CHAPTER 1

1. INTRODUCTION

In this chapter represents 6 topics viz, rationale and motivation, research objectives, scope and limitation of the dissertation, anticipated outcomes of the thesis dissertation, dissertation structure, and references.

Rationale and Motivation

According to the demand respond, increasing energy is required to reduce the cost, lead to be new and important regimes of research needed to convert thermal to electrical energy. Thermoelectric material has converted heat into electricity and vice versa, without moving part, environmentally friendly. The thermal to power generation relies greatly on the power factor (PF) that is defined as $PF = S^2T / \rho$, where S represents the Seebeck coefficient, T is the absolute temperature and ρ represents the electrical resistivity, respectively. Bulk TE materials for large scale energy harvesting applications need to demonstrate not only high thermoelectric performance but should also be composed from elements which are nontoxic, largely available in nature, and preferably be as light as possible for applications such as automobiles. Silicide based materials are considered as the best candidate for medium to high temperature on TE applications (400–600 °C) as their constituents are highly abundant, inexpensive, non-toxic and maintain a high stability (Ivanova, L.D., 2011, pp.965-970). Magnesium silicide-based materials possess a combination of these properties which are among the best candidates for these applications (Vasilevskiy, D., et al, 2015, pp. 523 – 531). The highest PF was reported about 3.8×10^{-3} Wm^{-1} K^{-2} for $Mg_2(Si_{0.4}Sn_{0.6})Sb_{0.018}$ sample preparing by twice mechanical alloying and spark plasma sintering process (Zheng, L., et al, 2016, pp. 452–457). Silicides have good properties for thermoelectric applications, and contain very abundant, inexpensive elements regarded as chemically and structurally stable. A high thermoelectric potential is associated with the higher manganese silicides (HMS), which behave as highly degenerate p-type semiconductors (Sadia, Madar, Kaler, & Gelbstein, 2015, pp. 1637-1643). HMS are represented by $MnSi_{2x}$, $MnSi_{1.75}$ and $MnSi_{1.8}$ compositions. They are consist of a homologous series of crystallographically distinct phases referred to as the Nowtony Chimney Ladder phases. Four distinct phases of HMS have been reported with the atomic positions determined by XRD: Mn_4Si_7, $Mn_{11}Si1_9$, $Mn_{15}Si_{26}$ and $Mn_{27}Si_{47}$ (Higgins, J., & Schmitt, A., 2008, pp. 16086–16094). HMS are semiconductors with band gap energy from 0.4 eV to 0.7 eV (Zwilling, V.G., & Aus, N., 1973, pp. 668–675.). Granger, G.B., et al, 2015, pp.403-412 were reported PF value of $MnSi_{1.75}$ preparing by SPS method about 1.82×10^{-3} Wm^{-1} K^{-2} at 773 K. Saleemi, M., et al, 2015, pp. 31-37 were reported the PF value of Yb doped on $MnSi_{1.73}$ preparing by BM, SSR and SPS method about 1.44×10^{-3} Wm^{-1} K^{-2} at 873 K. One problem with combining both *n*-type and *p*-type materials as unicouples in a module construction is caused by their relative difference in coefficients of thermal expansion (CTE) (Skomedal, G., et al, 2016, pp. 13-21). Generally, *n*-type silicides have CTE in the range $16–18 \times 10^{-6}$ K^{-1} for Mg_2(Si–Sn) whereas *p*-type HMS materials exhibit CTE's in the range of $9\text{-}13 \times 10^{-6}$ K^{-1}, which is very close to matching (Gao, P., et al, 2014, pp. 790–803), (Engström, I., & Lönnberg, B., 2014).

Therefore, this research has objective to synthesis thermoelectric materials; *p*-$Mn_{1-x}Ag_xSi_{1.75-y}Bi_y$ and *n*-$Mg_{2-x}Ag_xSi_{1-y}Bi_y$ (x=y=0, 0.01, 0.02, 0.03, 0.04, and 0.05), which has not reported Mg_2Si and $MnSi_{1.75}$ doped by Ag and Bi materials. And then, the best materials from doped condition are selected to fabricate thermoelectric devices.

Dissertation Objectives

1. To synthesize and develop thermoelectric materials of *p*-$Mn_{1-x}Ag_xSi_{1.75-y}Bi_y$ ($x = y = 0.01, 0.02, 0.03, 0.04$ and 0.05) and *n*-$Mg_{2-x}Ag_xSi_{1-y}Bi_y$ ($x = y = 0.01, 0.02, 0.03, 0.04$ and 0.05) by hot pressing method.

2. To study crystal structure, chemical composition, microstructure, thermoelectric properties and electronic properties of *p*-$Mn_{1-x}Ag_xSi_{1.75-y}Bi_y$ and *n*-$Mg_{2-x}Ag_xSi_{1-y}Bi_y$.

3 To fabricate and measure of thermoelectric device prototype from *p*-$Mn_{1-x}Ag_xSi_{1.75-y}Bi_y$ and *n*-$Mg_{2-x}Ag_xSi_{1-y}Bi_y$.

4 To study possibility of thermoelectric generator and refrigerator application.

Scope and Limitation of the Dissertation

1 Synthesis thermoelectric materials by Mechanical Alloying, Solid state reaction, and hot press method

2 The $MnSi_{1.75}$ base and Mg_2Si base was mixed by stainless steel and agate grinding jar in Ar atmosphere with sun wheel speed 200-400 rpm.

3 The Ag substituted on Mn site of $MnSi_{1.75}$ in ratio 1:0, 0.99:0.01, 0.98:0.02, 0.97:0.03, 0.96:0.04, and 0.95:0.05.

4 The Bi substituted on Si site of $MnSi_{1.75}$ in ratio 1.75:0, 1.74:0.01, 1.73:0.02, 1.72:0.03, 1.71:0.04, and 1.70:0.05.

5 The Ag substituted on Mg site of Mg_2Si in ratio 2:0, 1.99:0.01, 1.98:0.02, 1.97:0.03, 1.96:0.04, and 1.95:0.05.

6 The Bi substituted on Si site of Mg_2Si in ratio 1:0, 0.99:0.01, 0.98:0.02, 0.97:0.03, 0.96:0.04, and 0.95:0.05.

Anticipated Outcomes of the Thesis Dissertation

1 The *p*-$MnSi_{1.75}$ base and *n*-Mg_2Si base are high power factor.

2 Thermoelectric device should be high electrical power and medium temperature application.

3 The results can be published in ISI citation index journal.

4 Thermoelectric device fabrication process has been patented.

Dissertation Structure

The dissertation structure includes 5 chapters, namely, introduction, literature reviews, materials and methods, results and discussions, conclusions and suggestions. In the chapter 1 introduction consist rationale and motivation, dissertation objectives, scope and limitation of the dissertation, anticipated outcomes of the dissertation, and dissertation structure. The literature reviews of the thermoelectricity theorem, thermoelectric materials and thermoelectric device are present in chapter 2. In the chapter 3 are thermoelectric materials synthesis, crystal structure analysis, microstructure analysis, thermoelectric properties measurement, thermoelectric devices fabrication and thermoelectric power generation and refrigeration measurement. The results and discussion of experimental are present in chapter 4. In the final, chapter 5 are present the conclusions and suggestions of the work. In addition, the reference and appendix are present after chapter 5.