CHAPTER V
CONCLUSION AND SUGGESTION

In this research, the β–Zn_4Sb_3 powders was successfully synthesized using solid state reaction method via mechanical alloying technique. The crystallite structure was analyzed through X–ray diffraction technique. The oxidation states of Zn and Sb elements in the local structure of the synthesized β–Zn_4Sb_3 powder were investigated using X–ray absorption near–edge structure spectra at the Zn K–edge and Sb–L edges. The sintered β–Zn_4Sb_3 pellets were fabricated through a compression and sintering process under Ar gas flow system. Thermoelectric properties, including the Seebeck coefficient, electrical resistivity and power factor of the sintered β–Zn_4Sb_3 pellets were measured using Linseis LSR–3 equipment. The test cells of monolithic β–Zn_4Sb_3/ZnO TEG modules, with conditions β–Zn_4Sb_3 weight of 0.2 g, 0.5 g, 1 g, 2 g and 4 g were successfully fabricated using cyclical compression process, calcination method, and electrical connection method. Additionally, the monolithic multi–stack β–Zn_4Sb_3/ZnO TEG module was fabricated using the same procedures as the test cells. The electrical power output curves and IV–curves of both the test cells and the monolithic multi–stack β–Zn_4Sb_3/ZnO TEG module were evaluated and analyzed using a custom-built heating/cooling system with IV measurement capabilities. The conclusions of this research are divided into four sections: structure and characterization, thermoelectric properties, module analysis and evaluation, and suggestions for future work.

5.1 Structure and characterization

X–ray diffraction (XRD) pattern of the synthesized β–Zn_4Sb_3 powders, produced under conditions of excess Zn powders, were analyzed using XRD technique. The XRD patterns results indicated that optimal synthesis condition is adding 12 at.% Zn rich and calcination temperature of 450 °C for 3 hours. Under these conditions, the XRD patterns revealed a dominant crystalline phase of β–Zn_4Sb_3 with minor secondary phases of ZnSb, Zn and Sb. The XRD patterns of the synthesized β–Zn_4Sb_3 powders, with excess Zn powders 12 at.% and calcined at 450 °C for 3 hours, corresponds to the calculated XRD patterns β–Zn_4Sb_3 of Mozharivskyj’s model (Mozharivskyj *et al.*, 2006). The observed secondary phases of ZnSb, Zn and Sb are probably due to the limited temperature stability during calcination under argon gas flow, including the inversion of the crystalline phase of ZnSb during cooling process, resulting in the formation of crystalline phase ZnSb at across temperature of 100–200 °C (Zhang *et al.*, 2016).

The ionization energy of exciting core electrons for Zn and Sb elements in the synthesized β–Zn_4Sb_3 powders were investigated using X-ray absorption near-edge structure (XANES) spectroscopy. The ionization energies of exciting core electrons for Zn and Sb elements in local atoms structure of the synthesized β–Zn_4Sb_3 powders were measured at level K (Zn K–edge) and level L (Sb L–edges), respectively. The primary absorption edges at the Zn K-edge and Sb L-edges indicate that the ionization energies of the core electrons correspond to oxidation states of Zn^0 and Sb^0. The normalized XANES and derivative of normalized XANES spectra confirm that the synthesized β–Zn_4Sb_3 powders have an alloy structure, demonstrating the absence of ionic bonding and oxides.

5.2 Thermoelectric properties

The Seebeck coefficient, electrical resistivity, and power factor of the sintered β–Zn_4Sb_3 pellets were measured. The Seebeck coefficient of all sample increase with rising operating temperature, peaking around 300 °C, before gradually decreasing. Among the samples, the sintered β–Zn_4Sb_3 pellet pressed at 700 MPa and sintered at 500 °C exhibited the highest Seebeck coefficient of 255 μV/°C at an operating temperature of 320 °C. The positive Seebeck coefficient confirms that the sintered β–Zn_4Sb_3 pellets are p–type thermoelectric materials. The electrical resistivity of the sintered β–Zn_4Sb_3 pellets decreased steadily up to around 200 °C, after which it remained constant across the temperature range of 200–480 °C. While the electrical resistivity feature of all sintered β–Zn_4Sb_3 pellets were similar, the sintered β–Zn_4Sb_3 pellets under conditions of pressing pressure of 700 MPa with sintering temperature of 500 °C showed the lowest resistivity, making it the most favorable. The electrical power factor of all sample exhibited considerable fluctuations, likely due to inherent variations in the properties of the sintered β–Zn_4Sb_3 pellets or possible sensor issues with the measurement equipment. Despite these fluctuations, the results suggest that the optimal operating temperature for all sintered β–Zn_4Sb_3 pellets is across between 200–300 °C.

5.3 Module analysis and evaluation

The evaluation and performance of test cells of monolithic β–Zn_4Sb_3/ZnO TEG module was revealed using a custom-built heating/cooling system with IV measurement capabilities. The V_{op} and I_{sc} of test cells of monolithic β–Zn_4Sb_3/ZnO TEG module, with condition monolithic β–Zn_4Sb_3 weight of 0.5 g, 1.0 g, 2.0 g and 4.0 g revealed significant potential results. However, the 1 g test cell of monolithic β–Zn_4Sb_3/ZnO TEG module was the most efficient in terms of mass usage and produced the highest maximum electrical power output off 595 μW and the highest V_{op} of 45.4 V at an operating hot side temperature of 300℃ – ΔT=100 ℃.

The evaluation and performance of the monolithic multi–stack β–Zn_4Sb_3/ZnO TEG module also was revealed using a custom-built heating/cooling system with IV measurement capabilities. The V_{op} and I_{sc} of monolithic multi–stack β–Zn_4Sb_3/ZnO TEG module revealed that both incremental V_{oc} and I_{sc} increased with rising operating temperatures and ΔT. The IV–curve results of the multi–stack β–Zn_4Sb_3/ZnO TEG module at operating temperature of 300 ℃ shows the highest maximum electrical power output (P_{out}) of 550 μW and the highest V_{op} of 73.2 V, with similar steep slope under both T_h=300 ℃–ΔT=50 ℃ and T_h=300 ℃–ΔT=100 ℃ conditions. However, the optimal operating temperature for the monolithic multi–stack β–Zn_4Sb_3/ZnO TEG module was found to be the T_h=200 ℃–ΔT=50–100 ℃, as the electrical power output curves at this temperature demonstrated consistent performance under both temperature gradient conditions. The wide and consistent of IV–curves and electrical power output curves of the monolithic multi–stack β–Zn_4Sb_3/ZnO TEG modules suggest their potential for use in electrical generators that can withstand temperature fluctuations at an operating temperature of 200 ℃ with ΔT 50–100 ℃.

5.4 Suggestion

This work presents the invention of a thermoelectric generators module designed to recycle energy from industrial waste heat in industrial activities and public utilities, as mentioned in chapter I. The author aimed to use low cost materials and a simple fabrication method to invent a thermoelectric generators module that others can easily replicate. The author expected that the initial goal was for fabricated thermoelectric generator module to achieve at least V_{op}~1 volt and I_{sc}~0.1 A. hile the results of this work did not meet these expectations. However, the author hoped that the fabrication of monolithic multi–stack β–Zn_4Sb_3/ZnO TEG modules will contribute valuable insights and inspire future applications. Finally, the author would like to thank all readers and welcome any comments or suggestions.