.03841
8.31E-04	0.5005	0.04161	6.67E-04	0.49977	0.03333
8.31E-04	0.49897	0.04148	5.89E-04	0.50059	0.02949
8.31E-04	0.49894	0.04148	5.96E-04	0.50117	0.02987
8.31E-04	0.49898	0.04147	6.25E-04	0.50117	0.03131
8.31E-04	0.49903	0.04148	6.25E-04	0.50061	0.0313
8.45E-04	0.49908	0.04219	6.25E-04	0.50085	0.03132
9.09E-04	0.49898	0.04536	6.26E-04	0.50098	0.03135
9.06E-04	0.49839	0.04514	6.26E-04	0.50106	0.03134
9.06E-04	0.49843	0.04513	6.26E-04	0.50114	0.03136
7.68E-04	0.49941	0.03834	5.57E-04	0.50121	0.0279
7.68E-04	0.49947	0.03835	5.57E-04	0.50161	0.02792
7.68E-04	0.49951	0.03835	5.57E-04	0.50172	0.02793
7.68E-04	0.49954	0.03835	5.57E-04	0.50182	0.02795
7.68E-04	0.49956	0.03835	5.57E-04	0.5019	0.02794
7.68E-04	0.49958	0.03836	5.57E-04	0.50197	0.02796
7.24E-04	0.4996	0.03616	5.02E-04	0.50242	0.0252
7.13E-04	0.49985	0.03565	5.02E-04	0.50235	0.0252
7.14E-04	0.49971	0.03566	5.02E-04	0.50248	0.02521

APPENDICE J

TABLE OF OPEN-CIRCUIT VOLTAGE OF MEDIUM TEMPERATURE MODULE

Different	Open circuit	Different	Open circuit	Different	Open circuit
temperature	voltages	temperature	voltages	temperature	voltages
(K)	(∨)	(K)	(∨)	(K)	(∨)
7.003	0.00311	6.939	0.01783	11.304	0.00348
6.992	0.00668	6.935	0.01328	11.998	0.00325
6.986	0.00817	6.942	0.01319	12.741	0.03183
6.988	0.00817	6.942		13.518	0.03068
6.975	0.00692	6.941	0.02278	14.347	0.03855
6.968	0.00925	6.944		15.21	0.02816
6.967	0.00904	6.941		16.115	0.03586
6.96	0.01304	6.942	0.01094	17.06	0.03355
6.959	0.00819	6.936		18.036	0.05006
6.95		6.933		19.043	0.05279
6.951	0.02849	6.948		20.068	0.02204
6.937	0.00732	6.947	0.01153	21.113	0.02993
6.947	0.02934	6.972	0.00113	22.171	0.03173
6.944	0.01687	7.009		23.239	0.03469
6.934		7.054	0.01831	24.348	0.04378
6.944	0.0088	7.143	0.01616	25.469	0.04708
6.939	0.01981	7.274		26.614	0.05259
6.943		7.439	0.01551	27.766	0.05508
6.942		7.663		28.954	0.05746
6.943		7.917		30.129	0.06123
6.939	0.01158	8.25	0.01237	31.319	0.06635
6.942	0.02532	8.613	0.00221	32.535	0.06771
6.935	0.02174	9.051	0.00115	33.758	0.0697
6.938		9.532	0.00409	34.959	0.07149
6.941	0.00586	10.076	0.0043	36.156	0.07425
6.94	0.01645	10.661	0.00515	37.349	0.0799

Table 20 Open circuit voltages of medium-temperature module

Table 20	(Continued)
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Different	Open circuit	Different	Open circuit	Different	Open circuit
temperature	voltages	temperature	voltages	temperature	voltages
(K)	(∨)	(K)	(V)	(K)	(V)
38.559	0.08546	70.744	0.29807	98.636	0.42377
39.783	0.10129	71.891	0.30256	99.557	0.43855
41.022	0.10027	73.058	0.31433	100.487	0.44658
42.24	0.09558	74.194	0.33637	101.443	0.44122
43.426	0.10023	75.306	0.34619	102.415	0.44125
44.646	0.10383	76.423	0.35177	103.365	0.44208
45.859	0.10352	77.519	0.35413	104.292	0.44765
47.08	0.10722	78.597	0.35436	105.201	0.44964
48.294	0.10705	79.639	0.3563	106.082	0.44928
49.528	0.10798	80.725	0.3604	106.949	0.44942
50.73	0.11082	81.792	0.36247	107.802	0.44987
51.885	0.1102	82.846	0.36388	108.649	0.45045
53.088	0.11484	83.874	0.36405	109.497	0.45036
54.3	0.11675	84.886	0.36502	110.291	0.45017
55.509	0.11802	85.901	0.36513	111.051	0.45066
56.763	0.11887	86.958	0.36505	111.899	0.45218
57.973	0.11816	87.938	0.37436	112.741	0.45398
59.159	0.25193	88.919	0.37437	113.515	0.4521
60.337	0.26026	89.91	0.37437	114.303	0.45027
61.504	0.26732	90.903	0.37432	115.099	0.45127
62.713	0.28794	91.881	0.37426	115.928	0.45208
63.876	0.29153	92.866	0.37425	116.729	0.4511
65.028	0.29335	93.851	0.37428	117.371	0.45414
66.19	0.29443	94.829	0.38753	118.22	0.45357
67.34	0.29344	95.799	0.38751	118.957	0.4552
68.469	0.29551	96.765	0.39753	119.69	0.46891

APPENDICE K

TABLE OF THE I-V CHARACTERISTICS AND THE OUTPUT POWER MEASUREMENT WITH LOAD RESISTANCE OF MEDIUM TEMPERATURE

Current (mA)	Voltagos (V/)	Output power	
Current (MA)	volluges (v)	(mW)	
8.95E-04	0.39196	0.34308	
0.00655	0.35411	1.70982	
0.014	0.30108	3.1242	
0.0184	0.27835	3.77898	
0.0234	0.25055	4.22858	
0.02812	0.22783	4.57671	
0.0319	0.20762	4.72246	
0.0337	0.20002	4.7191	
0.0355	0.18992	4.66472	
0.04246	0.17981	4.29417	
0.0471	0.16718	3.82607	
0.05003	0.15707	3.46336	
0.0547	0.14193	2.74019	
0.06132	0.11665	1.2989	
0.0659	0.0889	0.1166	
0.007			

Table 21 The I–V characteristics and the output power measurement with load resistance medium temperature

APPENDICE L

TABLE OF OPEN-CIRCUIT VOLTAGE OF HIGH TEMPERATURE MODULE
Different	Open circuit	Different	Open circuit	Different	Open circuit
temperature	voltages	temperature	voltages	temperature	voltages
(K)	(∨)	(K)	(∨)	(K)	(∨)
0.636	7.97E-04	0.736	0.00305	1.299	0.00997
0.648	7.96E-04	0.735	0.00325	1.398	0.01029
0.652	8.01E-04	0.744	0.00346	1.571	0.01063
0.654	8.03E-04	0.747	0.00367	1.697	0.01096
0.659	8.06E-04	0.755	0.00389	1.902	0.0113
0.67	8.22E-04	0.747	0.00411	2.046	0.01165
0.67	8.37E-04	0.751	0.00434	2.277	0.01199
0.666	8.60E-04	0.755	0.00457	2.451	0.01234
0.666	8.92E-04	0.754	0.00481	2.712	0.01269
0.684	9.32E-04	0.762	0.00506	2.899	0.01305
0.68	9.84E-04	0.762	0.00531	3.19	0.01342
0.681	0.00104	0.776	0.00556	3.392	0.01378
0.695	0.00112	0.765	0.00582	3.701	0.01414
0.681	0.00119	0.766	0.0061	3.904	0.01451
0.699	0.00128	0.78	0.00636	4.242	0.01489
0.699	0.00138	0.776	0.00664	4.459	0.01527
0.71	0.0015	0.788	0.00692	4.801	0.01564
0.717	0.00161	0.784	0.0072	5.044	0.01603
0.71	0.00174	0.81	0.00749	5.401	0.01641
0.699	0.00188	0.813	0.00779	5.655	0.01681
0.714	0.00202	0.843	0.00808	6.025	0.0172
0.714	0.00218	0.879	0.00839	6.276	0.01759
0.736	0.00233	0.935	0.0087	6.669	0.01799
0.725	0.0025	0.982	0.00901	6.92	0.01839
0.721	0.00268	1.082	0.00933	7.317	0.0188
0.725	0.00287	1.163	0.00965	7.586	0.01921

Table 22 Open circuit voltages of high-temperature module

Table 22 (Continued)

Different	Open circuit	Different	Open circuit	Different	Open circuit
temperature	voltages	temperature	voltages	voltages temperature	
(K)	(∨)	(K)	(V)	(K)	(∨)
7.985	0.01961	18.412	0.0317	30.191	0.04546
8.259	0.02003	18.915	0.03219	30.548	0.04599
8.681	0.02046	19.258	0.03267	31.088	0.04652
8.961	0.02087	19.789	0.03315	31.435	0.04707
9.397	0.02129	20.136	0.03364	31.982	0.04758
9.692	0.02171	20.642	0.03413	32.322	0.04812
10.127	0.02214	20.981	0.03463	32.858	0.04865
10.426	0.02257	21.479	0.03514	33.215	0.0492
10.877	0.023	21.818	0.03562	33.748	0.04973
11.186	0.02344	22.304	0.03612	34.084	0.05028
11.637	0.02387	22.653	0.03663	34.597	0.05081
11.942	0.02433	23.195	0.03713	34.937	0.05136
12.415	0.02476	23.537	0.03763	35.465	0.0519
12.731	0.02521	24.053	0.03814	35.816	0.05242
13.203	0.02565	24.367	0.03865	36.378	0.05297
13.52	0.02611	24.866	0.03917	36.717	0.05351
14.015	0.02655	25.2	0.03969	37.246	0.05404
14.342	0.02702	25.735	0.0402	37.599	0.05459
14.825	0.02747	26.09	0.04072	38.126	0.0551
15.162	0.02793	26.643	0.04125	38.479	0.05562
15.642	0.0284	27.002	0.04176	38.992	0.05614
15.964	0.02886	27.533	0.04231	39.351	0.05666
16.451	0.02932	27.877	0.04282	39.871	0.05716
16.783	0.02979	28.404	0.04334	40.217	0.05765
17.261	0.03027	28.746	0.04386	40.758	0.05814
17.593	0.03076	29.28	0.0444	41.11	0.05864
18.091	0.03122	29.639	0.04493	41.656	0.05912

Table 22 (Continued)

Different	Open circuit	Different	Open circuit	Different	Open circuit
temperature	voltages	temperature	voltages	temperature	voltages
(K)	(V)	(K)	(V)	(K)	(V)
42.013	0.0596	53.695	0.07169	61.683	0.08295
42.55	0.06008	54.036	0.07211	62.206	0.08335
42.899	0.06056	54.436	0.07253	62.44	0.08376
43.426	0.06104	54.692	0.07296	62.702	0.08416
43.793	0.0615	55.126	0.0734	62.853	0.08457
44.324	0.06196	55.404	0.07381	63.148	0.08497
44.691	0.06242	55.827	0.07423	63.36	0.08536
45.24	0.06288	56.125	0.07465	63.641	0.08575
45.579	0.06335	56.536	0.07507	63.839	0.08615
46.123	0.06379	56.826	0.07553	64.13	0.08654
46.403	0.06425	57.198	0.07595	64.331	0.0869
47.001	0.0647	57.455	0.07637	64.633	0.08728
47.344	0.06515	57.752	0.07678	64.828	0.08769
47.88	0.0656	57.96	0.07721	65.098	0.08809
48.231	0.06605	58.254	0.07762	65.289	0.08848
48.788	0.06649	58.444	0.07803	65.539	0.08887
49.135	0.06693	58.726	0.07845	65.723	0.08926
49.61	0.06739	58.945	0.07886	66.021	0.08965
49.924	0.06781	59.255	0.07926	66.227	0.09002
50.402	0.06825	59.488	0.07968	66.572	0.09044
50.734	0.06869	59.784	0.08008	66.833	0.09084
51.241	0.06913	59.988	0.0805	67.254	0.09126
51.58	0.06956	60.272	0.08091	67.547	0.09168
52.087	0.06999	60.477	0.08132	67.993	0.09208
52.412	0.07042	60.79	0.08173	68.272	0.09248
52.899	0.07084	61.002	0.08213	68.697	0.09285
53.208	0.07127	61.362	0.08253	68.951	0.09324

Table 22 (Continued)

Different	Open circuit	Different	Open circuit	Different	Open circuit
temperature	voltages	temperature	voltages	voltages temperature	
(K)	(∨)	(K)	(V)	(K)	(∨)
69.328	0.09365	76.99	0.10392	83.026	0.11317
69.614	0.09403	77.239	0.10428	83.196	0.11349
69.947	0.09442	77.419	0.10465	83.407	0.1138
70.18	0.09481	77.676	0.10502	83.515	0.11412
70.574	0.09519	77.837	0.10539	83.649	0.11445
70.868	0.09557	78.057	0.10576	83.764	0.11478
71.264	0.09596	78.223	0.10612	83.983	0.11511
71.499	0.09635	78.498	0.10648	84.134	0.11546
71.812	0.09673	78.67	0.10684	84.392	0.11581
72.007	0.09713	78.904	0.1072	84.562	0.11615
72.257	0.09751	79.063	0.10759	84.838	0.11652
72.428	0.0979	79.308	0.10794	84.986	0.11685
72.744	0.09828	79.453	0.1083	85.211	0.1172
72.968	0.09867	79.742	0.10865	85.329	0.11754
73.355	0.09907	79.955	0.109	85.555	0.11788
73.604	0.09944	80.319	0.10935	85.63	0.1182
73.999	0.09982	80.485	0.10972	85.594	0.11856
74.255	0.1002	80.739	0.11004	85.589	0.1189
74.646	0.10058	80.927	0.11036	85.617	0.11924
74.895	0.10096	81.207	0.11069	85.699	0.1196
75.261	0.10133	81.402	0.11101	85.882	0.11993
75.513	0.1017	81.714	0.11135	86.156	0.12043
75.85	0.10207	81.924	0.11168	86.687	0.12059
76.054	0.10246	82.237	0.112	86.904	0.12091
76.333	0.10282	82.428	0.11228	87.102	0.12125
76.542	0.10317	82.614	0.11257	87.499	0.12158
76.806	0.10355	82.779	0.11287	87.941	0.1219

Table 22 (Continued)

Different	Open circuit	Different	Open circuit	Different	Open circuit
temperature	voltages	temperature	voltages	temperature	voltages
(K)	(∨)	(K)	(∨)	(K)	(V)
88.339	0.12225	93.001	0.13109	95.145	0.13934
88.783	0.12258	92.962	0.1314	95.315	0.13964
89.061	0.12292	92.876	0.13171	95.444	0.13993
89.522	0.12325	92.832	0.13202	95.632	0.14019
89.777	0.12358	92.966	0.13233	95.76	0.14046
90.154	0.12392	93.04	0.13264	95.927	0.14074
90.349	0.12424	93.166	0.13295	96.037	0.14101
90.67	0.12457	93.319	0.13326	96.287	0.14129
90.856	0.12489	93.548	0.13357	96.558	0.14155
91.138	0.12523	93.669	0.13387	97.025	0.1418
91.299	0.12556	93.844	0.13419	97.302	0.141
91.606	0.12588	93.97	0.1345	97.625	0.13985
91.669	0.12622	94.081	0.1348	97.777	0.1396
91.821	0.12655	94.124	0.13511	97.991	0.13854
91.895	0.12689	94.169	0.13542	98.168	0.13906
91.986	0.12721	94.21	0.13574	98.477	0.13956
92.013	0.12754	94.248	0.13604	98.685	0.13996
92.049	0.12787	94.303	0.13636	98.969	0.14034
92.084	0.1282	94.371	0.13666	99.14	0.14065
92.149	0.12851	94.455	0.13696	99.365	0.14095
92.238	0.12885	94.588	0.13727	99.523	0.14123
92.387	0.12917	94.673	0.13757	99.774	0.14147
92.554	0.1295	94.807	0.13787	99.954	0.14169
92.714	0.12983	94.892	0.13817	100.157	0.14189
92.758	0.13015	94.981	0.13847	100.259	0.14209
92.921	0.13047	95.018	0.13876	100.472	0.14229
93.009	0.13077	95.079	0.13905	100.632	0.14246

Table 22 (Continued)

Different	Open circuit	Different	Open circuit	Different	Open circuit
temperature	voltages	temperature	voltages	temperature	voltages
(K)	(∨)	(K)	(∨)	(K)	(∨)
100.875	0.14263	106.063	0.14561	105.972	0.14667
101.05	0.14281	106.147	0.14566	106.01	0.1467
101.274	0.14297	106.116	0.14572	106.044	0.14671
101.384	0.14313	106.103	0.14578	106.057	0.14672
101.582	0.1433	106.026	0.14583	106.083	0.14674
101.761	0.14344	106.001	0.14588	106.091	0.14675
102.08	0.14359	105.946	0.14592	106.077	0.14675
102.32	0.14374	105.917	0.14597	106.025	0.14676
102.726	0.14388	105.909	0.14602	105.938	0.14678
103.018	0.14399	105.815	0.14607	105.972	0.14678
103.318	0.14411	105.762	0.14613	106.06	0.1468
103.416	0.14424	105.718	0.14617	106.094	0.14679
103.586	0.14436	105.662	0.14621	106.131	0.14681
103.762	0.14447	105.6	0.14625	106.183	0.14682
104.04	0.14457	105.612	0.14629	106.227	0.14682
104.215	0.14465	105.632	0.14631	106.257	0.14683
104.978	0.14476	105.623	0.14635	106.294	0.14685
105.354	0.14485	105.611	0.14638	106.307	0.14685
105.56	0.14494	105.61	0.14642	106.318	0.14685
105.356	0.14503	105.616	0.14645	106.349	0.14687
105.522	0.14511	105.7	0.14648	106.4	0.14688
105.665	0.14519	105.765	0.1465	106.463	0.14689
105.807	0.14526	105.683	0.14654	106.512	0.1469
105.876	0.14534	105.663	0.14657	106.56	0.14691
105.952	0.14541	105.735	0.1466	106.58	0.14692
106.002	0.14547	105.813	0.14663	106.576	0.14693

APPENDICE M

TABLE OF THE I-V CHARACTERISTICS AND THE OUTPUT POWER MEASUREMENT WITH LOAD RESISTANCE OF HIGH TEMPERATURE

Current (mA)         Voltages (V)         Output powe (mW)           3.00E-06         0.1418         4.25E-07           6.00E-05         0.1402         8.41E-06           8.00E-05         0.1308         1.05E-05           8.00E-05         0.1304         1.04E-05
3.00E-06       0.1418       4.25E-07         6.00E-05       0.1402       8.41E-06         8.00E-05       0.1308       1.05E-05         8.00E-05       0.1304       1.04E-05
6.00E-050.14028.41E-068.00E-050.13081.05E-058.00E-050.13041.04E-05
8.00E-050.13081.05E-058.00E-050.13041.04E-05
8.00E-05 0.1304 1.04E-05
9.00E-05 0.1301 1.17E-05
1.30E-04 0.1285 1.67E-05
1.30E-04 0.12729 1.65E-05
2.40E-04 0.12735 3.06E-05
3.30E-04 0.12649 4.17E-05
5.90E-04 0.12412 7.32E-05
0.00109 0.12059 1.31E-04
0.00209 0.11418 2.39E-04
0.00315 0.10662 3.36E-04
0.0044 0.09833 4.33E-04
0.00712 0.08028 5.72E-04
0.01048 0.05841 6.12E-04
0.0128 0.043 5.50E-04
0.01441 0.03229 4.65E-04
0.0165 0.01852 3.06E-04

Table 23 The I–V characteristics and the output power measurement with load resistance high temperature

APPENDICE N

TABLE OF DATA FOR THE DAYLIGHT SOLAR RADIATION AND THE CORRESPONDING THEMPERATURE FOR PARABOLA DURING THE EXPERMEMTAL

Time (O'alask)	Color Dadiation		Ambient temperature
Time (U clock)	Solar Radiation	Hot side temperature	(К)
06:00	34	300	301.7
06:15	52	310.851	
06:30	84	311.705	
06:45	124	312.204	
07:00	124.8	313.383	302.8
07:15	124	318.727	
07:30	144.3	321.419	
07:45	209	324.252	
08:00	239.3	326.73	304.4
08:15	297.4	330.6	
08:30	345.3	332.78	304.4
08:45	409.5	335.528	
09:00	475.4	338.03	304.4
09:15	527	343.73	
09:30	580.3	347.69	314.4
09:45	674.3	350.56	
10:00	741.9	353.49	315.3
10:15	810.5	355.823	
10:30	871.6	357.65	317
10:45	923.5	359.28	
11:00	970.6	360.021	317.7
11:15	1045	360.062	
11:30	1063	360.29	317.6
11:45	1072	361.578	
12:00	108	361.82	319.1

Table 24 data for the daylight solar radiation and the corresponding temperature for parabola during the experimental

Table 24 (Continued)

Time (O'clock)	Solar Radiation	Hot side temperature	Ambient temperature (K)
12:15	1135	356.71	
12:30	1156.2	358.019	
12:45	1179.7	358.58	321.4
13:00	1190.5	358	
13:15	1195.4	358.61	319.7
13:30	1198.7	359.15	
13:45	1210.5	365.6	320.7
14:00	1195.5	364.06	
14:15	1204.8	364.4	320
14:30	1200.9	362	
14:45	1173.3	362.203	315.7
15:00	1145.8	361.86	
15:15	1052.7	359.81	317.4
15:30	1016.7	359.4	
15:45	934.8	359.18	319.1
16:00	880.8	358.86	
16:15	759.8	358.78	317
16:30	622	348.31	
16:45	507.5	326.32	316.9
17:00	377.6	320.96	
17:15	277.6	318.74	314.7
17:30	191.5	317.61	
17:45	87.9	318.43	313
18:00	21.4	318.034	
18:15	2	317.412	310.4

APPENDICE O

PUBLICATIONS

# First Author

- Pilasuta, P., Paengson, S., Singsoog, K., & Seetawan, T. (2021, September).
   P-Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>/n-Zn<sub>0.98</sub>Al<sub>0.02</sub>O module for high temperature thermoelectric generator. In Journal of Physics: Conference Series (Vol. 2013, No. 1, p. 012022). IOP Publishing.
- Pilasuta, P., Paengson, S., Singsoog, K., & Seetawan, T. (2022). Role of Al Substitution in the Enhancement of High–Temperature Thermoelectric Properties of ZnO Compound. Integrated Ferroelectrics, 222(1), 28–37.

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# P-Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>/n-Zn<sub>0.98</sub>Al<sub>0.02</sub>O module for high temperature thermoelectric generator

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Abstract. The thermoelectric generators can generate electrical power from different temperatures of the top and bottom side thermoelectric modules or devices using n - and p - types thermoelectric materials. We synthesized the p-type Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and n-type Zn<sub>0.98</sub>Al<sub>0.02</sub>O thermoelectric materials by solid-state reaction (SSR) and hot-pressing (HP) methods then measured thermoelectric properties such as Seebeck coefficient, electrical resistivity, and thermal conductivity. The thermoelectric module of  $\pi$ -shape was fabricated 2 pair p-n junction then measured the electrical voltage, power, and efficiency. It was found that we obtained the single phase of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and Zn<sub>0.98</sub>Al<sub>0.02</sub>O thermoelectric materials. The thermopower of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and Zn<sub>0.98</sub>Al<sub>0.02</sub>O thermoelectric cells was increased with increasing temperature difference from 28–603 K. The thermoelectric cells p-n junction 2 pairs generated a maximum voltage about 93.04 mV, power 8 mW and efficiency of 0.23 % at temperature difference of 735 K (hot side 976 K). So, the thermoelectric module has been feasible to fabricate thermoelectric generators and developed a method for fabrication of high stability modules.

Keywords: Oxide thermoelectric generator, thermoelectric module  $\pi$ -shape, synthesis oxide thermoelectric materials, thermoelectric properties, thermoelectric device

#### 1. Introduction

Nowadays, emerging global energy consumption drives the need for energy production, conservation, and management has intensified interest in the century due to the significant rate at which the world's energy demand is growing because of population growth and industrialization [1] therefore means of power generation research studies on alternative energy resources [2]. A thermoelectric (TE) device is viable clean energy that can convert thermal energy into electrical energy when a temperature gradient is present at the Seebeck effect. While a reverse phenomenon called the Peltier effect enables the TE device to generate thermal energy from electrical energy [3]. TE energy conversion plays a significant role in power generation by recovering waste heat released from many heat sources [4]. Thermoelectric generators (TEGs) can convert thermal energy directly into electricity through the Seebeck effect when

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a temperature difference is applied between their two sides [5]. However, TE devices have not been widely used for power generation because of their low conversion efficiencies [6] and TE modules and generators typically consist of p- and n-type TE legs connected electrically in parallel and series [7]. The efficiency of thermoelectric energy conversion is determined by the dimensionless figure of merit:

$$ZT = \frac{S^2 T}{\rho \kappa}$$
(1)

Where	S	is Seebeck coefficient,
	ρ	is electrical resistivity,
	κ	is thermal conductivity,
and	Т	is bsolute temperature [8].

In order to increase ZT, it is necessary to decreasing  $\rho$  and increasing S and reducing  $\kappa$  at the same time.

The thermoelectric device has two functions are thermoelectric generator and thermoelectric cooling, on the other hand, thermoelectric creating a cool side and a hot side by using an electric current, that is Peltier or cooling [9]. In addition, the thermoelectric materials have a three-temperature range, consisted of low-temperature range, medium temperature range, and high-temperature range [10]. In the low-temperature range materials, the most popular is bismuth telluride and antimony telluride [11]. In the medium temperature range, the silicide materials such as magnesium silicide and manganese silicide to use in this range. In the last of high-temperature range is an oxide material such as NaCo<sub>2</sub>O<sub>4</sub> [12–13] Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> [14–15], Zn<sub>5</sub>In<sub>2</sub>O<sub>8</sub> [16], SrTiO<sub>3</sub> [17–18], CaMnO<sub>3</sub> [19–20], and ZnO [21–25]. The over the years the performance of the oxide material has been enhanced by the addition of several depots, the improvement of the grain connection, and a variety of methodologies. However, the figure of merit of thermo-electric oxides is lower than 1 ZT about 0.1-0.8 at T = 800–1300 K [9, 26]. Among these oxide TE, Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> [27] and ZnO [28] have been considered as p- and n-type oxides, respectively, due to their relatively high ZT values at high temperatures.

Our work focuses on the generator function and high-temperature range from the oxide material, resist oxidation reaction, and feasibility of using for a long time. We choose p-type Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>/n-Zn<sub>0.98</sub>Al<sub>0.02</sub>O for the fabrication of the thermoelectric cells because p-type Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> showed low electrical resistivity and low thermal conductivity and slightly low Seebeck coefficient and n-type Zn<sub>0.98</sub>Al<sub>0.02</sub>O are shown high Seebeck coefficient, low thermal conductivity but high electrical resistivity, for this reason, we need to be matching for fabrication TE cell.

## 2. Materials and Methodology

# 2.1 Synthesis

Powders of p-type  $Ca_3Co_4O_9$  and n-type  $Zn_{0.98}Al_{0.02}O$  were prepared by conventional solid-state synthesis starting from the oxides and press to pelleted by hot pressing (HP) method. For n-type we chose  $Zn_{0.98}Al_{0.02}O$  as we found this concentration optimal for the thermoelectric properties. The next step was the sintering of the powders by HP to produce pellets for thermoelectric characterization and the production of cells.

# 2.1.1 Material Preparation and of p-type

Powders of p-type Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> were prepared from calcium carbonate powder CaCO<sub>3</sub> (99%, QRëC<sup>TM</sup>.) and cobalt oxide powder Co<sub>3</sub>O<sub>4</sub> (99.5%, Aldrich) then their powders were weighed in proper stoichiometric amounts. The precursor powder was mixed by a planetary ball mill (planetary ball mill PM400 RETSCH) was employed to mix Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> powder in agate grinding jar sizes 500 ml with by 5 mm diameter agate balls with the ball-per-powder 18 balls for 10 g at 350 rpm for 5 h, then Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> powder was pressed for pellets by a uniaxial HP at 1123 K with heating rate of 4 °C/min and under pressed 60 MPa for 1 h in Ar atmosphere after that Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> bulk sample was annealed at 1023 K in air.

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## 2.1.2 Material Preparation of n-type

Powders of n-type  $Zn_{0.98}Al_{0.02}O$  were prepared from ZnO (99.5%, QRëC<sup>TM</sup>.) and Al<sub>2</sub>O<sub>3</sub> (95%, Ajax Finechem Pty Ltd.) then their powders were weighed in proper stoichiometric amounts. and then mixed by the planetary ball mill using agate balls and vial in ethanol for 24 h at 350 rpm and dried at 353 K for 24 h. The mixed powder was calcined at 773 K for 5 h in air. The calcined powder was pressed for pellets by HP method (OTF-1200x-VHP-4). Which the HP has cylindrical graphite die with 20 mm inner-diameters and under pressed 60 MPa at 1173 K with heating rate 4 °C/min for 1 h in Ar atmosphere. The pellets were annealed by furnace at 1423 K for 5 h in the air.

The bulk Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and Zn<sub>0.98</sub>Al<sub>0.02</sub>O was cut to size  $3 \times 3 \times 15$  mm<sup>3</sup> for measurement of the Seebeck coefficient and electrical resistivity by ZEM-3(M10) was gauged in the temperature ranging from room temperature to 1023 K. The thermal conductivity was calculated from thermal diffusivity measured by the laser flash method using a Netzsch LFA-457 apparatus, with a sample size of diameter 9.5 mm and thickness 1 mm can be calculated from the equation:

$$\kappa = \alpha dC_p \tag{2}$$

where	κ	is Thermal conductivity	
	Ср	is heat capacity	
	α	is thermal diffusivity	
	d	is density	
Heat ca	pacity w	vas calculated from the equation of Dulong-Petit:	
		$C_p = 3nR$	(3)
where	n	is the number of atoms per formula unit	
	R	is the gas constant.	

## 2.2 Fabrication thermoelectric cells

Thermoelectric cells were designed by solid works program and assembly by silver plate. The design of thermoelectric cells was stated from assigning the substate size of  $25 \times 25 \times 1 \text{ mm}^3$  for 2 pair, Thermoelectric materials were used in size of  $3.5 \times 3.5 \times 6 \text{ mm}^3$  and as shown in Figure 1. The materials were cut into  $3.5 \times 3.5 \times 6 \text{ mm}^3$  rectangular legs; p-type Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and n-type Zn<sub>0.98</sub>Al<sub>0.02</sub>O then the materials were painted with silver paste on top and bottom, then annealed of 1073 K for 30 minutes in air heating and cooling used 5 K/min. The two-couple annealed p and n legs have been attached to an alumina substrate size of  $25 \times 25 \times 1 \text{ mm}^3$ , which etched two columns by using a silver paste, then the silver plate attached on top for joint p and n legs to  $\pi$ -shape. The  $\pi$ -shape TE cell was drying on hot plate 10 minutes for dried silver paste, then the TE cell metalized of 1073 K 30 minutes in air heating and cooling used 5 K/min. When the cell cooled at room temperature connected red and black wire for positive in p and negative in n legs, respectively, then test the power and the failure temperature limit temperature used for TE cell and module.



Figure 1. shows (a) cells design of thermoelectric device configuration and (b)  $\pi$ -shape thermoelectric cells.

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## 2.3 Power generation measurement of Thermoelectric generator

The power generation of Thermoelectric generator described above was installed a water cooling and was under a heater, placed over the cells. To measure the temperatures of hot and cold side temperatures, the two K-type thermocouples were attached on the thin mica plate of high temperature and low-temperature sides using an alumina substrate, respectively. A photograph of the output power measurement of thermoelectric module is shown in Figure 2. The output power (W) was calculated by the output voltage (V) and current (I) caused by changing a resistor.



Figure 2. Show (a) the schematic diagram of the power generation measurement of thermoelectric generator, (b) Performance measurement of thermoelectric generator.

# 3. Results and Discussion

X-ray diffraction pattern analysis by X-ray diffraction technique from  $10^{\circ}$  to  $80^{\circ}$  step  $0.02^{\circ}$  in 1 s, and 20 angle with CuK $\alpha$ -1 (l = 1.541 Å) at 40 kV and 30 mA, radiation utilizing a Shimadzu diffractometer, XRD-6100at room temperature from Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> powder, hot pressing the diffraction peaks, indexed, by comparison, was PDF# 00-058-0661, as shown in Figure 3 were accomplished for space group 8 Cm (C 1 m1) The main diffraction peaks indicate that the composites are composed of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> phases [29]. A little impurity phase can also be observed in the composites has shown a single phase with the Monoclinic structure. These observed peak positions are different from the calcined sample pack. The intensity of (002) peaks are initiated peaks for detected to the other (*hkl*) peaks conditions, the (002), (003), (004), (113), (020), (005), (202), (203) and (006) planes on the base of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> indicated a strong preference of all samples.



Figure 3. Indexed XRD patterns of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> from the hot pressing at 1123 K for 1 h in Ar atmosphere.

The XRD patterns analysis by X-ray diffraction technique from 30° to 80° step 0.02° in 1 s, and 20 angle with CuK $\alpha$ -1 (l = 1.541 Å) at 40 kV and 30 mA, radiation utilizing a Shimadzu diffractometer, XRD-6100at room temperature of Zn0.98Al0.02O are shown in Figure 4. Which all peaks were corresponded with the crystal structure of ZnO ICDD PDF #00-036-1451 and indicated a hexagonal wurzite structure space group of P6<sub>3</sub>mc (186) [30]. These observed peak positions are different from the calcined sample pack. The intensity of (101) peaks are initiated peaks for detected to the other (*hkl*) peaks conditions, the (100), (002), (002), (110), (103), (200), (112), (201), (204) and (202) planes on the base of Zn0.98Al0.02O indicated a strong preference of all samples. The obtained phase is pure and no peak was observed to correspond to aluminium, which may indicate that aluminium atoms were successfully incorporated in the ZnO lattice.



Figure 4. Indexed XRD patterns of Zn0.98Al0.02O from the hot pressing at 1173 K for 1 h in Ar atmosphere. The crystallite size was calculated by the Scherrer equation:

$$D = \frac{K\lambda}{\beta\cos(\theta)} \tag{4}$$

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where *D* is the mean particles size, *K* is a Scherrer constant = 0.9,  $\lambda = 1.5406$  Å is the wavelength of the used radiation CuK $\alpha$ 1.  $\beta$  is the FWHM and  $\theta$  is the Bragg diffraction angle [31]. The lattice parameters, *c/a* lattice ratio, density and relative density of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and Zn<sub>0.98</sub>Al<sub>0.02</sub>O [32] are shown in Table 1. The lattice parameters of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> (*a*, *b*, *c*) and volume unit cell (*V*) was calculated according to the following equation (5) and (6), respectively.

$$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left( \frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right)$$
(5)  
$$V = abc \sin \beta$$
(6)

The lattice parameters of  $Zn_{0.98}Al_{0.02}O$  (a, c) and volume unit cell (V) was calculated according to the following equation (7) and (8), respectively.

$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$
(7)

$$V = \frac{\sqrt{3}a^2c}{2} \tag{8}$$

Table 1. Show crystallite size, lattice parameter, c/a lattice ratio, density and relative density of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and Zn<sub>0.98</sub>Al<sub>0.02</sub>O.

Crevetallita		Lattice Parameter (Å)			c/a	volume	Density	Relative
Materials	Ciystallite	а	b	с	lattice	unit cell	(g/cm <sup>3</sup> )	density
	Size (IIII)				ratio	(Å <sup>3</sup> )		%
Ca <sub>3</sub> Co <sub>4</sub> O <sub>9</sub>	45.832	4.8734	4.4722	10.853	2.2270	211.460	4.478	92.60
Zn <sub>0.98</sub> Al <sub>0.02</sub> O	51.851	3.2490	3.2490	5.2064	1.6024	47.595	5.411	94.50

The morphology of the Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and Zn<sub>0.98</sub>Al<sub>0.02</sub>O powders is shown in Figure 5. After HP-sintering, the grain size of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> is observed that grain does grow larger after sintering and exhibited a dense microstructure of lamellar grains in size and strength. Zno.98Alo.02O presented randomly oriented grains and increasing aluminum content the morphological to Spherical shape with a homogeneous distribution of the particles which correspond to the report [33].



Figure 5. SEM images at magnifications 5000 of (a) Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and (b) Zn<sub>0.98</sub>Al<sub>0.02</sub>O.

The Seebeck coefficient (S) and electrical resistivity (p) of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and Zn<sub>0.98</sub>Al<sub>0.02</sub>O were measured by a ZEM-3 technique at room temperature to 1073 K figure 6 shows the dependence of the Seebeck coefficient of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and Zn<sub>0.98</sub>Al<sub>0.02</sub>O, which Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> shows positive-type and maximum value about 186 ( $\mu$ V/K) at 973 K and Zn<sub>0.98</sub>Al<sub>0.02</sub>O shown negative-type maximum about -408 ( $\mu$ V/K) at 1073 K together with references. It's what found that the Seebeck coefficient of our work at high temperature has a high value compared with references.

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Figure 6. The dependence of the Seebeck coefficient on the temperature of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and Zn<sub>0.98</sub>Al<sub>0.02</sub>O together with references.

The temperature dependence of the electrical resistivity  $Ca_3Co_4O_9$  and  $Zn_{0.98}Al_{0.02}O$  shows in figure 7.  $Ca_3Co_4O_9$  was similar behavior corresponding with metal to semiconducting transition in the range of 273–1073 K.  $Zn_{0.98}Al_{0.02}O$  showed a semiconducting behavior over the whole measured temperature range at room temperature to 1073 K and electrical resistivity value decreased with increasing of temperature content while  $Ca_3Co_4O_9$  value increased with increasing temperature content. The dependence of the thermal conductivity on the temperature of  $Ca_3Co_4O_9$  and  $Zn_{0.98}Al_{0.02}O$  shows in figure 8 found that he thermal conductivity of the results of all samples was decreased with increasing temperature. At temperature 1073 K  $Ca_3Co_4O_9$  thermal conductivity value decreased to 1.38 (W/m K)

and the Zn0.98Al0.02O thermal conductivity value decreased to 1.79 (W/m K) same temperature.



Figure 7. The dependence of the electrical resistivity on the temperature of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and Zn<sub>0.98</sub>Al<sub>0.02</sub>O together with references.





Figure 8. The dependence of the thermal conductivity on the temperature of  $Ca_3Co_4O_9$  and  $Zn_{0.98}Al_{0.02}O$  together with references.

The dependence of the Dimensionless figure of merit on the temperature of  $Ca_3Co_4O_9$  and  $Zn_{0.98}Al_{0.02}O$  shows in figure 9. The maximum ZT values of  $Ca_3Co_4O_9$ , and  $Zn_{0.98}Al_{0.02}O$  shown 0.0915 and 0.2882 at 1073 K. Plots of thermoelectric properties vs. temperature are reported while values at temperature 1073 K are summarized in Table 2.



Figure 9. The dependence of the Dimensionless figure of merit on the temperature of  $Ca_3Co_4O_9$  and  $Zn_{0.98}Al_{0.02}O$  together with references.

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Table 2. Summary of the thermoelectric properties of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and Zn<sub>0.98</sub>Al<sub>0.02</sub>O at 1073 K

Matamiala	Temperature	Thermoelectric properties			
Materials	HP (K)	<i>S</i> (μV/K)	$\rho$ (m $\Omega$ cm)	к (W/m K)	ZT
Ca <sub>3</sub> Co <sub>4</sub> O <sub>9</sub>	1123	186	15.9	1.38	0.0915
Zn0.98Al0.02O	1173	-408	51.1964	1.79	0.2882

Figure 10 shown the open-circuit voltage was an output voltage and current distribution of TEG with thermoelectric cells assembled in series, the open-circuit voltage of the thermoelectric module was increased with increasing temperature difference from 28–603 K. The 2 pairs p-n junction thermoelectric module generated maximum open-circuit voltage 87.92 (mV) at a temperature different 345 K at hot side temperature 976 K in a 30-time circle. Figure 11 shows the electric power shown at about 7.96 (mW) at a temperature different 345K, and the eclectic power is shown about 7.96 (mW) at hot side temperature 976 K in a 30-time circle. The module can be used at high temperature and stable with used in heat source 1473 K.



Figure 10. The dependence of the open circuit voltage on the temperature difference of TE cells 2 pairs.



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Figure 11. The dependence of the electric power on the temperature difference of TE cells.



Figure 12. The dependence of the electric current on the temperature difference of TE cells.

Figure 12 show the electric current on the temperature difference of TE cells 2 pairs can be was calculated according to the following equation:

*I* = (9) v is electric current (A) where I Р is electric power (W) V is voltage (V)

which data of P and V from Figure 10 and 11 the maximum value of the electric current is 93.9 mA at temperature difference 489 K.

and

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## 4. Conclusion

Successfully for synthesis Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>, and Zn<sub>0.98</sub>Al<sub>0.02</sub>O by solid-state reaction method and pelleted by the hot-pressing method be used to fabrication thermoelectric cells. The open-circuit voltage of thermoelectric cells was increased with increasing temperature difference from 28–603 K. The 2 pairs p-n junction thermoelectric cells generated maximum open-circuit voltage 87.92 (mV), and the eclectic power is shown about 7.96 (mW) at hot side temperature 976 K in a 30-time circle. The cells can be used at high temperature and stable with used in heat source 1473 K. The thermoelectric cells p-n junction 2 pairs generated maximum voltage about 93.04 mV, power 8 mW and efficiency of 0.229 % at temperature difference 735 K (hot size 976 K) The cells have been feasibilities to fabrication thermoelectric generator. The module has been feasible to fabricate thermoelectric generators and developed a method for fabricated high stability module. In future work, we will improvement of the thermoelectric properties of the materials and thermoelectric modules for the high performance of the module.

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- 3 Supasit Paengson, **Panida Pilasuta**, Kunchit Singsoog, Wanatchaporn Namhongsa Wairut Impho, Tosawat Seetawan, Improvement in thermoelectric properties of CaMnO<sub>3</sub> by Bi doping and hot–pressing Materials Today: Proceedings 4 (2017) 6289–629

APPENDICE P

INTERNATIONAL CONFERENCES

- P. Pilasuta, K. Singsoog, S. Paengsona, W. Namhongsa, S. Ruamruka, L. Sripasudab,c, S. suwannee, and T. Seetawan. "Thermoelectric power generation of p-Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>/n-Zn<sub>0.98</sub>Al<sub>0.02</sub>O legs" 4<sup>th</sup> Southeast Asia Conference on Thermoelectrics 2016. 15–18 December 2016, Sea Garden Hotel, Danang, Vietnam
- Panida Pilasuta, Supasit Paengson, Kunchit Singsoog, Tosawat Seetawan, "Role of Al substituted ZnO for improved electrical conductivity in high temperature thermoelectric material" The 5<sup>th</sup> International Conference on Smart Materials and Nanotechnology (SmartMat@2020) December 1 – 4, 2020, Pattaya, Thailand
- 3. Panida Pilasuta, Supasit Paengson, Kunchit Singsoog, Tosawat Seetawan, The Best Poster Presentation: "Thermoelectric generator of  $p-Ca_3Co_4O_9/n-Zn_{0.98}Al_{0.02}O$  for high temperature" The 5<sup>th</sup> Asian Conference on Thermoelectrics (ACT5) &The 6<sup>th</sup> Southeast Asia Conference on Thermoelectrics (SACT6) December 17, 2020, Thailand (Online conference, 1 Day)

APPENDICE Q

EXPERIENCE TO EXCHANGE STUDENT AT OSAKA PREFECTURE UNIVERSITY










## Synthesis of Cubic Ge12Sb2Te15 by Mechanical Alloying

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## ABSTRACT

The Ge<sub>12</sub>Sb<sub>2</sub>Te<sub>15</sub> this compound is a known phase change material with electronic properties that depend strongly on temperature because of superior electronic structures for both cubic and hexagonal phases, and potential thermoelectric material for the middle-temperature range, but its crystal structure is significantly affected by the preparation process, possibly leading to differences in the electrical properties depending on the preparation process. In this work, we are synthesized Ge<sub>12</sub>Sb<sub>2</sub>Te<sub>15</sub> by mechanical alloying (MA) of highly purity constituents of Ge, Sb and Te powders, ball milling in Nitrogen. The powder from ball milling was characterized by X-ray diffraction (XRD), and the microstructure change was investigated through scanning electron microscopy (SEM), confirm identify the elemental composition of materials is Ge<sub>12</sub>Sb<sub>2</sub>Te<sub>15</sub> by Energy Dispersive X-Ray Analysis (EDX).

Key words: Cubic Structure, Ge12Sb2Te15, Mechanical Alloying.

APPENDICE R

A BRIEF HISTORY OF RESEARCHER

## A BRIEF HISTORY OF RESEARCHER

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