CHAPTER I
INTRODUCTION

1.1 Background and motivation

The global demand for energy usage is rising significantly, which the electricity consumption is a major problem. Additionally, the crisis of using energy from crude oil, natural gas and nuclear power contributes to global warming, and emits radioactive pollutants that harm the environment. Therefore, it is crucial to explore and utilize alternative energy sources such as hydropower, wind energy, solar energy and geothermal energy. Research and innovation are essential for converting these alternative energies into electricity. For example, such as converting solar energy can be converted into electricity using solar cell devices, while hydropower and wind energy can be converted into electricity using dynamo, and Thermoelectric generators can generate electricity from natural heat sources and solar thermal energy.

Thermoelectric generator (TEG) modules are components used in electronic devices to directly convert heat to electrical current, serving as an electrical power source for the electronic devices. The heat to electricity conversion is known as the "Thermoelectric effect", first discovered by Thomas Johann Seebeck (Goldsmid, 2010). Normally, conventional TEGs, or longitudinal TEGs are typically constructed using a dual-leg model, which incorporates a couple of thermoelectric materials P–type and N–type. This dual-leg model allow for parallel flow of electric and heat transport with isotropic properties (Crawford, 2014). In contrast, a single leg model uses only one type of thermoelectric materials, either P–type or N–type. Both TEG model require alternative materials for electrical insulation materials for separating TEG cells and electrical conduction materials, i.e., ZO, SiO_2, Ag, Ag_2S–alloy (Lai *et al.*, 2022). To evaluate the efficiency of the initial thermoelectric materials use in fabricating TEGs, the dimensionless parameter known as the "the figure of merit (ZT is commonly employed. This parameter is given by the equation of $ZT = \frac{\alpha^2 \sigma T}{\kappa}$ where ZT, T, α, κ and σ are dimensionless figure of merit, operating temperature (K), Seebeck coefficient (V/K), thermal conductivity (W/Km) and electrical conductivity (S/m or $\Omega^{-1}m^{-1}$), respectively. This equation was defined and conceptualized by Edmund Altenkirch

(Saini *et al.*, 2021). Due to most industrials waste heat is released at temperatures of about 200–400°C (Minea, 2007). It presents a valuable opportunity as a recyclable energy source. This waste heat can generate electrical power through the use of high–temperature TEGs. A literatures survey of thermoelectric materials suitable for these temperatures includes β–Zn_4Sb_3, $NaPb_{20}SbTe_{22}$ (salt), PbTe, PbTe–PbS, $AgSbTe_2$–GeTe (TAGS), $Ba_{0.08}La_{0.05}Yb_{0.04}Co_4Sb_{12}$ (skutterudite) and $AgPb_{18}SbTe_{20}$ (LAST) (Caillat *et al.*, 1997; Poudeu *et al.*, 2006; Biswas *et al.*, 2012; Levin *et al.*, 2012; Shi *et al.*, 2011; Hsu *et al.*, 2004; Rull–Bravo *et al.*, 2015). Among these materials, β–Zn_4Sb_3 is considered the most effective due to its high ZT at value at waste heat temperatures, inexpensive materials, and uncomplicated crystalline structure. Originally, Zn_4Sb_3 has three polymorphs: α–Zn_4Sb_3, β–Zn_4Sb_3 and γ–Zn_4Sb_3, each with unique thermoelectric properties (Seebeck, 1895; Mönkemeyer, 1905; Beer and Cochran, 1952; Mayer *et al.*, 1978). However, the β–Zn_4Sb_3 polymorph in space group R$\overline{3}$c is the most efficient, exhibiting a significant Seebeck coefficient at operating temperature about 200–400 °C, with a maximum figure of merit (ZT) of approximately 1.3 (Caillat *et al.*, 1997).

The monolithic architecture of TEG modules offers an all-in-one structural design that simplifies fabrication processes. A monolithic $Ag_2S_{0.2}Se_{0.8}$/ Ag_2S /$Bi_{0.5}Sb_{1.5}Te_3$ TEG module and fabrication process were reported by Huajun L. and research team. This dual leg series TEG module comprises three alloys materials: $Ag_2S_{0.2}Se_{0.8}$, $Bi_{0.5}Sb_{1.5}Te_3$, Ag_2S as n–type, p–type and insulator materials respectively (Lai *et al.*, 2022; Dreßler *et al.*, 2015). However, this TEG module is limited to low-temperature applications due to the properties of $Ag_2S_{0.2}Se_{0.8}$ and $Bi_{0.5}Sb_{1.5}Te_3$ (Mansouri *et al.*, 2021; Singh *et al.*, 2020). Additionally, the Ag_2S components are prepared separately to create Ag_2S spacer layers, which adds complexity to the fabrication process.

This report presents the fabrication of single-leg series monolithic β–Zn_4Sb_3/ZnO TEG modules, designed for easier manufacturing processes and the recycling of industrial waste heat. The design incorporates a modified zigzag electrical connection circuit. In this configuration, β–Zn_4Sb_3 is used as the p-type thermoelectric materials, while ZnO serves as the insulator materials (Jantrasee *et al.*, 2016). The β–Zn_4Sb_3 powers were synthesized by solid–state reaction and calcination under Ar gas flow. The prepared powders were characterized and then used to produce sintered β–Zn_4Sb_3 pellets. Then, thermoelectric properties of the sintered β–Zn_4Sb_3 pellets were evaluated. The performance efficiency of the monolithic β–Zn_4Sb_3/ZnO TEG modules was assessed based on their electrical power output. This was calculated using the equation of $P_{out} = NI^2R_L = N\left[\frac{S(T_h - T_c)}{R_g + R_L}\right]^2 R_L$ where P_{out}, N, S, T_h, T_C, I, R_g and R_L are electrical power output, number of TEG cells, Seebeck coefficient, temperature of the hot side, temperature of the cold side, electrical current, thermal resistance and load resistance (Goldsmid, 2010), respectively.

1.2 Objectives of the research

1.2.1 To synthesize zinc antimony alloy beta phase (β–Zn_4Sb_3) powders using solid state reaction and calcination under Ar gas flow.

1.2.2 To characterize the synthesized β–Zn_4Sb_3 powders using advanced X–ray measurement techniques (XRD–D8), X–ray absorption near–edge structure (XANES) spectra, and derivative of normalized XANES techniques.

1.2.3 To study and analyze thermoelectric properties of the synthesized β–Zn_4Sb_3 powders (Seebeck coefficient, electrical resistivity and power factor) using Linseis LSR–3 equipment.

1.2.4 To fabricate monolithic β–Zn_4Sb_3/ZnO thermoelectric generator (TEG) modules.

1.2.5 To develop custom-built heating/cooling system with IV measurement capabilities for evaluating the performance of the fabricated monolithic β–Zn_4Sb_3/ZnO TEG modules.

1.2.6 To evaluate IV characteristics and electrical power output of the monolithic β–Zn_4Sb_3/ZnO TEG modules.

1.2.7 To analyze the performance of the monolithic β–Zn_4Sb_3/ZnO TEG modules by varying operating temperature.

1.3 Scope and limitation

1.3.1 The research focuses on synthesis zinc antimony alloy beta phase (β–Zn_4Sb_3) powders using solid state reaction and calcination under Ar gas flow. It also includes fabricating monolithic β–Zn_4Sb_3/ZnO thermoelectric generator modules base on the synthesized β–Zn_4Sb_3 powders and developing custom-built heating/cooling system with IV measurement capabilities to evaluate its performance.

1.3.2 The crystalline structure phase and ionization energy of core electrons in the synthesized β–Zn_4Sb_3 powders were analyzed using a literatures review and compared with standard data and model.

1.3.3 Thermoelectric properties of sintered β–Zn_4Sb_3 pellets and the performance of the monolithic β–Zn_4Sb_3/ZnO TEG modules were investigated and evaluated.

1.4 Location of the research

1.4.1 Advanced Materials Physics Laboratory (AMP), School of Physics, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima, Thailand.

1.4.2 Facility Building 10 (F10), Suranaree University of Technology, Nakhon Ratchasima, Thailand.

1.4.3 Synchrotron Light Research Institute (BL 5.2), Nakhon Ratchasima, Thailand.

1.4.4 Department of Physics, Faculty of Science, Khon Kaen University, Khon Kaen, Thailand.

1.5 Outline of thesis

This thesis consists of five chapters. The first chapter introduces the background and motivation for this research. Chapter II represents literatures reports, providing information on zinc antimony materials, the theory of thermoelectric effect and relevant equations, process synthesis, characterization techniques, fabrication methods for thermoelectric generator modules, and development of a custom-built heating/cooling system with IV measurement capabilities. It also covers the investigation and evaluation of thermoelectric properties and the performance of thermoelectric generator modules respectively. Chapter III describes the preparation of β–Zn_4Sb_3 powders and sintered β–Zn_4Sb_3 pellets, characterization techniques, investigation methods, and the fabrication of monolithic β–Zn_4Sb_3/ZnO thermoelectric generator modules, including custom-built heating/cooling system with IV measurement capabilities. Chapter IV presents experimental results and discussions. Finally, Chapter V summarized the conclusion and offers suggestion.