MG₂(SI,SN)-BASED THERMOELECTRIC MATERIALS AND DEVICES

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ABSTRACT

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Thermoelectric effects are phenomena found in materials that can achieve direct conversion between heat flow and electricity. One important application of thermoelectric effects is thermoelectric generators, which can generate electricity when a temperature gradient is applied. Thermoelectric generators make use of various sources of heat and it is considered a promising solution for waste heat recovery.

The conversion efficiency of thermoelectric generators depends on the materials used in the devices. Significant improvement in the performance of thermoelectric materials has been made in the past few decades. However, most of the good thermoelectric materials being investigated have limitations, such as the high materials cost, high materials density and toxicity of the constituent elements. The Mg₂(Si,Sn)-based materials studied in this work are promising candidates for thermoelectric generators in the mid-temperature range and have drawn increasing research interest in recent years because these materials are high performance thermoelectrics that are low cost, low-density and non-toxic.

In this work, systematic studies were performed on the Mg₂(Si,Sn) thermoelectric materials. Thermal phase stability was studied for different compositions of Mg₂Si_{1-x}Sn_x and Mg₂Si_{0.4}Sn_{0.6} was used as base material for further optimization. Both *n*-type and *p*-type samples were obtained by doping the materials with different elements. Peak $ZT \sim 1.5$ for the *n*-type and $ZT \sim 0.7$ for the *p*-type materials were obtained, both of which are among the best reported results so far.

Experimental work was also done to study the techniques to develop the $Mg_2Si_{0.4}Sn_{0.6}$ materials into working devices. Different electrode materials were tested in bonding experiment for this compound, and copper was found to be the best electrode material for $Mg_2Si_{0.4}Sn_{0.6}$. Preliminary work was done to demonstrate the possibility of fabricating a $Mg_2Si_{0.4}Sn_{0.6}$ -based thermoelectric generator and the result is promising.

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Chapter 1 Introduction to Thermoelectrics

1.1 The Thermoelectric Effects

Thermoelectric effects can be interpreted as phenomena in which a temperature gradient directly creates a difference in electrical potential or vice versa. Thermoelectric effects include the Seebeck effect, the Peltier effect and the Thomson effect.



Figure 1 Illustration of the Seebeck effect.

Figure 1 shows a schematic circuit of two different conductors, A and B, with junctions at temperature *T* and $T + \Delta T$. A voltage is observed between A and B when ΔT is applied and proportional to the temperature gradients:

$$V_{\rm AB} = S_{\rm AB} \cdot \Delta T \tag{1}$$

where V_{AB} is the voltage between A and B. This is known as the Seebeck effect and S_{AB} is defined as the Seebeck coefficient for the A-B junction, or the relative Seebeck coefficients between material A and B [1].

The Peltier effect is schematically shown in Figure 2. When an electric current runs through a circuit composed of two different conductors A and B, heat is liberated at one junction and absorbed at the other, as a result of charge carriers crossing the interface of the junction between two different materials. The rate of heat absorption or evolution of heat at the junctions is proportional to the current *I*:

$$Q_{\rm AB} = \pi_{\rm AB} \cdot I \tag{2}$$

where the proportionality constant π_{AB} is defined as the Peltier coefficient for the A-B junction, or the relative Peltier coefficient between material A and B [2].



Figure 2 Illustration of the Peltier effect.

Unlike the Seebeck effects and the Peltier effects, both of which deal with the heatelectricity conversion at the interface of two different materials, the Thomson effect describes the heat evolution or absorption within one single homogeneous conductor in a temperature gradient when an electric current passes through it, as shown in Figure 3. It could be observed in a single material. The rate at which the heat is liberated or absorbed, \dot{q}_A , is expressed as



Figure 3 Illustration of the Thomson effect.

where β_A is the Thomson coefficient for material A and dT/dx is temperature gradient. The Thomson coefficient is the reversible change of the heat content within a single conductor per unit temperature gradient per unit current flow. Thomson termed it the "specific heat of electricity" as it describes the energy change when a hot charge carrier becomes a cold carrier, or vice versa.

The three thermoelectric effects are related to each other. Thomson investigated the thermoelectric circuit as shown in Figure 4 by approximating it as a reversible heat engine, where no Joule heating due to electrical resistance exists [3]. In the circuit, the colder junction is kept at temperature *T* and the hotter junction is at $T + \Delta T$. Both junctions are maintained by heat

reservoirs. The Seebeck voltage generated by the temperature difference is V_{AB} . The electrical energy is

$$I \cdot V_{\rm AB} = I \cdot \frac{dV_{\rm AB}}{dT} \Delta T \tag{4}$$

The thermal energy involved in this circuit includes the Peltier heat at the hot junction,

 $I \cdot \pi_{AB(T+\Delta T)}$, the Peltier heat at the cold junction, $-I \cdot \pi_{AB(T)}$, the Thomson heat in conductor B, $I \cdot \beta_B \Delta T$, and the Thomson heat in conductor A, $-I \cdot \beta_A \Delta T$. As this is a reversible heat engine, the total thermal and electrical energy must be equal



Figure 4 An ideal thermoelectric circuit for the derivation of Thomson relations.

Dividing both sides of the equation by $I \cdot \Delta T$ yields

$$\frac{dV_{AB}}{dT} = \frac{\pi_{AB(T+\Delta T)} - \pi_{AB(T)}}{\Delta T} + (\beta_{B} - \beta_{A})$$
(6)

The first term on the right side of the equation is the change of Peltier coefficient with respect to temperature so the above equation could be further reduced to

$$\frac{dV_{\rm AB}}{dT} = \frac{d\pi_{\rm AB}}{dT} + (\beta_{\rm B} - \beta_{\rm A}) \tag{7}$$

The entropy change of the system can be expressed as

$$-\frac{I \cdot \pi_{AB(T+\Delta T)}}{T+\Delta T} + \frac{I \cdot \pi_{AB(T)}}{T} - \frac{I \cdot \beta_B \cdot \Delta T}{T+\frac{\Delta T}{2}} + \frac{I \cdot \beta_A \cdot \Delta T}{T+\frac{\Delta T}{2}} = 0$$
(8)

The total entropy change is zero because this is a reversible heat engine. The entropy change of conductor A and B are evaluated at the midpoint where the temperature is $T + \Delta T/2$. Equation 8 could be rearranged so that

$$\frac{-\frac{I \cdot \pi_{AB(T+\Delta T)}}{T+\Delta T} + \frac{I \cdot \pi_{AB(T)}}{T}}{\Delta T} \cdot \Delta T - \frac{I \cdot \beta_{B} \cdot \Delta T}{T+\frac{\Delta T}{2}} + \frac{I \cdot \beta_{A} \cdot \Delta T}{T+\frac{\Delta T}{2}} = 0$$
(9)

$$-\frac{d}{dT}\left(\frac{\pi_{AB}}{T}\right) \cdot \Delta T - \frac{\beta_B \cdot \Delta T}{T + \frac{\Delta T}{2}} + \frac{\beta_A \cdot \Delta T}{T + \frac{\Delta T}{2}} = 0$$
(10)

Let $\Delta T = 1 K$, since T is much greater than ΔT , Equation 10 could be further reduced to

$$\frac{d}{dT}\left(\frac{\pi_{\rm AB}}{T}\right) = \frac{\beta_{\rm A}}{T} - \frac{\beta_{\rm B}}{T} \tag{11}$$

Applying the chain rule of derivative yields

$$\frac{\pi_{\rm AB}}{T} = \frac{d\pi_{\rm AB}}{dT} + \beta_{\rm B} - \beta_{\rm A} \tag{12}$$

Equation 12 could be treated as the dependence of the Peltier coefficient on both the Thomson coefficient and temperature. If a maximum Peltier coefficient exists, $(d\pi_{AB})/dT = 0$. Equation 12 becomes

$$\pi_{\rm AB} = \beta_{\rm B} \cdot T - \beta_{\rm A} \cdot T \tag{13}$$

Substituting Equation 13 to Equation 7 yields

$$\pi_{\rm AB} = \frac{dV_{\rm AB}}{dT} \cdot T = S_{\rm AB} \cdot T \tag{14}$$

Differentiating Equation 14 with respect to temperature yields

$$S_{AB} + T \cdot \frac{dS_{AB}}{dT} = \frac{d\pi_{AB}}{dT} = \frac{\pi_{AB}}{T} + \beta_A - \beta_B$$
(15)

Substituting Equation 14 into 15,

$$\frac{dS_{\rm AB}}{dT} = \frac{\beta_{\rm A} - \beta_{\rm B}}{T} \tag{16}$$

Equation 14 and 16 are known as the Thomson relations that relates the Seebeck, Peltier and Thomson effects. Equation 16 also clarifies the definition of the absolute Seebeck coefficient as the integration of Equation 16 gives

$$S_{\rm AB} = \int \frac{\beta_{\rm A}}{T} dT - \int \frac{\beta_{\rm B}}{T} dT \tag{17}$$

where the first and term on the right side are defined as the absolute Seebeck coefficient for materials A and B, respectively.

$$S_{\rm AB} = S_{\rm A} - S_{\rm B} \tag{18}$$

1.2 Thermoelectric Power Generator and Its Efficiency

If an electrical load is connected into the open circuit in Figure 1, the load could make use of the Seebeck voltage and the thermoelectric circuit works as a power generator. A more common configuration of a thermoelectric power generator is shown in Figure 5, where two different thermoelectric materials were connected by a metal plate on the hot side while electrical leads on the cold side are connected to the external load. All thermoelectric power generators use semiconductors as the thermoelectric materials and one leg should be a p-type semiconductor while the other one should be n-type. The structure in Figure 5 is known as the thermoelectric uni-couple and it is the basic element for a thermoelectric module, which usually consists of an array of large number of uni-couples.



Figure 5 Illustration of a thermoelectric power generation uni-couple.

Like the efficiency for traditional heat engine, the efficiency for the thermoelectric generator is defined as the output power divided by the total heat imported from the heat source per unit time. To find the theoretical conversion efficiency, a few assumptions are commonly made: 1) the metal plate has zero resistance and 2) the heat is transferred from the heat source to the heat sink solely by conduction along the two legs of thermoelectric materials [3].

For the uni-couple in Figure 5, once the temperature difference ΔT is established between the two ends by the heat source, the voltage produced by the uni-couple is

$$V = S_{\rm pn} \cdot (T_{\rm h} - T_{\rm c}) = S_{\rm pn} \cdot \Delta T \tag{19}$$

where S_p and S_n are the Seebeck coefficients for the *p*-type and *n*-type materials. The current in the circuit is

$$I = \frac{S_{\rm pn} \cdot \Delta T}{R_{\rm p} + R_{\rm n} + R_{\rm L}} \tag{20}$$

where R_p , R_n and R_L are the electrical resistivity for the *p*-type leg, *n*-type leg and the external load.

The thermal energy is transferred from the heat source to the thermoelectric generator in different forms. The thermal conductance through the two legs due to the temperature gradient is $(K_p + K_n) \cdot \Delta T$, where K_p and K_n are the thermal conductance for the materials. Heat is also transferred by the Peltier effect, $(\pi_P - \pi_n) \cdot I = (S_P - S_n) \cdot T_h \cdot I$, where T_h is the temperature of the heat source. It could also be shown that to maintain a constant temperature gradient, the Joule heating due to the electrical resistance should be distributed evenly towards the cold and hot ends and the portion returned to the heat source is given by $I^2(R_p + R_n)/2$. Thus the total heat input from the heat source to the thermoelectric generator is

$$Q = (K_{\rm p} + K_{\rm n}) \cdot \Delta T + I \cdot S_{\rm pn} \cdot T_{\rm h} - I^2 (R_{\rm p} + R_{\rm n})/2$$
⁽²¹⁾

so the efficiency of the thermoelectric generator could be calculated as

$$\eta = \frac{W}{Q} = \frac{I^2 \cdot R_{\rm L}}{\left(K_{\rm p} + K_{\rm n}\right) \cdot \Delta T + S_{\rm pn} \cdot T_{\rm h} \cdot I - I^2 \left(R_{\rm p} + R_{\rm n}\right)/2}$$
(22)

Substituting Equation 20 into Equation 22 yields

$$\eta = \frac{\left[\frac{S_{\rm pn} \cdot \Delta T}{R_{\rm p} + R_{\rm n} + R_{\rm L}}\right]^2 \cdot R_{\rm L}}{\left(K_{\rm p} + K_{\rm n}\right) \cdot \Delta T + \frac{S_{\rm pn}^2}{R_{\rm p} + R_{\rm n} + R_{\rm L}} \cdot \Delta T \cdot T_{\rm h} - \left[\frac{S_{\rm pn} \cdot \Delta T}{R_{\rm p} + R_{\rm n} + R_{\rm L}}\right]^2 \frac{\left(R_{\rm p} + R_{\rm n}\right)}{2}$$
(23)

To find the maximum efficiency, the external load R_L should be adjusted so that $d\eta/dR_L = 0$, solving this equation gives

$$R_{\rm L} = \left(R_{\rm p} + R_{\rm n}\right) \sqrt{1 + \frac{S_{\rm pn}^{2}}{\left(K_{\rm p} + K_{\rm n}\right)\left(R_{\rm p} + R_{\rm n}\right)} \cdot \frac{T_{\rm h} + T_{\rm c}}{2}}{2}$$
(24)

Using

$$Z = \frac{S_{\rm pn}^{2}}{(K_{\rm p} + K_{\rm n})(R_{\rm p} + R_{\rm n})}$$
(25)

Then the maximum efficiency can be written as

$$\eta_{\max} = \frac{T_{h} - T_{c}}{T_{h}} \cdot \frac{\sqrt{1 + Z \cdot \frac{T_{h} + T_{c}}{2}} - 1}{\sqrt{1 + Z \cdot \frac{T_{h} + T_{c}}{2}} + \frac{T_{c}}{T_{h}}}$$
(26)

Equation 26 shows that once the working temperature is set, the efficiency of the thermoelectric generator depends solely on the parameter Z. A higher Z leads to a higher efficiency. Rewriting Z

in terms of absolute Seebeck coefficient (S_p and S_n), electrical resistivity (ρ_p and ρ_n), thermal conductivity (κ_p and κ_n), cross-sectional area (A_p and A_n) and length (L_p and L_n) of the legs gives

$$Z = \frac{\left(S_{\rm p} - S_{\rm n}\right)^2}{\left(\frac{\kappa_{\rm p}A_{\rm p}}{L_{\rm p}} + \frac{\kappa_{\rm n}A_{\rm n}}{L_{\rm n}}\right)\left(\frac{\rho_{\rm p}L_{\rm p}}{A_{\rm p}} + \frac{\rho_{\rm p}L_{\rm n}}{A_{\rm n}}\right)}$$
(27)

and *Z* can be maximized when $L_n A_p / L_p A_n = \sqrt{\rho_p \kappa_n / \rho_n \kappa_p}$. This gives a *Z* that only depends on materials intensive properties

$$Z = \frac{\left(S_{\rm p} - S_{\rm n}\right)^2}{\left[\sqrt{\rho_{\rm p}\kappa_{\rm p}} + \sqrt{\rho_{\rm n}\kappa_{\rm n}}\right]^2} \tag{28}$$

This form of Z is known as the figure-of-merit for thermoelectric devices. The unit of Z is the inverse of temperature so the product of Z and T becomes the dimensionless figure-of-merit for thermoelectrics, which is more commonly used in practice.

Figure 6 shows the dependence of the thermoelectric conversion efficiency on *ZT*. For comparison, the blue line representing the ideal Carnot efficiency and the red line representing the actual efficiency of a modern coal-burning power plant are also shown. As *ZT* approaches infinity, the thermoelectric generator efficiency would approach the ideal Carnot efficiency defined by $\frac{T_{\rm h}-T_{\rm c}}{T_{\rm h}}$. To make thermoelectric generator comparable to coal burning power plant, *ZT* needs to exceed 10.



Figure 6 The dependence of thermoelectric generator efficiency on ZT.

As will be discussed in following paragraphs, current thermoelectric generators only operate at $ZT \approx 1$. Thermoelectric devices cannot compete with traditional heat engine in the near future. However, thermoelectric generators have their own advantages. No moving parts are involved in the energy conversion process which makes it stable for long term application. The thermoelectric conversion efficiency is size independent so thermoelectric devices could be made small enough to cool computer CPUs or large enough to power electrical devices on space ships. Thermoelectric generator could also make use of low-level waste heat energy that could not be used or recycled by traditional heat engines. Theoretically, up to 7-8% of the waste heat energy in the burning exhaust of coal-burning plant could be converted to electricity and increase the overall efficiency of current power plant [4,5]. It also has been shown that thermoelectric

waste heat recovery devices on automobile could potentially increase the overall fuel efficiency of vehicles by up to 10% [6].

1.3 Approaches to High *ZT*

The definition of *ZT* in Equation 28 involves properties of two different materials. In real cases the materials properties *S*, ρ and κ to are temperature dependent so numerical computation needs to be carefully done to calculate *ZT*. Thus, it is difficult to evaluate the thermoelectric performance of a single material by using Equation 28. Practically, a simplified form of Equation 28 is used

$$ZT = \frac{S^2}{\rho\kappa}T = \frac{S^2\sigma}{\kappa}T$$
(29)

where σ is the electrical conductivity of the material and $S^2\sigma$ is usually referred to as the power factor for thermoelectrics. Equation 29 is only equivalent to Equation 28 when both the *p*-type and *n*-type materials have the same transport properties except the sign of the Seebeck coefficient. In most practical cases, materials in a combination that gives a high *ZT* in Equation 28 also have high *ZT* as defined by Equation 29 for each material. Thus, the definition of *ZT* in Equation 29 is more commonly used to evaluate thermoelectric materials individually. If not specifically mentioned, the right most form in Equation 29 will be used as the definition for *ZT* for the remainder of this dissertation.

High ZT is needed to obtain high energy conversion efficiency for thermoelectric generators. The following discussion will be focused on relating the transport properties S, σ and

 κ to the materials parameters such as crystal structure and composition to introduce the concepts of good thermoelectric materials.

Most good thermoelectric materials are heavily doped semiconductors in which a major type of charge carrier dominates. (holes for *p*-type material and electrons for *n*-type material) Taking an *n*-type semiconductor for example, according the single parabolic band model, the carrier concentration *n* is calculated by [7]

$$n = \frac{4}{\sqrt{\pi}} \left(\frac{2\pi k_B m^* T}{h^2}\right)^{3/2} F_{1/2}(\eta) \tag{30}$$

where k_B is the Boltzmann constant, m^* is the density of states (DOS) effective mass, η is the reduced Fermi level and $F_{1/2}(\eta)$ is the Fermi-Dirac.

$$\eta = \frac{E - E_F}{k_B T} \tag{31}$$

$$F_{\lambda} = \int_{0}^{\infty} x^{\lambda} \frac{1}{1 + e^{x - \eta}} \,\mathrm{d}x \tag{32}$$

where *E* is the energy of electrons, E_F is the Fermi level of the material and λ is the scattering mechanism. The electron mobility is calculated as

$$\mu = q \cdot \frac{\tau}{m_{\mu}^*} \tag{33}$$

where q is the charge for each electron, τ is the scattering time for electrons and m_{μ}^* is the mobility effective mass for electrons. Thus the electrical conductivity is

$$\sigma = q \cdot n \cdot \mu = q^2 \cdot \frac{4}{\sqrt{\pi}} \left(\frac{2\pi k_B m^* T}{h^2}\right)^{3/2} F_{1/2}(\eta) \cdot \frac{\tau}{m_{\mu}^*}$$
(34)

The Seebeck coefficient could be calculated by the Mott equation as [8]

$$S = \frac{1}{\sigma} \cdot \frac{k_B}{q} \int_0^\infty \sigma(E) \frac{E - E_F}{k_B T} \left[\frac{\partial F_\lambda(E)}{\partial E}\right] dE$$
(35)

where the Fermi-Dirac distribution function is the same as defined in Equation 32. After proper substitution, differentiation and integration, Equation 35 becomes

$$S = -\frac{k_B}{q} \left[\frac{(\lambda + 5/2)F_{\lambda + 3/2}(\eta)}{(\lambda + 3/2)F_{\lambda + 1/2}(\eta)} - \eta \right]$$
(36)

If multiple bands are involved in the electrical conduction, the overall electrical conductivity and Seebeck coefficient should be the weighted sum of the contribution from each band.

$$\sigma_{\text{total}} = \sum_{i} \sigma_{i} , \quad S_{\text{total}} = \frac{1}{\sigma_{\text{total}}} \sum_{i} S_{i} \cdot \sigma_{i}$$
 (37)

The total thermal conductivity κ consists of three components

$$\kappa = \kappa_{\rm e} + \kappa_{\rm l} + \kappa_{\rm bi} \tag{38}$$

where κ_e is the electronic thermal conductivity arising from the movement of the charge carriers (electrons or holes), κ_1 is the lattice thermal conductivity and κ_{bi} is the bipolar thermal conductivity. The bipolar thermal conductivity only becomes significant at a certain transition temperature for semiconductor materials and it is negligible below the transition temperature. The electronic thermal conductivity is related to the materials electrical conductivity by the Wiedemann-Franz law [9]

$$\kappa_{\rm e} = L \cdot \sigma \cdot T \tag{39}$$

where *L* is the Lorenz number

$$L = \left(\frac{k_B}{q}\right)^2 \left\{ \frac{(\lambda + 7/2)F_{\lambda+5/2}(\eta)}{(\lambda + 3/2)F_{\lambda+1/2}(\eta)} - \left[\frac{(\lambda + 5/2)F_{\lambda+3/2}(\eta)}{(\lambda + 3/2)F_{\lambda+1/2}(\eta)}\right]^2 \right\}$$
(40)

Heat is conducted in the crystal lattice by phonons, which could be considered analogous to electrons in electrical conduction. The general form of the lattice thermal conductivity could be expressed as

$$\kappa_{\rm l} = \frac{1}{3} \cdot \frac{v}{V_{\rm M}} \int_0^{\omega_D} C_{\rm v}(\omega) \cdot l(\omega) \, d\omega \tag{41}$$

where v is the average phonon velocity, $V_{\rm M}$ is the molar volume, $C_{\rm v}$ is the molar specific heat at constant volume, l is the mean free path of the phonons, ω is phonon frequency and $\omega_{\rm D}$ is the phonon frequency at the Debye temperature $\theta_{\rm D}$. At high temperature the specific heat solid is almost constant according to the Dulong–Petit law. The mean free path could be related to the relaxation time by $1/\tau = v/l$, where τ is the relaxation time for phonons.



Figure 7 Normal process (N-process) and Umklapp process (U-process).

Phonon-phonon scattering is the dominant scattering mechanism for materials have a carrier concentration on the level of 10^{19} to 10^{20} cm⁻³. Below the Debye temperature, only long-wavelength phonons exist and the interaction of two phonons results in a third phonon and the phonon momentum is conserved during this process. This is called a normal process (N-process). The normal process only changes the momentum distribution of phonons and does not hinder the heat conduction. Above the Debye temperature, phonons have higher energies and the interaction of two phonons will result in a phonon the wave vector of which extends outside the first Brillouin zone for phonons. Once the wave vector exceeds the first Brillouin zone, it is cut-off by the reciprocal lattice vector \vec{G} and translated back into the first Brillouin zone. The overall effect is $\vec{k_1} + \vec{k_2} \rightarrow \vec{k_3} + \vec{G}$ because some phonon momentum is lost to the lattice by \vec{G} . This process is called the Umklapp process (U-process) in which the momentum of phonons is not conserved, resisting the heat conduction in the lattice. The U-process is the origin of thermal resistivity in a perfect crystal, without which a material would have infinite thermal conductivity. The phonon relaxation in a U-process is [10, 11]

$$\tau_U^{-1}(x) = \frac{k_B^2 \gamma^2}{\hbar M v^2 \theta_D} \cdot \left(\frac{\hbar \omega}{k_B T}\right)^2 \cdot T^3 \cdot e^{-\frac{\theta_D}{3T}}$$
(42)

where \hbar is the reduced Planck constant, γ is the Gruneisen parameter which characterizes the anharmonicity of the lattice and *M* is average mass of atoms.

Real crystals are not perfect and there exists different types of defects such as point defect (impurity atoms, vacancies, etc), line defects (dislocations) and planar defects (grain boundaries or phase boundaries). Different types of defects have different relaxation time. For the phononpoint defect

$$\tau_D^{-1}(x) = \frac{k_B^4 \cdot \Gamma \cdot V_A}{4\pi\hbar^4 v^3} \cdot \left(\frac{\hbar\omega}{k_B T}\right)^4 \cdot T^4$$
(43)

where Γ is the impurity scattering parameter and V_A is the average volume per atom. For scattering by boundaries or interfaces, the common expression for scattering rate is

$$\tau_B^{-1}(x) = \frac{\nu}{C_g} \tag{44}$$

where C_g is the grain size. The total relaxation time is the sum of all the participating scattering mechanisms in the materials

$$\tau^{-1} = \sum_{i} \tau_{i}^{-1} \tag{45}$$

Despite the large number of physical parameters through Equation (30 - 45), there are only a few key variables that are significant to ZT. To increase ZT, a high power factor ($S^2\sigma$) and a low thermal conductivity (κ) is needed.

Based on previous analysis, the reduced Fermi level η affects *S*, σ and κ (κ_e) differently and an optimal value is needed to balance the three parameters to increase *ZT*. The reduced Fermi level determines the Fermi-Dirac distribution and directly affects the carrier concentration once the band structure is fixed. In other words, by adjusting the carrier concentration, the reduced Fermi level could be optimized to increase *ZT*. The general dependence of *S*, σ and κ (κ_e) on the carrier concentration *n* could be approximated as shown in Figure 8 [4]. The optimal carrier concentration level for good thermoelectric materials is usually $10^{19} - 10^{20}$ cm⁻³.



Figure 8 Dependence of thermoelectric transport properties on the carrier concentration *n*.

Another factor that affects the thermoelectric transport properties is the band structure of the materials. The band structure is characterized by the band gap, band degeneracy and the shape of the band. Good thermoelectric materials are usually narrow band gap semiconductors with energy gap close to $10k_BT$ at the working temperature T [12]. High band degeneracy allows more carriers to participate in the transport (Equation 37) and could potentially improve the power factor. The shape of the band is characterized by the DOS effective mass $m^* = \hbar^2 \cdot$ $(d^2E/dk^2)^{-1}$ and a high effective mass would increase the carrier concentration. Meanwhile, the mobility of the carriers is inversely proportional to the mobility effective mass m_{μ}^* . To increase the electrical conductivity, the density of states effective mass should be high while the mobility effective mass should be reduced. The band structure engineering has been successfully applied in the Na-doped PbTe by manipulating the band convergence. By substituting Te with Se, the energy of the high degeneracy valence band was tuned to converge with the low energy band and the power factor was successfully improved [13, 14].

The thermal conductivity should be reduced to improve *ZT*. Because the electronic part of the thermal conductivity is coupled with the electrical conductivity, it is unlikely to solely adjust the κ_e without changing $S^2\sigma$. For the lattice thermal conductivity, as the phonons have different scattering mechanism from electrons, it is possible to reduce κ_1 without affecting $S^2\sigma$. Thus, reducing the lattice thermal conductivity has been an important strategy to improve *ZT*.

A classic approach to reducing the lattice thermal conductivity is to form solid-solutions by introducing impurity atoms to the pristine crystal. The impurity atoms act as point defects without causing structural change and will strongly enhance the phonon-defect scattering as described in Equation 43. As pointed out by Ioffe [3], in most cases, those point defects scatter phonons more strongly than electrons so the net effect is a reduced thermal conductivity and an increased *ZT*. Successfully examples include $Bi_{2-x}Sb_xTe_3$ and $Si_{1-x}Ge_x$ solid solutions, both of which are among the best thermoelectric materials so far [15, 16].

For crystals with a large unit cell, it is possible to fill the interstitial sites with heavy atom and those foreign atoms "rattle" in the cage, scattering phonons without affecting the transport properties governed by the host crystal matrix [17]. Skutterudites (such as CoAs₃ or CoSb₃) have open structures in the nit cell large enough to accept such rattling atoms. The filled or partially filled skutterudites have a lattice thermal conductivity that is more than one order of magnitude less than the unfilled skutterudites, making skutterudites one of the most promising thermoelectric materials for domestic applications [18-20]. Nano structuring is another common method to reduce the lattice thermal conductivity. One way is to directly reduce the grain size to the nano level so that the phonon-grain-boundary scattering is enhanced. However, in most cases the grain boundary scattering is detrimental to electron transport. Another approach is to introduce nano precipitates into the host matrix by forming endotaxial structures. Such endotaxial structures maintain the crystallinity across the nanoparticle to host matrix interface so as to minimize the scattering potential for electrons. In these materials mass fluctuations between nanoparticles and host matrix can scatter phonons such that the lattice thermal conductivity is effectively reduced without sacrificing the power factor. The PbTe-PbS [21] and PbTe-SrTe [22] systems are successful examples of this method and presently the best *ZT* ever reported in bulk materials is found in the PbTe-SrTe material.

1.4 The State of the Art Thermoelectric Materials and the Motivation of Current Work

Currently most thermoelectric materials have *ZT* that peaks around unity. Figure 9 displays the figure of merit of the most bulk thermoelectric materials that have been or is being investigated [23].

The Bi_2Te_3 material is mature material that has been successfully applied in commercial applications, such as thermoelectric refrigerators and coolers. For the purpose of high temperature power generation, Si-Ge is a proven reliable material that has been used in Radioisotope Thermoelectric Generators (RTG) for space missions by NASA.



Figure 9 Figure of merit for state of the art thermoelectric materials.

The mid-temperature range (400K – 800K) is the typical range for thermoelectric waste heat recovery because most waste heat, such as exhaust gas and hot steam are in this temperature range. Materials that have high *ZT* in this range could be categorized into three major types: 1) lead chalcogenides such as PbTe, PbS and PbSe, 2) skutterudites such as CoAs₃ and CoSb₃, and 3) half Heusler compounds, which are (Hf,Zr)Ni(Sn,Sb)-based alloys [24, 25]. However, these materials have their own limitations that prevent them from being used for domestic applications. Lead chalcogenides showed the best ever reported *ZT* (*ZT* > 2), but the Pb element is toxic and it could cause potential environmental problems. Most lead chalcogenides are fragile, which limited their application in automotive industry. The cost of thermoelectric devices would be increased if the thermoelectric materials contain large amount of noble elements such as Te, Bi, Co and Hf.

A low cost and efficient material is needed for thermoelectric generators in domestic applications. The $Mg_2(Si,Sn)$ material is a good candidate for such applications because of its low density (1.99 – 3.59 g/cm³), low material cost and non-toxicity. In this work, the $Mg_2(Si,Sn)$

materials were synthesized and optimized to get *ZT* that is comparable to traditional thermoelectric materials. In addition to the materials study, engineering of thermoelectric device based on $Mg_2(Si,Sn)$ was also initiated. The success of this research would prove the possibility of fabricating light, cheap and high efficiency thermoelectric modules by only using $Mg_2(Si,Sn)$ as the thermoelectric material.

Chapter 2 Experimental Setup

2.1 Materials Synthesis

The B₂O₃-flux method was used for the synthesis of all the Mg₂(Si,Sn) samples in this work [26]. Powder materials were purchased from Alfa Aesar. The powders were weighed using a high-precision digital scale to get a stoichiometric powder mixture. The mixture was then loaded into Al_2O_3 crucibles (Almath Crucibles Ltd, OD = 22 mm, Height = 80 mm). The powder mixture was stirred by a stainless steel sampling spoon and then placed on a sieve shaker (Retsch AS 200) to perform a 20 min shaking for better mixing. The mixed powder was cold pressed in the crucible by hand and covered by two layers of graphite foil. The B₂O₃ powder was then compacted on top of the graphite foil. All the steps mentioned above were done in an argonpurged glovebox (Mbraun UNIIab 2000). The Al₂O₃ crucible containing the reactant materials and B₂O₃ was transferred from the glovebox to a Benchtop Muffle Furnace (MTI Corporation, EQ-KML1100X) which was pre-heated to 973 K. The powder mixture was annealed at 973 K for 12 hours. Once it naturally cooled down to room temperature, the crucible was broken and the cast ingot was obtained (Figure 10). The top of the ingot was B_2O_3 and the bottom part was the Mg₂(Si,Sn) solid solution. The graphite foil put in between them earlier made it easy to separate the B_2O_3 from the $Mg_2(Si,Sn)$.

The as-synthesized $Mg_2(Si,Sn)$ ingot was porous and inhomogeneous. The ingot was pulverized using an agate mortar and pestle in the glovebox for 1-3 hours. The ground powders were passed through a 53 µm sieve. To get a dense specimen for transport and mechanical property measurements, the powders were densified using a Pulsed Electrical Current Sintering (PECS) system (Thermal Technology LLC, SPS10-2). The PECS process, also known as Spark Plasma Sintering (SPS), is a current-activated pressurized consolidation technique. The heating rate could be up to 2000 K/min in PECS, so it can attain high density samples in a shorter time compared to the traditional hot pressing technique. Some researchers claimed that PECS could improve the thermoelectric properties of materials as the grain growth is suppressed due to the short processing time in PECS [22]. For the powder consolidation PECS experiments, the pressure was set at 30 MPa, the temperature was at 973 K and the processing time was between 15 - 20 minutes. The die and punch materials of the PECS was stainless steel (SS 304). Graphite foils were used between the powder and the die/punch to prevent the materials stick to the die/punch. The consolidated sample has a disk-like shape and has a diameter of 12.7 mm. The thickness of the samples may vary from 1 mm to 6 mm, depending on how much material is used.



Figure 10 The cast ingot, consolidated sample and the PECS powder consolidation setup.

2.2 Diffusion Bonding in PECS

The PECS-assisted diffusion bonding was used to bond $Mg_2(Si,Sn)$ samples and different alloys/metals. The alloys or metals serve as electrode to output the power generated by the thermoelectric materials to the external load. The quality of the bonding interface affects the efficiency of the device significantly. If the interface has a high resistance, it could cause significant power loss.

The diffusion bonding experimental setup in PECS is shown in Figure 11. It is similar to the setup used in the powder consolidation step. A layer of alloy or metal was added to both ends of the $Mg_2(Si,Sn)$ sample. The metal/alloy had direct contact with $Mg_2(Si,Sn)$ so that the diffusion would occur during the PECS process. In most diffusion bonding experiments, graphite dies and punches were used instead of SS 304. Most samples were already densified before the diffusion bonding experiment and they had smaller diameter than the inner diameter of the die, so the radial stress caused by the CTE mismatch could be neglected. The pressure, temperature and processing time were adjusted depending on the alloys or metals used as the electrode material.



Figure 11 A sample bonded with electrode and the experimental setup.
2.3 Crystallography, Microstructure and Composition Analysis

The phase purity of samples was examined by performing powder X-ray diffraction (XRD) analysis on a Rigaku Miniflex II bench-top X-ray diffractometer with Cu K_{α} radiation (wavelength = 0.154187 nm). The powders were obtained by grinding a portion of each sample with an agate mortar and pestle set. The XRD patterns were evaluated using a Jade 9.0 software package, which includes a JCPDS XRD database.

Some samples were also analyzed by neutron scattering on the Vulcan beamline at the Oak Ridge National Lab. The data were analyzed by the GSAS package through the EXPGUI interface. Standard data were taken from the Inorganic Crystal Structure Database (ICSD) and used as reference during the analysis.

The microstructures of the samples were observed using a JEOL 6610LV Scanning Electron Microscope (SEM). For most samples, compositional analysis was done using the energy dispersive X-ray spectroscopy (EDX) in the SEM. Some samples contain light elements (e.g. Li and Na) which could not be detected by EDX. Those samples were dissolved in 2 wt% nitric acid (HNO₃) solutions with trace amount of hydrofluoric acid (HF). The sample solutions were analyzed using a Varian 710-ES Axial Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) instrument.

2.4 Transport Property Measurement

The room temperature densities ρ_0 of the densified samples were measured by the Archimedes method using ethanol as the medium. A Netzsch DIL 402 C dilatometer was used to

measure the linear coefficient of thermal expansion α of the sample. Then the temperature dependent densities could be calculated as

$$\rho = \rho_0 / [1 - 3\alpha \cdot (T - T_0)] \tag{46}$$

A laser flash technique was used to measure the thermal diffusivities D and specific heat capacities C_p of the samples on a Netzsch LFA 457 MicroFlash system. Disk-shaped samples that had thickness of ~ 2 mm and diameter of 12.7 mm were used for the measurement. The thermal conductivities of the samples were calculated as

$$\kappa = D \cdot \rho \cdot C_p \tag{47}$$

The temperature-dependent electrical conductivities σ and Seebeck coefficients *S* were measured using a ULVAC ZEM-3 system on pieces cut from the sample disk after the thermal diffusivity measurement. The photo of the ZEM-3 system is shown in Figure 12, as well as the schematic wiring setup.



Figure 12 The ZEM-3 system and its schematic wiring setup.

Electrical resistivity was measured using a four-probe DC technique. The wires made of the same material from the two thermocouples measured the voltage drop across distance d_{probe} along the sample when an electric current *I* was applied through the sample. To eliminate the Peltier effect of the current, the current direction was flipped during the measurement and the results were the average of flipped measurements. The electrical conductivity was calculated as:

$$\sigma = \frac{I}{V_{\rm h} - V_{\rm c}} \cdot \frac{d_{\rm probe}}{\rm width \cdot depth}$$
(48)

To measure the Seebeck coefficient, the current through sample was turned off and the heater within the sample stage was turned on to create a steady temperature difference in the sample. The temperature difference as well as the voltage difference was recorded by the thermocouple. The Seebeck coefficient was then calculated as

$$S = \frac{V_{\rm h} - V_{\rm c}}{T_{\rm h} - T_{\rm c}} \tag{49}$$

The temperature-dependent carrier concentrations n and Hall mobilities μ were measured using a laboratory-built Hall measurement apparatus (room temperature to 600K) and a Quantum Design Versalab system (70K to room temperature) on thin pieces cut from the sample disk. Both measurement systems have similar wiring setup except the heating/cooling units. The wiring setup for the Hall measurement is shown in Figure 13.



Figure 13 The schematic wiring setup for the Hall measurement.

When a current, *I*, passes through the sample and a magnetic field, *B*, is applied perpendicular to the sample, the Lorentz force causes the charge carriers to drift towards one side of the sample until the accumulated charge creates a transverse electric field that balances the Lorentz force. At equilibrium,

$$R_{\rm H} = \frac{V_{\rm A} - V_{\rm c}}{I \cdot B} \cdot \text{thickness}$$
(50)

where $R_{\rm H}$ is known as the Hall coefficient and the carrier concentration in the materials is calculated as

$$n = \frac{R_{\rm H}}{q} \tag{51}$$

Then the mobility could be calculated by Equation 33.

The estimated uncertainties in the high temperature measurements for the electrical conductivity, Seebeck coefficient, thermal diffusivity and specific heat are 7%, 7%, 3% and 5%, respectively.

2.5 Mechanical Property Measurement

Knowledge on the mechanical property of the thermoelectric materials is crucial for the fabrication of the thermoelectric devices. As the thermoelectric devices work in places where can be significant temperature gradient, stress could be induced due to thermal expansion and thermal shock. For automotive application, vibration induced stress is also expected. The mechanical property also gives information on the crystal lattice, which might be helpful in understanding the lattice thermal conductivity of the materials.

In collaboration with Professor Eldon Case's group at Michigan State University, mechanical properties were measured for some samples in this work. The materials hardness and fracture toughness were measured by Vickers indentation method. The elastic moduli and acoustic wave speeds of the materials were measured by the Resonant Ultrasound Spectroscopy (RUS). Samples were excited with mechanical vibration in a frequency range of 20 – 600 kHz and the resonance modes of the samples were recorded. The mechanical properties were then calculated from the resonance frequencies along with the mass, shape, and the dimensions of the samples using the commercial software package (RUSpec, Magnaflux Quasar, Albuquerque, NM, USA). Details on the RUS measurement technique can be found in related articles [27-29].

2.6 Contact Resistance

The quality of the interface formed by the diffusion bonding experiment was evaluated by measuring the contact resistance. Electrically conductive interface of low resistance are desired for thermoelectric devices.



Figure 14 The experimental setup the contact resistance measurement.

The contact resistance was measured in a room temperature scanning probe station shown in Figure 14. The motorized probe scans the sample surface across the interface along certain directions. The voltage profile gives information on the contact resistance. A large discontinuity in the voltage profile indicates significant contact resistance with the contact resistance found as:

$$R_{\rm contact} = \frac{V_{\rm contact}}{I} \tag{52}$$

where V_{contact} is the voltage change across the interface and I is the current.

2.7 Module Fabrication and Testing

Some preliminary modules were fabricated in this work to demonstrate the possibility of making $Mg_2(Si,Sn)$ -based thermoelectric devices. Details on the design, fabrication and testing of the modules could be found in Chapter 7.

Chapter 3 Mg₂(Si,Sn) Solid Solutions

3.1 Crystal Structure and Phase Diagram

 $Mg_2(Si,Sn)$ is a solid solution system formed by Mg_2Si and Mg_2Sn . Solid solutions formed by different ratios of these endpoint members all have the anti-fluorite crystal structure (Fm-3m). In the unit cell of Mg_2Si (Figure 15), the Si atoms occupy the face centered cubic (FCC) sites and Mg atoms fill the tetrahedral sites. The solid solution $Mg_2Si_{1-x}Sn_x$ is formed as some of the Si atoms in the Mg_2Si unit cell are replaced with Sn atoms. The lattice constant is 6.338 Å for Mg_2Si and 6.765 Å for Mg_2Sn . The band gap at 0 K for Mg_2Si is 0.78 eV and it is 0.38 eV for Mg_2Sn . $Mg_2Si_{1-x}Sn_x$ solid solutions have been shown to follow Vegard's Law, and the lattice constant and band gap of $Mg_2Si_{1-x}Sn_x$ can be calculated by a linear combination of the properties of the two endpoint members [30].



Figure 15 Unit cell of Mg₂Si anti-fluorite structure with the Fm-3m space group.

A single phase solid solution only exists in a certain range for Mg₂Si_{1-x}Sn_x (Figure 16). A quasi binary phase diagram for Mg₂Si_{1-x}Sn_x has been known for decades [31]. For $x \le 0.35$, a Sirich single solid solution phase is expected while for $x \ge 0.65$, a Sn-rich single solid solution phase is expected. The Si-rich and Sn-rich solid solution phases would coexist if $0.35 \le x \le 0.65$, creating the miscibility gap in the phase diagram.



Figure 16 The quasi binary phase diagram for Mg₂Si_{1-x}Sn_x.

3.2 Thermal Phase Stability of Mg₂Si_{1-x}Sn_x

Two phases coexist for $Mg_2Si_{1-x}Sn_x$ when $0.35 \le x \le 0.65$, as shown by the miscibility gap in the phase diagram. Similar to the grain boundaries (Equation 44), the interface between different phases, i.e. phase boundaries, scatter both electrons and phonons as well. The phase boundary scattering might be detrimental to the thermoelectric properties of Mg₂Si_{1-x}Sn_x, however, $ZT \approx 1.2$ has been reported on Mg₂Si_{0.5}Sn_{0.5}, in which single phase solid solution was claimed to exist [32]. There are other reports in the literature that contradict the existing phase diagram as well, where single phase solid solution was claimed to exist for the Mg₂Si_{0.5}Sn_{0.5} composition [33-36]. To get a better understanding on the phase diagram, the thermal phase stability study was performed for the Mg₂Si_{1-x}Sn_x system.



Figure 17 Illustration of the neutron scattering experiment setup.

The thermal phase stability study was conducted in two manners, *in*-situ neutron scattering and *ex*-situ neutron scattering. An incident beam of 4.32 Å bandwidth was selected by running the chopper at 20 Hz. Cylindrical samples (5 mm in diameter) were prepared for the experiments.

For the *in*-situ experiment, the $Mg_2Si_{1-x}Sn_x$ (x = 0.3, 0.4, 0.5, 0.6 and 0.7) samples were synthesized and PECS-processed at 973 K. The samples were then placed in vanadium sample

holders and loaded into a vacuum furnace, as shown in Figure 17. The samples were heated to different temperatures and kept at each temperature for 1 - 1.5 hours. The neutron scattering data were collected during the whole process so that the live phase transition could be observed directly. For the *ex*-situ experiment, three batches of Mg₂Si_{1-x}Sn_x (x = 0.3, 0.4, 0.5, 0.6 and 0.7) samples were synthesized and PECS-processed at 673 K – 923 K. Each batch of samples was vacuum sealed in quartz tubes and annealed at 723 K, 823 K and 973 K for two days, respectively. After annealing, the quartz tubes were taken from the furnace and immediately quenched in water, so the equilibrium phases at different annealing temperatures were attained for each sample. The samples were then loaded to the apparatus as shown in Figure 17 for neutron scattering experiment at room temperature.

The *in*-situ data are shown in Figure 18 – 22. For x = 0.3, 0.4, 0.6 and 0.7, the major peaks in the materials are solid solution phases (Fm-3m) of different compositions, which is in agreement with the phase diagram. Small amount of MgO phase could be found in all the samples, which is an impurity that could not be eliminated during the synthesis of the Mg₂Si₁. _xSn_x materials [32-36]. For some of the single-phase compound, there is a "shoulder" next to the major solid solution phase. The shoulder phase is the solid solution phase with slight change in the composition, possibly caused by gravity during the PECS process [37, 38]. As temperature increases, the peak positions of each solid solution phase shift right, due to the increased lattice constant caused by thermal expansion. For the x = 0.5 compound (Mg₂Si_{0.5}Sn_{0.5}), the Rietveld fitting results show that the composition of the major solid solution phase is close to Mg₂Si_{0.3}Sn_{0.7}. The MgO impurity phase was found in the compound as well. Besides, Mg (P6₃/mmc) and Mg_{0.98}Si_{0.02} (P6₃/mmc) were found to be the cause of the impurity peaks located at *d*-spacing = 2.74 Å and 2.81 Å, respectively. The creation of the Mg_{0.98}Si_{0.02} is likely due to the phase separation of $Mg_2Si_{0.5}Sn_{0.5}$. As temperature increases, the intensities of the Mg and $Mg_{0.98}Si_{0.02}$ impurity peaks do not change significantly, indicating that the sample is close to an equilibrium state. This result confirms that $Mg_2Si_{0.5}Sn_{0.5}$ is not a single solid solution phase. However, due to the limitations of the profile fitting programs, a perfect fitting could not be achieved for the profile of $Mg_2Si_{0.5}Sn_{0.5}$. The accurate boundaries of the miscibility gap boundaries have not been determined yet.



Figure 18 The *in*-situ neutron scattering pattern for Mg₂Si_{0.3}Sn_{0.7}.



Figure 19 The *in*-situ neutron scattering pattern for Mg₂Si_{0.4}Sn_{0.6}.



Figure 20 The *in*-situ neutron scattering pattern for Mg₂Si_{0.5}Sn_{0.5}.



Figure 21 The *in*-situ neutron scattering pattern for Mg₂Si_{0.6}Sn_{0.4}.



Figure 22 The *in*-situ neutron scattering pattern for Mg₂Si_{0.7}Sn_{0.3}.

The *ex*-situ data are shown in Figure 23 – 27. When the annealing temperature of 675 K or 775 K was used, only one major solid solution phase was found in Mg₂Si_{1-x}Sn_x for x = 0.3, 0.4, 0.6 and 0.7, similar to the results in the *in*-situ experiments. For x = 0.5, however, multiple impurity phases are found in the compound, which is possibly due to phase separation. Besides, the Mg (P6₃/mmc) and Mg_{0.98}Si_{0.02} (P6₃/mmc) phases found in the *in*-situ experiments, a Si (Fd-3mS) phase was also found in the sample. For those samples annealed at 975 K, except for

 $Mg_2Si_{0.3}Sn_{0.7}$, all other samples showed a second solid solution phase in the neutron scattering pattern, which had a lattice constant close to 6.7 Å (corresponding to the $Mg_2Si_{0.15}Sn_{0.85}$ composition).



Figure 23 The *ex*-situ neutron scattering pattern for Mg₂Si_{0.3}Sn_{0.7}.



Figure 24 The *ex*-situ neutron scattering pattern for Mg₂Si_{0.4}Sn_{0.6}.



Figure 25 The *ex*-situ neutron scattering pattern for Mg₂Si_{0.5}Sn_{0.5}.



Figure 26 The *ex*-situ neutron scattering pattern for Mg₂Si_{0.6}Sn_{0.4}.



Figure 27 The *ex*-situ neutron scattering pattern for Mg₂Si_{0.7}Sn_{0.3}.

Comparing the *in*-situ and *ex*-situ results, it could be concluded that for $Mg_2Si_{0.4}Sn_{0.6}$, $Mg_2Si_{0.6}Sn_{0.4}$, $Mg_2Si_{0.7}Sn_{0.3}$, the equilibrium state is the single phase solid solution below 775 K while a Sn-rich phase is generated at 975 K. For the $Mg_2Si_{0.3}Sn_{0.7}$ sample, single solid solution phase is the equilibrium state up to 975 K. For the $Mg_2Si_{0.5}Sn_{0.5}$ sample, the equilibrium state contains a solid solution phase plus a P6₃/mmc-structured $Mg_{0.98}Si_{0.02}$ phase and an Fd-3mS-structured Si phase.

Thus, to avoid phase separation in the operation of thermoelectric devices, the x = 0.5 composition should be avoided. The x = 0.3, 0.4 and 0.6 compositions should be long-term safe for application below 775 K and the x = 0.7 composition could be used up to 975 K.

3.3 Intrinsic Properties of Mg₂Si_{0.4}Sn_{0.6}

As mentioned in Chapter 1, forming a solid solution is an effective way to reduce the lattice thermal conductivity of materials. The lattice thermal conductivity for the whole range $Mg_2Si_{1-x}Sn_x$ materials have been studied [38-40]. The lowest lattice thermal conductivities were found for the x \approx 0.6 compound.

For the Mg₂Si_{1-x}Sn_x materials, the band structure can also be engineered by adjusting the compositions of the solid solution. The band structure engineering in the Mg₂Si_{1-x}Sn_x materials was first studied by Zastaiv [39] and further investigated by Liu [40]. It has been found that there is a heavy conduction band and a light conduction band for Mg₂Si_{1-x}Sn_x. The two bands converge when $x = 0.6 \sim 0.7$. As a result, the density of states effective mass is increased and the Seebeck coefficient is increased. The mobility effective mass is not changed significantly, so the overall power factor could be increased to get a high *ZT*. For the valence bands, the band degeneracy is not sensitive to the change in the solid solution composition [30].

Based on the thermal phase stability study and the literature review on the intrinsic properties of the $Mg_2Si_{1-x}Sn_x$ materials, $Mg_2Si_{0.4}Sn_{0.6}$ was chosen as the base compound for further improvement in this dissertation. Some mechanical properties of the intrinsic $Mg_2Si_{0.4}Sn_{0.6}$ material were measured and listed in Table 1 [28].

Coefficient of thermal expansion	Debye temperature	Young's Modulus	Shear Modulus	Bulk modulus
$2.0 \times 10^{-5} \mathrm{K}^{-1}$	394 K	88.07 GPa	36.63 GPa	49.28 GPa

Table 1 Room temperature mechanical properties of the intrinsic $Mg_2Si_{0.4}Sn_{0.6}$.

Chapter 4 Optimization of the *n*-type Mg₂Si_{0.4}Sn_{0.6} Materials

The intrinsically low lattice thermal conductivity of $Mg_2Si_{0.4}Sn_{0.6}$ makes it a promising candidate for thermoelectric power generation application in mid-temperature range from 400 K to 800 K. Intrinsic $Mg_2Si_{0.4}Sn_{0.6}$ is an *n*-type semiconductor with a band gap of 0.54 eV (0 K) [30], however, the *ZT* of the intrinsic $Mg_2Si_{0.4}Sn_{0.6}$ is below 0.3 due to the low electrical conductivity. The low electrical conductivity is mainly caused by the low carrier, so the *ZT* could be potentially increased if the carrier concentration is adjusted to an optimal level. Doping is the most common method used in adjusting carrier concentration. For *n*-type materials, dopants are usually chosen to fill in the Si/Sn sites [41]. Thus the dopant elements should have one or more valence electrons relative to Si/Sn so the extra electron(s) will become unbounded and contribute to charge transport. The dopant elements should also have compatible sizes with the Mg/Si/Sn atoms to minimize distortion of the crystal lattice. Such distortion of the lattice can increase the scattering of charge carriers and thus reduce the carrier mobility and the electrical conductivity. In this work, Sb and Bi were used as dopants to adjust the carrier concentrations of $Mg_2Si_{0.4}Sn_{0.6}$.

4.1 Sb-doped Mg₂Si_{0.4}Sn_{0.6}

Samples with nominal compositions of $Mg_{2.08}Si_{0.4-x}Sn_{0.6}Sb_x$ (x = 0, 0.012, 0.024, 0.036, 0.048, 0.060 and 0.072) were synthesized and prepared as described in Chapter 2. The excess Mg was used to compensate for the loss of the Mg during synthesis and PECS processing.

The powder XRD patterns of the samples are shown in Figure 28. As mentioned in the neutron scattering phase study, all $Mg_{2.08}Si_{0.4-x}Sn_{0.6}Sb_x$ samples formed single phase solid solutions, despite the change in the Sb content in the samples. For some samples a small amount of MgO impurity phase was also detected.



Figure 28 The powder XRD patterns for Mg_{2.08}Si_{0.4-x}Sn_{0.6}Sb_x.

The temperature dependent transport properties of the $Mg_{2.08}Si_{0.4-x}Sn_{0.6}Sb_x$ samples are shown in Figure 29 – 33. Generally the Sb-doping effectively changed the transport properties of the $Mg_{2.08}Si_{0.4-x}Sn_{0.6}Sb_x$ materials.

The Seebeck coefficients of the Mg_{2.08}Si_{0.4-x}Sn_{0.6}Sb_x samples are shown in Figure 29. All the Sb-doped samples show negative Seebeck coefficients, indicating the *n*-type semiconducting behavior. As the Sb content increases in the sample, the absolute Seebeck coefficient value decreases. This is caused by the increased the carrier concentration (Figure 30) introduced by the Sb dopants and this trend has been shown and discussed in Figure 8. For all the samples, the absolute values of the Seebeck coefficients increase up to a certain temperature and decrease afterwards. This rollover is known to be caused by the bipolar effect [42]. $Mg_{2.08}Si_{0.4}Sn_{0.6}$ is a narrow band gap semiconductor (0.54 eV at 0 K) and the activation of intrinsic carriers across the band gap could be easily achieved at elevated temperatures. This activation process produces an equal number of intrinsic holes and electrons in the material. According to Equation 37, the overall Seebeck effect should be the weighted sum of the contribution from both the holes and electrons. As holes have opposite Seebeck coefficients to electrons, when the intrinsic holes concentration become comparable to the overall electron concentrations (extrinsic plus intrinsic electrons), the absolute value of the overall Seebeck coefficient decreases. Generally the rollover temperature increases as the Sb content increases in the material. In a more heavily Sb-doped sample, the extrinsic electron concentration is higher, so more intrinsic holes are needed to make the bipolar effect significant and this could only happen at higher temperatures.



Figure 29 The temperature dependent Seebeck coefficients for Mg_{2.08}Si_{0.4-x}Sn_{0.6}Sb_x.



Figure 30 The temperature dependent carrier concentrations for Mg_{2.08}Si_{0.4-x}Sn_{0.6}Sb_x.

The temperature dependent electrical conductivities of the $Mg_{2.08}Si_{0.4-x}Sn_{0.6}Sb_x$ samples are shown in Figure 31. As the Sb content increases, the electrical conductivity increases appreciably. As shown in Figure 32, the carrier mobilities of the samples were not significantly affected by the Sb-doping, so the increased electrical conductivity should be attributed to the increase in the carrier concentration. For the doped samples, all of which are extrinsic semiconductors, the electrical conductivities generally decrease as the temperature increases, mainly due to the decreased carrier mobilities caused by enhanced phonon scattering at elevated temperatures.



Figure 31 The temperature dependent electrical conductivities for Mg_{2.08}Si_{0.4-x}Sn_{0.6}Sb_x.

The temperature dependence of the Hall mobility generally follows the equation below.

$$\mu \propto T^j \tag{53}$$

where *j* is determined by the scattering mechanism. (-0.5 for alloy scattering and -1.5 for acoustic phonon scattering) As shown in Figure 32, most of the mobility data points fall in the range between -1.5 and -0.5, indicating mixed scattering mechanism. An empirical equation was used to evaluate the contributions from both scattering mechanisms [43].

$$\frac{1}{\mu} = \frac{1}{\mu_{\text{alloy}}} \left(\frac{T}{300 \text{ K}}\right)^{0.5} + \frac{1}{\mu_{\text{phonon}}} \left(\frac{T}{300 \text{ K}}\right)^{1.5}$$
(54)

where μ_{alloy} and μ_{phonon} are fitting parameters related to alloy scattering and phonon scattering, respectively. A high value indicates weak scattering to electrons and a low value means strong scattering to electrons. The values of μ_{alloy} and μ_{phonon} were determined by least-square fitting of the data and the fitting results are shown in Table 2. The value of μ_{alloy} for the undoped sample is extremely high compared with other samples. As discussed by Liu [44], Mg₂Si_{0.4}Sn_{0.6} compound has a low alloy scattering potential (~ 0.7 eV) which helps explain the weak alloyelectron scattering in the undoped sample. The alloy-electron scattering increases upon Sbdoping as indicated by μ_{alloy} significantly increasing in the doped samples. Meanwhile, the values of μ_{phonon} do not change as much as μ_{alloy} do between the undoped and doped samples. It is therefore concluded that increasing the Sb content enhances the alloy-electron scattering while the effect on the phonon-electron scattering is more subtle.



Figure 32 The temperature dependent Hall mobilities for Mg_{2.08}Si_{0.4-x}Sn_{0.6}Sb_x.

	x = 0.000	x = 0.012	x = 0.024	x = 0.036
$\mu_{\rm alloy}({\rm cm}^2/{\rm V}\cdot{\rm s})$	1750.55	65.16	68.37	52.52
$\mu_{\rm phonon} ({\rm cm}^2/{\rm V}\cdot{\rm s})$	62.51	171.88	26.08	206.59

Table 2 Empirical fitting results for the Hall mobility.

The SEM-EDX compositional analysis results for two batches of the $Mg_2Si_{0.4-x}Sn_x$ samples are shown in Table 3. The compositions were normalized so that the relative concentration of Si, Sn and Sb added up to unity, so if the relative concentration of Mg is less than two it would suggest Mg-deficiency in the sample. The nominal Mg compositions for all samples are below the nominal values, despite the fact that excess Mg (4%) was added during the synthesis of the samples. All the samples are Mg-deficient based on the SEM-EDX compositional analysis.

1st batch	x = 0.000	x = 0.012		x = 0.024		x = 0.036	
Mg	1.86	1.84		1.66		1.80	
Si	0.37	0.38		0.38		0.33	
Sn	0.63	0.58		0.	58	0.62	
Sb	0	0.038		0.040		0.053	
2nd batch	x = 0.000	x = 0.012	x = 0.024	x = 0.036	x = 0.048	x = 0.060	x = 0.072
Mg	1.74	1.78	1.61	1.76	1.71	1.82	1.81
Si	0.37	0.36	0.30	0.30	0.31	0.26	0.31
Sn	0.63	0.64	0.67	0.66	0.65	0.69	0.60
Sb	0	0	0.041	0.044	0.047	0.058	0.085

Table 3 SEM-EDX compositional analysis results of the Mg_{2.08}Si_{0.4-x}Sn_{0.6}Sb_x sample.

It is highly likely that Mg vacancies exist if the sample is Mg-deficient. As discussed by Nolas [45], Dasgupta [46] and Jiang [47], vacancies in materials act as point defects and they could potentially scatter electrons, this could be the reason for the enhanced alloy-electron scattering in the doped samples (Table 2). Mg vacancies also act as electron acceptors in the material, with the formation of each vacancy creating two holes [48]. Thus, more donors (Sb) would be needed to get the same number of electrons in a sample containing Mg vacancies than in a sample without Mg vacancies. Table 4 listed the carrier concentrations (n) and the

corresponding compositions from literature reports on the Sb-doped $Mg_2(Si,Sn)$ compounds. In this work, much more Sb is needed to obtain a comparable carrier concentration levels compared with similar work. This is also consistent with higher Mg vacancies existing in our samples.

	ZT	n / cm^{-3}	Composition
This work	1.51	2.35×10 ²⁰	$Mg_{2.08}Si_{0.364}Sn_{0.6}Sb_{0.036}$
Zaitsev [39]	1.0	2.99×10 ²⁰	$Mg_2Si_{0.4}Sn_{0.6}$ with Sb doping
Liu [32]	1.25	1.92×10 ²⁰	$Mg_{2.11}Si_{0.52}Sn_{0.48}Sb_{0.0056}$
Gao [26]	0.9	2.6×10 ²⁰	$Mg_{2+z}Si_{0.487}Sn_{0.5}Sb_{0.013}^{*}$
Søndergaard [38]	1.0	1.6×10 ²⁰	$Mg_{2.2}Si_{0.5925}Sn_{0.4}Sb_{0.0075}$

Table 4 Nominal Sb content from different literatures on Sb-doped Mg₂(Si,Sn).

* The exact composition (z value) was not specified in Gao's original paper.

The total thermal conductivities of the $Mg_{2.08}Si_{0.4-x}Sn_{0.6}Sb_x$ samples are shown in Figure 33. The lattice and electronic thermal conductivities were calculated based on a single parabolic band model using Equation (31, 32, 36 and 38 - 40) and plotted in Figure 34. Generally the total thermal conductivity of the material increases as the Sb doping concentration increases in the material. This can be attributed to the increase in the electrical conductivity, which caused increase in the electronic thermal conductivity.



Figure 33 The temperature dependent thermal conductivities for Mg_{2.08}Si_{0.4-x}Sn_{0.6}Sb_x.



Figure 34 The lattice and electronic thermal conductivities for Mg_{2.08}Si_{0.4-x}Sn_{0.6}Sb_x.

A peak $ZT \approx 1.50$ was obtained at 716 K for Mg_{2.08}Si_{0.364}Sn_{0.6}Sb_{0.036}. This is a combining effect of a high power factor (optimal values for *S* and σ) and reduced lattice thermal conductivity (the x = 0.036 sample has the lowest lattice thermal conductivity).

The Sb-doped samples showed promising thermoelectric properties and they could be potentially used as the *n*-type leg for a thermoelectric module. However, the origin of the high degree of Mg deficiency in the Sb-doped materials is still not clear. Liu has shown that the thermoelectric properties of the Mg₂(Si,Sn) compounds are sensitive to the Mg content in the materials [32]. Without a comprehensive solution to precisely control the Mg deficiency, the repeatability of the sample synthesis could be a problem. Whether the Mg deficiency could create defects that are unstable in long term application also needs to be investigated in the future.



Figure 35 The ZT for $Mg_{2.08}Si_{0.4-x}Sn_{0.6}Sb_x$.

4.2 Bi-doped Mg₂Si_{0.4}Sn_{0.6}

As mentioned in Chapter 1, the *ZT* defined in Equation 28 needs to be carefully evaluated because all the material parameters are temperature dependent. An approximation to evaluate Equation 28 in the working temperature range is to evaluate the average value of Equation 29 in the desired working temperature range. So a material that has a wide temperature range of peak *ZT* or tunable high *ZT* in a wide range of temperatures is desirable for practical thermoelectric application. It has been reported that Bi-doping could tune the peak *ZT* (> 1) of the n-type Mg₂Si_{0.5}Sn_{0.5} material to a lower temperature [49]. Thus, Bi-doped was applied to our Mg₂Si_{0.4}Sn_{0.6} samples, to better understand its influence on the peak *ZT* in our samples.

Samples with nominal compositions of $Mg_{2.08}Si_{0.4-x}Sn_{0.6}Bi_x$ (x = 0, 0.005, 0.010, 0.015, 0.020 and 0.030) were synthesized and prepared as described in Chapter 2. Excess Mg was added to compensate for the loss of the Mg during the synthesis and PECS processing.

The powder XRD patterns for the $Mg_{2.08}Si_{0.4-x}Sn_{0.6}Bi_x$ samples are shown in Figure 36. Similar to the Sb-doped samples, the major phase in these samples is the target solid solution.



Figure 36 The powder XRD patterns for $Mg_{2.08}Si_{0.4-x}Sn_{0.6}Bi_x$.

The temperature dependent Seebeck coefficients and electrical conductivities are shown in Figure 37 and 38. Similar to the Sb-doped samples, all the Bi-doped samples showed negative Seebeck coefficients, indicating *n*-type behavior for the doped samples. The electrical conductivity increases while the Seebeck coefficient decreases as the Bi-doping concentration increases. This is because more Bi atoms introduced more electrons to the sample, as seen in the carrier concentration for the samples (Figure 39).



Figure 37 The Seebeck coefficients for $Mg_{2.08}Si_{0.4-x}Sn_{0.6}Bi_x$.



Figure 38 The electrical conductivities for Mg_{2.08}Si_{0.4-x}Sn_{0.6}Bi_x.


Figure 39 The carrier concentrations for Mg_{2.08}Si_{0.4-x}Sn_{0.6}Bi_x.

The total thermal conductivity of the $Mg_{2.08}Si_{0.4-x}Sn_{0.6}Bi_x$ samples are shown in Figure 40. Generally the total thermal conductivity increases as the Bi content increases, which should be attributed to the increased electronic thermal conductivity.

For the Bi-doped samples, a more detailed analysis was performed to accurately evaluate the lattice thermal conductivity. The bipolar contribution to the total thermal conductivity as well as the electronic thermal conductivity was calculated. In this case, Equation 37 becomes:

$$S = \frac{\mu_{\rm n} n S_{\rm n} + \mu_{\rm p} p S_{\rm p}}{\mu_{\rm n} n + \mu_{\rm n} p} \tag{55}$$

where S_n (S_p), n (p) and μ_n (μ_p) are the Seebeck coefficients, carrier concentration and mobility



Figure 40 The total thermal conductivities for Mg_{2.08}Si_{0.4-x}Sn_{0.6}Bi_x.

for electrons (holes). The reduced chemical potential for electrons (η) and holes (η_p) are determined by an iterative method using the experimental Seebeck coefficient data.

$$S_{\rm n} = -\frac{k_{\rm B}}{q} \left[\frac{(\lambda + 5/2)F_{\lambda + 3/2}(\eta)}{(\lambda + 3/2)F_{\lambda + 1/2}(\eta)} - \eta \right]$$
(56)

$$S_{\rm p} = \frac{k_{\rm B}}{q} \left(\frac{5}{2} + \lambda - \eta_{\rm p}\right) \tag{57}$$

$$\eta + \eta_{\rm p} = -\frac{E_{\rm g}}{k_{\rm B}T} \tag{58}$$

Then the carrier concentrations were estimated by

$$n = \frac{1}{2\pi^2} \left(\frac{2m_{\rm n}^* k_{\rm B}T}{\hbar^2}\right)^{3/2} F_{1/2}(\eta)$$
⁽⁵⁹⁾

$$p = \frac{1}{2\pi^2} \left(\frac{2m_{\rm p}^* k_{\rm B} T}{\hbar^2} \right)^{3/2} e^{\eta}$$
(60)

where the effective mass for electrons (m_n^*) and holes (m_p^*) were taken from literature values [30, 50]. The mobilities for the two types of carriers were measured experimentally as shown in Figure 41, where the *p*-type sample Mg_{2.005}Si_{0.4}Sn_{0.6}Ag_{0.075} was synthesized and processed in the same methods as the *n*-type samples. The electronic thermal conductivity was calculated using Equation 39 and the bipolar thermal conductivity was calculated as

$$\kappa_{\rm bi} = \frac{\mu_{\rm n} n \times \mu_{\rm p} p}{\mu_{\rm n} n + \mu_{\rm p} p} \left(S_{\rm n} - S_{\rm p} \right)^2 T \tag{61}$$



Figure 41 High temperature Hall mobilities for the *n*-type $Mg_{2.08}Si_{0.4-x}Sn_{0.6}Bi_x$ and *p*-type $Mg_{2.005}Si_{0.4}Sn_{0.6}Ag_{0.075}$ sample.

Using these results, the lattice thermal conductivity could be estimated using Equation 38. The estimated electronic thermal conductivity and bipolar thermal conductivity are shown in Figure 42 and the lattice thermal conductivity is shown in Figure 43.



Figure 42 The electronic and bipolar thermal conductivities for Mg_{2.08}Si_{0.4-x}Sn_{0.6}Bi_x.



Figure 43 The lattice thermal conductivities for Mg_{2.08}Si_{0.4-x}Sn_{0.6}Bi_x.

The reliability of the above calculation was verified by calculating the pure lattice thermal conductivity of the undoped samples using the Slack's formula and the mechanical property data [51].

$$\kappa_{\rm l} = A \frac{\overline{M} \theta^3 V^{1/3}}{\gamma^2 n_{\rm V}^{2/3} T} \tag{62}$$

$$\gamma = \frac{3\beta B V_{\rm m}}{C_{\rm V}} \tag{63}$$

where *A* is a collection of physical constants and a value of $A = 3.1 \times 10^{-7} \text{ s}^{-3} \text{ K}^{-3}$ was used in our calculation [51-53], \overline{M} is the average mass of the atoms in the crystal, *V* is the average volume occupied by an atom, n_V is the number of atoms per primitive cell, $\beta = 6.0 \times 10^{-6} \text{ K}^{-1}$ is the volume thermal expansion coefficient, *B* is the bulk modulus, V_m is the molar volume and C_V ($\approx C_P$) is the isochoric specific heat per mole. The Debye temperature θ (394 K) and the Grüneisen parameter γ (1.73) were calculated based on the mechanical properties shown in Chapter 3. The κ_1 calculated by Equation 62 is displayed by the solid line in Figure 43 and shows good agreement with the result derived from Equation 56-61.

In Figure 43, the lattice thermal conductivity decreases as the Bi content increases. The reduction is close to 13% in the most heavily doped sample $Mg_{2.08}Si_{0.37}Sn_{0.6}Bi_{0.03}$. An empirical formula has been proposed by Ioffe [54-56] to explain the influence of impurities on the intrinsic lattice thermal conductivity for various semiconductor materials

$$\frac{\kappa_0}{\kappa_l} = 1 + \chi \frac{N_D \, l_0}{N_0 \, a} \tag{64}$$

where κ_0 is the lattice thermal conductivity for the pristine crystal and κ_1 is that for the doped crystal. $N_{\rm D}$ is the impurity concentration, N_0 is the number of atoms per unit volume, l_0 is the mean free path of phonons in the materials, a is the lattice constant and χ is a parameter determined by the effective scattering area of the impurity atoms. Interstitial impurities have in χ > 1 and substitutional impurities have χ < 1. The temperature dependent lattice thermal conductivity of the Mg_{2.08}Si_{0.4-x}Sn_{0.6}Bi_x samples were fit to Equation 64 to find the parameter χ , as shown in Figure 44. There are no reported values for l_0 in Mg₂Si_{0.4}Sn_{0.6} at this moment, but a range of 10 ~ 100 Å for l_0 in Mg₂Si has been reported [57]. If l_0 of 10 ~ 100 Å was used, the calculated χ was in the range of 2.0 ~ 51. The lattice thermal conductivities of Mg₂Si_{0.4}Sn_{0.6} are much lower than that of Mg₂Si due to the formation of a solid solution [39], so a smaller l_0 should be expected in Mg₂Si_{0.4}Sn_{0.6}. Thus, the real values of χ should be close to the high end of the range $2.0 \sim 51$, which is expected to be much greater than 1. This indicates that there is at least a portion of the Bi atoms occupy interstitial sites in the Mg₂Si_{0.4}Sn_{0.6} matrix. The only possible interstitial site in the Mg₂(Si,Sn) matrix is the 4b site, which is the center of the octahedron formed by Si/Sn in the FCC frame. Assuming that the lattice constant for Mg₂Si_{0.4}Sn_{0.6} is 6.60 Å [30], the atomic radius for Mg, Si, Sn and Bi is 1.36, 1.17, 1.40 and 1.52 Å, respectively [9], the maximal radius of the 4b interstitial site is calculated to be about 2.00 Å. This indicates that it is possible for Bi atoms to enter the 4b interstitial site. Such interstitial Bi atoms would act as strong phonon scattering centers and reduce the lattice thermal conductivities.

The empirical nature of Equation 64 requires further study to confirm the existence of the interstitial Bi atoms. It has been reported that the fitting parameter χ is 7 for Te and 3 for Se in the GaSb lattice; for isovalent impurities such as Si in Ge lattice, Sn in Si lattice and Se in PbTe

lattice, the value of χ were close to unity [56]. As Bi is not an isovalent impurity compared with Si or Sn, so the behavior of Bi in Mg₂Si_{0.4}Sn_{0.6} might be closer to the case of Te/Se in GaSb. One possible explanation for origin of the off-site Bi atoms might be the solubility limit of Bi in the Mg₂Si_{0.4}Sn_{0.6} materials [58].



Figure 44 The lattice thermal conductivities for Mg_{2.08}Si_{0.4-x}Sn_{0.6}Bi_x.

While the lattice thermal conductivity is reduced, the Bi doping increases the power factors of the sample significantly compared with the undoped sample (Figure 45). Because the scattering effect of Bi, the mobilities and the power factor of the Bi-doped samples are slightly lower than those of the Sb-doped samples. Overall, due to the reduction in the lattice thermal conductivity, all Bi-doped samples showed peak ZT > 1 and increasing with increasing Bi content. A maximum $ZT \sim 1.55$ was obtained at 773 K for x = 0.030 (Figure 46). Based on the current results it is likely that the peak ZT could be pushed to a higher value for x > 0.030.

However, the *ZT*s of our Bi-doped samples still peak above 650 K and the low temperature (below 500 K) *ZT* is not significantly increased compared with the Sb-doped sample. The reason might be the different Si : Sn ratio used in our samples compared with that used in Zhang's work. They also used a spin melting synthesis method and nano-structures were found in their samples. Nano structures could affect the thermoelectric properties of the sample but no nano-structuring was found in our sample.



Figure 45 The power factor for Mg_{2.08}Si_{0.4-x}Sn_{0.6}Bi_x.



Figure 46 The dimensionless figure of merit (ZT) for Mg_{2.08}Si_{0.4-x}Sn_{0.6}Bi_x.

As mentioned previously, one drawback of the Sb-doped samples is the uncontrollable high Mg deficiency level and the possible defects that may result from it. Table 5 shows the EDX compositional analysis results for the $Mg_{2.08}Si_{0.4-x}Sn_{0.6}Bi_x$ samples where all the measured compositions are in close agreement with the nominal compositions. No systematic Mg deficiency could be seen other than the uncertainty of the EDX instrument.

	x = 0.005	x = 0.010	x = 0.015	x = 0.020	x = 0.030
Mg	1.95	1.98	2.05	1.94	2.04
Si	0.32	0.32	0.35	0.34	0.39
Sn	0.67	0.67	0.64	0.65	0.60
Bi	0.0048	0.0098	0.013	0.015	0.017

Table 5 SEM-EDX compositional analysis results of the Mg_{2.08}Si_{0.4-x}Sn_{0.6}Bi_x samples.

4.3 Summary of the Chapter

The *n*-type Mg₂Si_{0.4}Sn_{0.6} materials were synthesized and doped with Sb and Bi. Both dopants were found to be effective in improving the thermoelectric performance of the materials. Peak ZT > 1.50 were obtained in both the Sb-doped and Bi-doped samples. The Sb-doping seemed to cause Mg deficiency in the materials while Bi-doping did not have such a problem. In addition to improving the power factor, Bi impurity could potentially enter the interstitial site of the Mg₂Si_{0.4}Sn_{0.6} lattice, act as phonon scattering center and reduce the lattice thermal conductivity.

Chapter 5 Optimization of the *p*-type Mg₂Si_{0.4}Sn_{0.6} Materials

As shown in Equation 28, the conversion efficiency of a thermoelectric generator depends on the properties of both the *n*-type and the *p*-type materials. In Chapter 4 it has been shown that the peak *ZT* of the *n*-type Mg₂Si_{0.4}Sn_{0.6} could be improved to ~ 1.5. The *p*-type material should have comparable Seebeck coefficient, electrical conductivity and thermal conductivity to the *n*type material. For practical concern, the coefficient of thermal expansion (CTE) of the *p*-type materials should also be close to the *n*-type materials. There are *p*-type materials with *ZT* > 1 available such as PbTe [21, 22] or tetrahedrite [59, 60]. However, PbTe exhibits a relatively low fracture toughness [61], and the power factor of tetrahedrite is much lower than *n*-type Mg₂Si_{0.4}Sn_{0.6}, thus *p*-type Mg₂Si_{0.4}Sn_{0.6} was investigated. The adjustments of the electronic and thermal transport properties for *p*-type Mg₂Si_{0.4}Sn_{0.6} are discussed in this chapter.

5.1 Dopant and Doping Agent for *p*-type Mg₂Si_{0.4}Sn_{0.6}

The choice of dopant is critical to the performance of the *p*-type Mg₂Si_{0.4}Sn_{0.6} as it has been shown that the hole mobility strongly depends on the dopant element [62-64]. Silver (Ag) has been the most commonly used p-type dopant for Mg₂(Si,Sn) materials. However, as shown in Figure 41, the hole mobility of the Ag-doped Mg₂Si_{0.4}Sn_{0.6} sample is only 1/3 - 1/2 of the electron mobilities in the *n*-type samples. Lithium (Li) is a recently discovered effective *p*-type dopant for the Mg₂(Si,Sn) materials that could create high mobility holes in the material. A peak $ZT \sim 0.5$ has been reported [65] for the Li-doped material which makes it worth investigating further improvement of the material. The handling of the Li metal involves complicated procedures that require some specially designed equipment. For example, a glovebox that could contain liquid (for commercial Li metal that is stored in oil) and razor safe (commercial Li metal is only available in chunks) is needed. An alternative would be to use some stable lithium compound to deliver Li to the Mg₂Si_{0.4}Sn_{0.6} matrix, where the compound acts as a doping agent. It has been shown that sodium acetate could be used as a doping agent to dope Mg₂(Si,Sn) with sodium (Na). Inspired by this, lithium acetate (LiCH₃COOH), lithium carbonate (Li₂CO₃) and lithium oxide (Li₂O) were chosen as possible Li doping agent candidates. First Li₂O was ruled out because of its high reactivity with moisture. Then Li₂CO₃ was chosen over LiCH₃COOH because Li₂CO₃ had a higher Li content and a lower price. The possible decomposition of Li₂CO₃ could generate CO₂ gas. This could cause pressure built-up problem if the material is synthesized using sealed quartz tube. However, the B₂O₃ encapsulation method used in this work does not have this problem as the B₂O₃ layer could deform or move to balance the pressure.

5.2 The *p*-type Mg₂Li_xSi_{0.4}Sn_{0.6} Synthesized Using Li₂CO₃ as the Doping Agent

Elemental powders of Mg, Si and Sn were mixed stoichiometrically, as described in Chapter 2. Different amounts of Li₂CO₃ powders (Jade Scientific, 99.0%) were added to the Mg₂Si_{0.4}Sn_{0.6} mixture for a nominal composition of Mg₂Li_xSi_{0.4}Sn_{0.6} where $0 \le x \le 0.100$. No excess Mg was used here because excess Mg could fill the interstitial site (4b site) and act as donors [48, 66], which contradict our efforts to make a *p*-type material. The synthesis and processing of the samples were the same as described in Chapter 2.

The powder XRD patterns of the $Mg_{2-x}Li_xSi_{0.4}Sn_{0.6}$ are shown in Figure 47. Similar to the *n*-type samples, the major phase is the single phase solid solution between pure Mg_2Si (#65-

2988) and Mg₂Sn (#07-0274) [67, 68]. There is no appreciable lattice constant shift as the doping level increased. This could be explained by the similar ionic radii of Mg^{2+} and Li^+ ions [65, 69, 70].



Figure 47 Powder XRD patterns of $Mg_2Li_xSi_{0.4}Sn_{0.6}$ with different Li contents (MgO peaks are denoted by Δ).

Besides the major phase, there is also a minor MgO impurity phase in all the samples. Figure 47 also shows that the intensity of the MgO impurity peak increases as the lithium content increases. The volume fraction of MgO was estimated using a Relative Intensity Ratio (RIR) method. The RIR values of MgO (3.03) and Mg₂Si_{0.4}Sn_{0.6} (7.08) were taken from literature values [31, 71]. The estimated MgO volume fractions are shown in Figure 48. The undoped sample has the lowest MgO amount, below 1 vol%, indicating the high effectiveness of the B₂O₃ encapsulation layer in protecting samples from atmospheric oxygen. The MgO impurity concentration monotonically increases as the lithium concentration in the sample increases. All the samples were prepared under the same conditions so the surface oxidation (which could occur during PECS) was expected to be on the same level. We thus attribute the increased MgO level to be most likely caused by the Li₂CO₃ in the reactant as the amount of Li₂CO₃ is the only parameter that was different among all the samples.



Figure 48 The actual Li content and MgO volume fraction in the Mg₂Li_xSi_{0.4}Sn_{0.6} samples.

The MgO phase could also be found in the SEM images. Figure 49 includes the SEM image and EDX elemental mapping for the undoped sample. All the elements are uniformly distributed in the undoped sample. Figure 50 was taken from a doped sample and the EDX-mappings show clear oxygen-concentrated areas, which overlap with the magnesium-concentrated areas. Such oxygen-magnesium concentrated areas were interpreted as the MgO impurity phase and the size of the MgO particle was on micron level. No aggregation or larger particle of the MgO phase was observed.

Due to the limitation of EDX, the actual Li composition in each sample was determined by the ICP-OES technique and shown in Figure 48. All the samples the have Li compositions that are lower than the nominal compositions. This might be caused by the evaporation or diffusion of the lithium ion. The actual compositions show good linear correlation to the nominal compositions, indicating that the doping efficiency of Li_2CO_3 is consistent. The nominal compositions will be used in the remainder of the dissertation.



Figure 49 The SEM image and EDX mappings of the undoped sample.



Figure 50 The SEM image and EDX mappings of the doped sample.

The Seebeck coefficients of the $Mg_2Li_xSi_{0.4}Sn_{0.6}$ samples are shown in Figure 51. The undoped sample has negative Seebeck coefficient, similar to the results in Chapter 2 although no excess Mg was used during the synthesis. All the doped samples have positive Seebeck coefficients, indicating that Li_2CO_3 is an effective *p*-type doping agent. The doped samples have lower absolute Seebeck coefficients than the undoped samples due to the increased hole concentration (Figure 52). The Seebeck coefficients of the doped samples increase with increasing temperature until a certain temperature at which intrinsic carrier activation becomes significant and the bipolar transition occurs.



Figure 51 The Seebeck coefficients for Mg₂Li_xSi_{0.4}Sn_{0.6} samples.

The temperature dependent Hall measurement results are shown in Figure 52 and 53. The hole concentrations increase from ~ 8×10^{19} cm⁻³ to ~ 1.4×10^{20} cm⁻³ as the doping concentration increases from x = 0.025 to x = 0.100. Weak dependence of the hole concentration on temperature is observed, which is typical of heavily doped semiconductors. At ~ 70 K, the least doped sample has the highest mobility of ~ $55 \text{ cm}^2/(\text{V} \cdot \text{s})$ and the most doped sample has the lowest mobility of ~ $40 \text{ cm}^2/(\text{V} \cdot \text{s})$. However, due to the scattering by phonons, the mobilities for all the samples drop quickly to $20 - 35 \text{ cm}^2/(\text{V} \cdot \text{s})$ as temperature increases to 300 K. Compared with the room temperature Hall mobilities in Figure 41, Mg₂Li_{0.025}Si_{0.4}Sn_{0.6} has lower mobility than the *n*-type samples. But compared with the Ag-doped Mg₂Si_{0.4}Sn_{0.6}, which has a room temperature mobility of ~ $20 \text{ cm}^2/(\text{V} \cdot \text{s})$, Mg₂Li_{0.025}Si_{0.4}Sn_{0.6} shows a significant increase in the hole mobility, which is in agreement with Zhang's report [65].



Figure 52 The carrier concentrations for Mg₂Li_xSi_{0.4}Sn_{0.6} measured from 70 K to 300 K.



Figure 53 The Hall mobilities for Mg₂Li_xSi_{0.4}Sn_{0.6} measured from 70 K to 300 K.

The electrical conductivity (Figure 54) of the Mg₂Li_xSi_{0.4}Sn_{0.6} samples increases as the doping concentration increases, mainly due to increased carrier concentration after doping. The undoped sample has an electrical conductivity that increases with increasing temperature due to enhanced thermal activation across the bad gap as the temperature increases. From 300 K to 600 K, increasing temperature causes a decrease in the electrical conductivities, due to stronger phonon scattering at high temperatures. Above 650 K, the bipolar conduction becomes significant when enough minority carriers are thermally activated. The doped samples enter the intrinsic region and show increased electrical conductivities as the temperature continues to increase.



Figure 54 The electrical conductivities for the Mg₂Li_xSi_{0.4}Sn_{0.6} samples.



Figure 55 The thermal conductivities for the Mg₂Li_xSi_{0.4}Sn_{0.6} samples.

The thermal conductivities for the Mg₂Li_xSi_{0.4}Sn_{0.6} samples are shown in Figure 55. Below 500 K the thermal conductivity of the doped samples are higher than the undoped samples. In the temperature region above 500 K the undoped sample has a higher thermal conductivity. The electronic thermal conductivity κ_e , which is caused by the conduction of holes, was estimated by the Wiedemann-Franz law using Equation 31, 32, 36 and 38 – 40 and shown in Figure 56. Below 500 K, the bipolar thermal conductivity κ_{bp} should be negligible [30, 62] and the lattice thermal conductivity κ_1 could be calculated by subtracting κ_e from the total thermal conductivity (Figure 57).



Figure 56 The electronic thermal conductivities for the $Mg_2Li_xSi_{0.4}Sn_{0.6}$ samples.



Figure 57 The lattice thermal conductivities for the Mg₂Li_xSi_{0.4}Sn_{0.6} samples.

Figure 56 shows that samples with higher electrical conductivities also have higher electronic thermal conductivities. The electronic thermal conductivities remain constant up to the bipolar transition temperature. For the lattice thermal conductivities, more heavily doped samples seem to have higher lattice thermal conductivities as well. As shown in Figure 48, more heavily doped samples have more MgO impurity. The increased MgO content could be the cause of the increased lattice thermal conductivities in doped samples.

The existence of the MgO impurity phase makes the sample a two-phase particulate composite. The thermal conductivity of such a composite system could be estimated by the methods proposed by by Hashin and Shtrikman [72, 73]. The thermal conductivity of the composite should fall into a region defined by a lower and upper bound.

$$\kappa_{lower} \leq \kappa^* \leq \kappa_{upper}$$
 (64)

$$\kappa_{lower} = \kappa_m + A_m / (1 - \alpha_m A_m) \tag{65}$$

$$\kappa_{upper} = \kappa_n + A_n / (1 - \alpha_n A_n) \tag{66}$$

$$A_s = \sum_{i=1}^{2} v_i [(\kappa_i - \kappa_s)^{-1} + (3\kappa_s)^{-1}]^{-1}$$
(67)

$$\alpha_s = (3\kappa_s)^{-1}, \qquad s = m, n \tag{68}$$

where v_i is the volume fraction for each phase and it could be calculated using the RIR method discussed in Figure 47 and 48. The subscripts *m* and *n* denote the phase with minimum and maximum thermal conductivity, respectively. The room temperature thermal conductivity of MgO is 28.4 W·m⁻¹·K⁻¹ [74].

Using Equation 64 - 68, the upper and lower limit for the composites have been calculated and shown in Figure 58, together with the lattice thermal conductivities of the Mg₂Li_xSi_{0.4}Sn_{0.6} samples at 300 K. The experimental values fall between the lower and upper limit predicted by Hashin and Shtrikman and show the same increasing trend as the MgO amount increases.



Figure 58 The lattice thermal conductivity for the Mg₂Li_xSi_{0.4}Sn_{0.6}-MgO composite.

The dimensionless figure of merit *ZT* was calculated using the transport data from Figure 51, 54 and 55 and shown in Figure 59. All the doped samples showed appreciable enhancement in *ZT* compared with the undoped sample. Among the doped samples, the least doped sample $Mg_2Li_{0.025}Si_{0.4}Sn_{0.6}$ exhibited the highest *ZT* \approx 0.7 at 675 K.



Figure 59 The ZT for the $Mg_2Li_xSi_{0.4}Sn_{0.6}$ samples.

Our results are comparable with those reported by Zhang (peak $ZT \approx 0.5$ around 750 K). The difference in the ZT might be caused by the difference in the Si : Sn ratio. As shown in Liu's work [40], a different Si : Sn ratio could cause a difference in the band structure and the lattice thermal conductivity, which could lead to significant difference in the transport properties and the ZT. Our samples have lower lattice thermal conductivities than those reported by Zhang, which is in agreement with Liu's work that Mg₂Si_{0.4}Sn_{0.6} has the lowest lattice thermal conductivity in the Mg₂(Si,Sn) material system. Another significant difference is that Zhang's work showed a higher doping efficiency by using pure Li metal. For similar Li content levels, Zhang's samples have much higher carrier concentration than ours. This could be attributed to the different reaction/doping mechanism of using different doping agents (pure Li metal or

 Li_2CO_3), and it should be investigated in the future. Similar to Zhang's work, color changes on the surface of the samples were observed in our samples (Figure 60). The thermal stability of those samples should be further studied.



Figure 60 Photo of the $Mg_2Li_{0.1}Si_{0.4}Sn_{0.6}$ sample before and after the transport property measurement up to 775K.

5.3 The Reaction and Doping Mechanism of the Li₂CO₃ Doping Agent

The transport data has shown that p-type Mg₂Si_{0.4}Sn_{0.6} was successfully synthesized using Li₂CO₃ as a doping agent. The reaction and doping mechanism are not clearly revealed by the transport measurement results. The following discussion will be focused on the reaction and doping mechanism.

For the reaction mechanism, a replacement reaction between Li_2CO_3 and the Mg-Si-Sn mixture is not thermodynamically possible but the decomposition of Li_2CO_3 could occur at 1573 K [75].

$$Li_2CO_3 \rightarrow Li_2O + CO_2$$
 I

The synthesis temperature in our experiment was set at 973 K. Although the actual temperature of the reactant mixture might be higher due to latent heat from reaction, it is hard to determine whether or not the local temperature reached 1573 K during synthesis. It has been reported that the decomposition temperature can be lowered if CO_2 is instantly purged from the system [76]. In the synthesis environment, magnesium could react with CO_2 easily and consume the CO_2 produced by the decomposition of Li_2CO_3 , making Reaction I possible at lower temperatures. Overall the following reaction is proposed.

$$Li_2CO_3 + Mg \rightarrow Li_2O + MgO + CO$$
 II

Reaction II explains the increasing MgO content in the final product. More experimental or theoretical evidence is needed to verify this reaction route.

For the doping mechanism, the consequence of Reaction II is the consumption of Mg during the reaction, which could potentially create magnesium vacancies (V_{Mg}) in the sample. It is well accepted that V_{Mg} acts as acceptor in the Mg₂(Si,Sn) materials system, so the *p*-type behaviour in our samples could be attributed to the effect of V_{Mg} as well. To address this question, two Mg₂Si_{0.4}Sn_{0.6} samples were synthesized using same amount of Na₂CO₃ and K₂CO₃ as doping agent, respectively. The reaction mechanism for Na₂CO₃ and K₂CO₃ are similar to Reaction II. Similar transport properties should be expected if V_{Mg} was the origin of the holes as all three different carbonates consume Mg in the same manner. The Seebeck coefficients and electrical conductivities of the Li₂CO₃, Na₂CO₃ and K₂CO₃ doped samples are shown in Figure 61 and they exhibit different values and temperature dependence. Meanwhile, our transport data are comparable to those reported by Zhang, who used pure Li metal as a doping agent to make *p*-

type $Mg_2Si_{0.3}Sn_{0.7}$ (Figure 62). Thus, it is unlikely that the major source of holes in our samples is from magnesium vacancies and it should be related to the Li.



Figure 61 Transport property of Li₂CO₃, Na₂CO₃, and K₂CO₃ doped Mg₂Si_{0.4}Sn_{0.6} samples.

Another possible source of holes is the substitutional lithium (Li_{Mg}). The formation energies of Li_2O (466 kJ/mol) and MgO (492 kJ/mol) are very similar and the reactant mixture is a Mg-rich environment for Li_2O , the following reaction could possibly take place [75]

$$Mg + Li_2O \leftrightarrow MgO + 2Li$$
 III



Figure 62 Transport data of Mg_{1.94}Li_{0.06}Si_{0.3}Sn_{0.7} ($n_p \approx 1.4 \times 10^{20} \text{ cm}^{-3}$)[65] and Mg₂Li_{0.05}Si_{0.4}Sn_{0.6} ($n_p \approx 1.3 \times 10^{20} \text{ cm}^{-3}$) in this work (symbols represent Seebeck coefficients and line-symbols represent electrical conductivities).



Figure 63 "Ionization" percentages of Li in the Mg₂Li_xSi_{0.4}Sn_{0.6} samples.

The 'free' Li could react with the Mg-Si-Sn reactant mixture and form Li_{Mg} as proposed by Zhang, who reported Li ionization percentages below 30% for all the samples [65]. The carrier concentration was divided by the ICP-OES measured Li content to calculate the "ionization" percentages for our samples (Figure 63). The results in Figure 63 are comparable to those reported by Zhang, however, lithium is an easily activated element and the carrier concentration data do not show temperature dependent activation behaviour. This implies that all Li_{Mg} should be fully ionized and what limits the doping efficiency seems to be the fact that not all Li become Li_{Mg}, i.e. some might become interstitial Li (Li_i) on the 4b site. As shown in the literature, Mg₂Si/Mg₂Sn is a system that can easily accommodate Li at both the interstitial site and the Mg-substitutional site [77-79]. A pristine Mg₂Sn and a fully doped Li₂MgSn are shown in Figure 64. The site preference of Li is still not clear and more theoretical research on the formation energy of Li_{Mg} and Li_i in the Mg₂(Si,Sn) system is needed to better understand the point defects that could be created by Li in this system.



Figure 64 Structural representations for Mg₂Sn and Li₂MgSn (Li atoms occupy both substitutional and interstitial sites in Li₂MgSn).

5.4 Summary of the Chapter

Lithium (Li) was chosen for investigation as a *p*-type dopant for the Mg₂Si_{0.4}Sn_{0.6} due to the high hole mobilities in Li-doped samples. Lithium carbonate (Li₂CO₃) was used as the doping agent to deliver Li to the Mg₂Si_{0.4}Sn_{0.6} materials. Li₂CO₃ turned out to be an effective *p*type doping agent that is much easier to handle than pure Li metal. Using Li₂CO₃ as the doping agent also increased the MgO impurity concentration in the sample, which increased the lattice thermal conductivities of the sample. Peak $ZT \approx 0.7$ at 675 K was found in the Mg₂Li_{0.025}Si_{0.4}Sn_{0.6} sample, which is the state of art result for the *p*-type Mg₂Si_{0.4}Sn_{0.6}. The reaction and doping mechanism were discussed, but further study is needed.

Chapter 6 Diffusion Bonding in PECS

In Chapter 4 and 5, we have developed both *n*-type and *p*-type $Mg_2Si_{0.4}Sn_{0.6}$ materials with state of the art thermoelectric properties, which makes them very promising for practical thermoelectric power generation applications. One crucial step in making a thermoelectric generator is to bond the thermoelectric materials to electrodes. To minimize the power loss, high electrical conductivity and thermal conductivity are needed in the electrodes and across this junction. For practical concern, the interface must be strong enough so that the bond does not break or fail during the operation of the thermoelectric generator. The bonding process for the $Mg_2Si_{0.4}Sn_{0.6}$ materials was studied and the quality of the bonding interfaces was tested in this work.

6.1 Diffusion Bonding in PECS

The bonding experiment is usually done by pressing together two or more materials to be bonded and increasing the temperature until the bonding is made by the atomic diffusion across the interface. This process is usually done in vacuum, inert gas, or reducing gas to avoid the oxidation on the interface. The pressure is applied by springs or clamps [80]. All the conditions required by a bonding experiment could be met by a PECS system, where the temperature, atmosphere and pressure can all be controlled by program or manually. The high heating rate in PECS might be able reduce the bonding time and speed up the whole process, which usually takes hours in a traditional bonding experiment set up [81]. The PECS process could potentially clean the grain boundary or interface between different materials [82, 83], which improves the quality of the bond. Another advantage of the bonding experiment in PECS is that powders of materials might be directly used so that the sintering of $Mg_2Si_{0.4}Sn_{0.6}$ and the bonding with different electrode materials could be completed in one step. This could speed up the whole thermoelectric generator fabrication process significantly. All the bonding experiments in this work were done in the PECS instrument.

6.2 Screening of the Electrode Materials

The electrode material is also an important parameter that determines the outcome of a bonding experiment, besides the experimental conditions such as temperature and pressure.

The temperature of the bonding experiment depends on the melting point of the electrode material and $Mg_2Si_{0.4}Sn_{0.6}$. The bonding temperature is usually 50 - 80 % of the melting point of the more fusible metal [84]. The melting point of $Mg_2Si_{0.4}Sn_{0.6}$ is about 1100 K (Figure 16), so an ideal electrode material should have a melting point close to 1100 K. If the melting point of the electrode material is too low, the electrode might fail before the thermoelectric materials do. If the melting point of the electrode is too high, the bonding experiment would take too much time to complete.

To minimize the stress at the bonding interface, the electrode materials should have similar coefficients of thermal expansion (CTE) to $Mg_2Si_{0.4}Sn_{0.6}$. The CTE of $Mg_2Si_{0.4}Sn_{0.6}$ is 2.0×10^{-5} K⁻¹ which is a relatively high value. Thus, material with a high CTE is preferred for the electrode material.

The electrode material itself should also have high electrical conductivity as well as high thermal conductivity. With those factors considered, some materials were selected as the candidates for the electrode materials (Table 6). The materials listed in Table 6 were not selected solely due to the physical properties. For example, aluminum can be a good electrode material but aluminum was never used in the bonding experiment because of two reasons. Aluminum powder is active and flammable, making the operation with aluminum powders dangerous. The aluminum plate/foil is difficult to bond to other materials because the surface oxide layer acts as a diffusion barrier that prevents the inter-diffusion between materials [84].

Material	Melting Point / K	CTE / 10 ⁻⁶ K ⁻¹	Electrical conductivity / S·cm ⁻¹	Thermal conductivity / W·m ⁻¹ ·K ⁻¹
Aluminum	933	23	3.8×10^5	205
Copper	1357	17	6.0×10^5	401
Nickel	1728	13	1.4×10^5	91
Iron	1808	12	1.0×10^5	80
430 Stainless Steel	1783	11	4.4×10^4	26
Silver	1234	18	6.3×10^5	429

Table 6 Candidate electrode materials Mg₂Si_{0.4}Sn_{0.6} bonding experiment.

Most electrode materials investigated are metals and metal-semiconductor interfaces were formed after the bonding experiment. Both the *n*-type and *p*-type Mg₂Si_{0.4}Sn_{0.6} materials that have high *ZT* in this work are heavily doped and they have carrier concentration on the order of 10^{20} cm⁻¹. For heavily doped semiconductor, tunneling current is the main current across the metal-semiconductor interface. The contact resistance across such an interface strongly depends on the carrier (doping) concentration of the semiconductor. For carrier concentration higher than 10^{20} cm⁻¹, the contact resistance can be neglected and ohmic contact can be easily obtained between the heavily doped semiconductor and most metals [7]. In theory all the metals/alloys listed in Table 6 should be able to form ohmic contact with the doped Mg₂Si_{0.4}Sn_{0.6} material. Thus, the main focus of this part of the dissertation was on adjusting the processing techniques to get a low-resistance interface.

6.3 One Step Sintering and Bonding in PECS

As mentioned in the first part of this chapter, it is possible to achieve sintering and bonding in one experiment in PECS. Similar one step experiment design has been successfully applied to the fabrication of skutterudite-based thermoelectric modules, where the hot press technique was used instead of PECS [85].Powders of $Mg_2Si_{0.4}Sn_{0.6}$, metals and alloys were used in the one step sintering and bonding experiment in PECS. The experiment setup is as shown in Figure 11 and some of the experiment results are shown in Table 7. The PECS parameters were shown in the form of "Temperature (in K) –Pressure (in MPa) –Time (in min)".

Unfortunately, none of the one-step experiments showed satisfactory bonding results. The photos of some samples from the one-step experiments are shown in Figure 65 – 67. The length of each sample is about 12 mm. Most samples in the one-step experiment suffered from the cracking within the Mg₂Si_{0.4}Sn_{0.6} layer, which should be due to the CTE mismatch.

Silver was found to be able to produce a good bonding interface without cracking the $Mg_2Si_{0.4}Sn_{0.6}$ or the electrode layer, which was attributed to the similar CTE between silver and $Mg_2Si_{0.4}Sn_{0.6}$. However, appreciable amount of material melted and leaked from the PECS assemble during the experiment. The PECS sintering experiment with only $Mg_2Si_{0.4}Sn_{0.6}$ was
done at 973 K and small amount of melting was only observed rarely. The Ag-Mg₂Si_{0.4}Sn_{0.6} sintering and bonding experiment was done at a lower temperature (923 K) but significant melting was observed. The ternary phase diagram of Ag-Mg-Sn shows that the mixture is in liquid state at 823 K when the silver atomic percentage (at.%) is between 63 at.% and 68 at.% or higher than 76 at.% [86-97]. The Ag-Mg₂Si_{0.4}Sn_{0.6} inter-diffusion area could be heavy in silver on the silver side and fall into the liquid composition, causing the melting of the material. To avoid the melting at the interface the experiment temperature should be below 823 K, at which the Mg₂Si_{0.4}Sn_{0.6} layer could not be densified.

Electrode	PECS Parameter	Results		
		$Mg_2Si_{0.4}Sn_{0.6}$	Electrode	Interface
Ni	973-30-25	Fractured	Densified	Bonded
Ni	973-40-10	Fractured	Densified	Bonded
Ni	923-40-10	Fractured	Densified	Bonded
Ni	873-40-10	Fractured	Densified	Bonded
Ni	823-40-10	Fractured	Densified	Partially bonded
Ni	673-60-15	Powder	Densified	Partially bonded
Ni	673-30-15	Good	Densified	Not bonded
Fe	923-40-10	Cracks	Densified	Yes
Ag	923-40-10	Densified	Densified	Partially bonded
CoSi ₂	923-40-10	Cracks	Powder	Not bonded
CoSi ₂	973-40-10	Cracks	Densified	Bonded
CoSi ₂	1023-40-10	Cracks	Densified	Bonded

Table 7 Results of the one step sintering and bonding experiments.



Figure 65 The one step sintering and bonding using Fe as the electrode.



Figure 66 The one step sintering and bonding using Ni as the electrode.



Figure 67 The one step sintering and bonding using Ag as the electrode.

6.4 Bonding Experiment with Braze Materials

Inspired by the successful experiment done by previous group members, a braze material was used between $Mg_2Si_{0.4}Sn_{0.6}$ (MST) and the electrode to improve the quality of the interface. In those experiments, the $Mg_2Si_{0.4}Sn_{0.6}$ layer was previously sintered by PECS. The electrode materials were powders. Foils of the braze material from McMaster-Carr (Part#76965A66, Ag50%-Cu20%-Zn28%-Ni2%) were used.

The braze material turned out to be effective in improving the quality of the bonding interface. It could be seen in Figure 68 and 69 that the bonding interfaces are clean and there are no visible cracks in the $Mg_2Si_{0.4}Sn_{0.6}$ layer. The gaps in Figure 68 were not cracks but the space intentionally left between the $Mg_2Si_{0.4}Sn_{0.6}$ pieces.



Figure 68 The Cu-Braze-MST-Braze-Cu_773K-5MPa sample.



Figure 69 The Fe-Braze-MST-Braze-Fe_773K-5MPa sample.

The voltage profile for the Fe-Braze-MST-Braze-Fe_773K_5MPa sample was obtained using the voltage scanning probe (Figure 14) and data is shown in Figure 70. The Fe-Braze-

MSS-Braze-Fe_773K_5MPa sample showed high contact resistance as a large voltage discontinuity was observed across the interface. The resistance across the interface is almost seven times higher than the resistance of the whole $Mg_2Si_{0.4}Sn_{0.6}$ layer.



Figure 70 The voltage profile for the Fe-Braze-MST-Braze-Fe_773K-5MPa sample.

The SEM images and EDX mapping of this sample are shown in Figure 71. In the braze layer, no significant diffusion of Cu or Zn was observed. Ag and Ni showed different distribution. Ni was concentrated in one thin layer, while the Ag spread across the braze layer and some Ag even diffused into the Mg₂Si_{0.4}Sn_{0.6} layer. It was suspected that Ag might be the cause of the high contact resistance at the interface. The Mg₂Si_{0.4}Sn_{0.6} layer used in the sample was *n*-type sample. Silver could act as acceptor in Mg₂Si_{0.4}Sn_{0.6}. At the interface, Mg₂Si_{0.4}Sn_{0.6} were could be doped by Ag from the braze material. Once some electrons in *n*-type Mg₂Si_{0.4}Sn_{0.6} were

neutralized by Ag, the $Mg_2Si_{0.4}Sn_{0.6}$ was no longer heavily doped and the contact resistance could rise due to the work function difference between the electrode and $Mg_2Si_{0.4}Sn_{0.6}$ [7].



Figure 71 The SEM image and EDX mapping results for the Fe-Braze-MST-Braze-Fe_773K-5MPa sample.

6.5 Bonding Experiment with Nickel Silver and Copper

As silver was suspected to be the cause of the high contact resistance in the braze-bonded sample, a silver-free braze was investigated. Removing silver from the commercial braze used previously, a Cu-Ni-Zn alloy was obtained. It was found that a commercial materials known as "Nickel Silver" was one type of the Cu-Ni-Zn alloy. The general composition of the nickel silver is 47-64% for Cu, 10-25% for Ni and 15-42% for Zn. The melting point of this alloy is between 1173 K and 1300 K and the CTE is between 17×10^{-6} K⁻¹ and 20×10^{-6} K⁻¹, both of which can be adjusted by changing the concentration of each element. More information on this material could be found from the materials suppliers. Rod of the nickel silver (ASTM B151) was purchased (Shinwonmetal Co. from South Korea) and cut into thin (~ 0.5 mm) discs. The discs of the nickel silver were directly used as the electrode. Previously sintered disk-shaped Mg₂Si_{0.4}Sn_{0.6} samples were used in the bonding experiment.



Figure 72 The Nickel Silver-MST-Nickel Silver _823K-5MPa sample before and after cutting.

Figure 72 showed one sample from a bonding experiment using nickel silver. Like most samples using nickel silver disc as the electrode, the sample was intact after the bonding

experiment but the $Mg_2Si_{0.4}Sn_{0.6}$ layer broke near the interface when the sample was cut using a low speed diamond saw to reveal the cross section.

The voltage profile was scanned on some of the interfaces that remained intact after cutting. Figure 73 shows the voltage profile of the sample in Figure 72. There is no appreciable change in the voltage when the probe scans across the interface, indicating low contact resistance. The interface is mechanically strong and electrically conductive.



Figure 73 The voltage profile for the Nickel Silver-MST-Nickel Silver _823K-5MPa sample.

However, the disadvantage of nickel silver is as obvious as its advantage. As mentioned above, it tends to break the $Mg_2Si_{0.4}Sn_{0.6}$ layer. The CTE of nickel silver (17 - 20×10^{-6} K⁻¹) is very close to that of $Mg_2Si_{0.4}Sn_{0.6}$ but nickel silver is a very hard (85-190 HB) material compared with $Mg_2Si_{0.4}Sn_{0.6}$, making $Mg_2Si_{0.4}Sn_{0.6}$ the weakest part in the junction. Even a small CTE mismatch might be able to build up and break the $Mg_2Si_{0.4}Sn_{0.6}$ layer as $Mg_2Si_{0.4}Sn_{0.6}$ is more

brittle than nickel silver. Besides, nickel silver is not a good conductor compared with pure metals. The room temperature electrical resistance of nickel silver is on the level of 10^4 S·cm⁻¹ and the thermal conductivity is about 30 W·m⁻¹·K⁻¹.

Copper was investigated as a possible electrode material as well. As listed in Table 6, copper has close CTE to $Mg_2Si_{0.4}Sn_{0.6}$ and is an excellent conductor of both heat and electricity. The major component of nickel silver turns out to be copper as well. Thus, bonding experiments were conducted using ~ 0.5 mm thick copper (Cu 110 - ASTM B152) disc as the electrode in the bonding experiments in PECS.

Figure 74 shows threes samples processed at 823 K and 5 MPa using Cu disks as the electrode for $Mg_2Si_{0.4}Sn_{0.6}$. The thickness of the $Mg_2Si_{0.4}Sn_{0.6}$ layer was 2 mm, 4 mm and 6 mm for each sample in Figure 74. All the samples show clean and well-bonded interfaces. The voltage profiles for the three samples are shown in Figure 75. All the samples show nearly zero contact resistance.



Figure 74 The Cu-MST-Cu_823K-5MPa samples with different Mg₂Si_{0.4}Sn_{0.6} layer thickness.



Figure 75 The voltage profiles for Cu-MST-Cu_823K-5MPa samples with different $Mg_2Si_{0.4}Sn_{0.6}$ layer thickness.

The success of copper might be attributed to the softness of copper compared with nickel silver. The Brinell hardness of copper is only 35 HB. Copper might be able to deform during the bonding process to accommodate the CTE mismatch and prevent the $Mg_2Si_{0.4}Sn_{0.6}$ from breaking.

Thermal stability of the Cu electrode was tested by annealing the bonded sample at 733 K for 24 hours in an Ar purged environment. The voltage profiles before and after annealing are shown in Figure 76. No significant changes in the voltage profile was observed after annealing, indicating that interface did not degrade after the annealing.



Figure 76 The voltage profiles for Cu-MST-Cu_823K-5MPa samples before and after annealing.

The SEM images and EDX line scans were also collected on the sample before and after the annealing. No voids or cracks were observed at the interface after annealing (Figure 77). The thickness of the inter-diffusion layer (the $20 - 80 \mu m$ regime in Figure 78 and 79) did not show significant changes. This also indicates that the interface is thermally stable at 733 K for 24 hours.



Figure 77 The SEM images for Cu-MST-Cu_823K-5MPa samples before (top) and after (bottom) annealing.



Figure 78 The EDX line scan for Cu-MST-Cu_823K-5MPa samples before annealing.



Figure 79 The EDX line scan for Cu-MST-Cu_823K-5MPa samples after annealing.

6.6 Bonding Experiment for *p*-type Mg₂Si_{0.4}Sn_{0.6}

All the bonding experiments shown above were done using the *n*-type $Mg_2Si_{0.4}Sn_{0.6}$ samples, either Sb-doped or Bi-doped. Bonding experiments were also done for *p*-type $Mg_2Si_{0.4}Sn_{0.6}$ samples doped by Na_2CO_3 as well. The experiment setup was the same as that used for the *n*-type materials. Mechanically strong and electrically conductive bonding interface were also obtained using copper electrodes (Figure 80).



Figure 80 The bonding experiment sample using *p*-type Mg₂Si_{0.4}Sn_{0.6} and its voltage profile.

6.7 Summary of the Chapter

Bonding experiments in PECS were conducted to find the good electrode materials and process parameters for $Mg_2Si_{0.4}Sn_{0.6}$. The one-step sintering and bonding experiments were not successful. The commercial braze improved the mechanical bonding but showed high contact resistance. Nickel silver could create low resistance interface but also resulted in fracturing of the $Mg_2Si_{0.4}Sn_{0.6}$ material. Copper was found to be the best electrode material for $Mg_2Si_{0.4}Sn_{0.6}$. Mechanically strong and electrically conductive bonding interfaces were obtained for both *n*-

type and *p*-type samples. The copper electrode also showed good thermal stability after 24 hours annealing test at 733 K to the *n*-type samples.

Chapter 7 Module Fabrication and Testing

Some preliminary work on the module fabrication and testing was done, using the $Mg_2Si_{0.4}Sn_{0.6}$ materials and the bonding techniques developed in this dissertation. The manufacturability of a $Mg_2Si_{0.4}Sn_{0.6}$ -based thermoelectric generator was investigated.

A uni-couple forms a simple thermoelectric generator, which only has one *p*-type leg and one *n*-type leg. To get a higher output voltage, multiple uni-couples are connected in series. An array of uni-couples is shown in Figure 81 and this is a common design for most thermoelectric modules. To make such a module, multiple legs of *p*-type and *n*-type material need to be bonded to the electrodes simultaneously. The experimental setup in Figure 11 could not achieve such a goal and some modification of the experimental setup is needed.



Figure 81 Illustration of a thermoelectric generator module consisting of multiple uni-couples.

7.1 The 4-leg Module

The initial design was a simple 4-leg module as shown in Figure 82 and the mold used for the bonding experiment is shown in Figure 83. The mold consists of three graphite parts: A, B1

and B2. Part B1 and part B2 are the same. When the three parts were put together, cubes $(2.5 \times 2.5 \text{ mm})$ of the *p*-type Li-doped Mg₂Si_{0.4}Sn_{0.6} and *n*-type Bi-doped Mg₂Si_{0.4}Sn_{0.6} were placed in the four square holes formed between A, B1 and B2. The top and bottom of the A-B1-B2 assembly were then covered by Cu discs and processed in PECS for the boding experiment (Figure 84). When the PECS was finished, the Cu discs were bonded to the cubes of Mg2Si0.4Sn0.6 and the mold could be separated from the materials by pulling A, B1 and B2 in the directions shown in Figure 83.



Figure 82 Illustration of the 4-leg thermoelectric generator module.



Figure 83 The mold design for the 4-leg thermoelectric generator module.



Figure 84 The PECS setup for the fabrication of a 4-leg thermoelectric module.



Figure 85 The 4-leg thermoelectric generator module before (left) and after (right) cutting the Cu electrode.

One 4-leg module was fabricated and the module is shown in Figure 85. Before cutting the Cu discs to the shape in Figure 82, the module looked intact. During the cutting process, two legs broke from the Cu disc and only one uni-couple survived. The uni-couple was tested in Dr. Harold Schock's lab with the help of Mr. Edward Timm. The I-V curve and the power output curve of the uni-couple were tested when the hot side temperature was 710 K and the cold side

temperature was 380 K. A maximum power output of 117 mW was obtained when the current was 2 A, which was comparable to some test results done before on skutterudite-based modules.



Figure 86 The I-V and power output curves for the uni-couple from the 4-leg module.

7.2 The 8-leg Module

It was speculated that the breaking of the 4-leg module was cause by the stress during the cutting. To avoid cutting the Cu electrode after the bonding experiment, a new mold was designed which could accommodate 8 legs of $Mg_2Si_{0.4}Sn_{0.6}$. The design of the 8-leg module is illustrated in Figure 87 and the mold is shown in Figure 88. All the mold parts were made in graphite. There were engraved pockets on part A and E, where the copper plates would fit in. The assembly, processing and disassembly was similar to the 4-leg module.



Figure 87 Illustration of the 8-leg thermoelectric generator module.



Figure 88 The mold design for the 8-leg thermoelectric generator module.

Photos of the mold parts A and E and the PECS assembly are shown in the left column of Figure 89. The module was shown in the right column of Figure 89. Part A, E and C could be easily separated from the module. However, copper pads deflected during the bonding experiment and pinched part B and D, making it difficult to remove part B and D from the module. When part B and D were removed by force, the module was damaged and no uni-couple survived.



Figure 89 The photos of the 8-leg thermoelectric generator module.

7.3 Summary of the Chapter

We have presented two designs for the fabrication of the $Mg_2Si_{0.4}Sn_{0.6}$ -based thermoelectric generator. A 4-leg module and an 8-leg module were obtained. A uni-couple from the 4-leg module was tested and showed a maximum power output of 117 mW when the hot side temperature was 710 K and the cold side temperature was 380 K. The fabrication technique needs improvement in the future to avoid the breaking of the module during the cutting or separation process after the bonding experiment.

Chapter 8 Conclusions and Future Work

The objective of this work has been to investigate the $Mg_2(Si,Sn)$ -based thermoelectric materials and develop the techniques to fabricate $Mg_2(Si,Sn)$ -based thermoelectric generators.

The Mg₂(Si,Sn)-based material represents a solid solution system formed by Mg₂Si and Mg₂Sn. Single phase solid solution could only be obtained in certain ranges of Mg₂Si : Mg₂Sn ratios. The thermal phase stability of the Mg₂Si_{1-x}Sn_x (x = 0.3, 0.4, 0.5, 0.6 and 0.7) materials were studied using neutron scattering. Both *in*-situ (up to 750 K) and *ex*-situ (up to 973 K) neutron scattering experiments were conducted in the Oak Ridge National Laboratory. Mg₂Si_{0.4}Sn_{0.6} was found to be a stable single solid solution phase up to 775 K. Mg₂Si_{0.4}Sn_{0.6} was known to have high degeneracy in the conduction band, which was good for obtaining a high Seebeck coefficient for the material. The Mg₂Si_{0.4}Sn_{0.6} phase also had the lowest lattice thermal conductivity among all the Mg₂Si_{1-x}Sn_x compositions studied.

Further optimization of the thermoelectric properties was conducted through doping studies on the Mg₂Si_{0.4}Sn_{0.6} material. Antimony (Sb) and bismuth (Bi) were used as *n*-type dopant to adjust the transport properties of *n*-type Mg₂Si_{0.4}Sn_{0.6} material. Both Sb and Bi were found to be effective dopant and peak ZT > 1.50 were obtained in both Sb-doped and Bi-doped samples. The Sb-doped samples showed high Mg deficiency, which made it difficult to control the composition of the sample and might cause thermal stability problems with the creation of Mg vacancies. No such problems were found in the Bi-doped samples. The study also suggests that the Bi atoms can enter the interstitial sites of the Mg₂Si_{0.4}Sn_{0.6} lattice and act as phonon scattering centers to reduce the lattice thermal conductivity of Mg₂Si_{0.4}Sn_{0.6}.

The *p*-type Mg₂Si_{0.4}Sn_{0.6} material was synthesized using lithium carbonate (Li₂CO₃) as the doping agent to deliver lithium (Li) to the Mg₂Si_{0.4}Sn_{0.6} matrix. This synthesis approach avoided the handling of the highly reactive pure Li metal and to our knowledge is the first time this doping agent has been reported. Using Li₂CO₃ as the doping agent inevitably increased the amount of MgO impurity phases in the samples and led to an increased lattice thermal conductivity. Our samples showed comparable thermoelectric properties compared with pure Li metal doped samples. A peak $ZT \approx 0.75$ was obtained in the Mg₂Li_{0.025}Si_{0.4}Sn_{0.6} sample at 675 K, which, to the best of our knowledge, is the highest result ever reported for *p*-type Mg₂Si_{0.4}Sn_{0.6} materials.

The interfaces between $Mg_2Si_{0.4}Sn_{0.6}$ and several different metals and alloys were studied, as an important part of the fabrication of $Mg_2Si_{0.4}Sn_{0.6}$ -based thermoelectric generators. Mechanically strong and electrically conductive interface was realized by using copper (Cu, ASTM B152) as the electrode material. Both *n*-type and *p*-type $Mg_2Si_{0.4}Sn_{0.6}$ material could form strong low-resistance interface with Cu. Preliminary thermal stability test showed that the Cu electrode did not degrade at 733 K for up to 24 hours.

A 4-leg module and an 8-leg were fabricated, using the knowledge acquainted in the research on the materials synthesis and bonding of the electrode. The uni-couple from the 4-leg showed peak power output of 117 mW when $T_{\rm h} = 710$ K and $T_{\rm c} = 380$ K. This result is promising and demonstrated the possibility of building environmentally friendly, low-cost, light-weight and high-efficiency thermoelectric generators by only using Mg₂Si_{0.4}Sn_{0.6} as the thermoelectric material.

For future work, the thermal stability research for both the doped Mg₂Si_{0.4}Sn_{0.6} materials and the bonding interface between Cu electrode and Mg₂Si_{0.4}Sn_{0.6} should be systematically studied. Especially for the *p*-type Mg₂Si_{0.4}Sn_{0.6} material, the existence of Li in the sample would always raise the question about the diffusion of Li at high temperatures. Although our thermal cycle measurement results did not show significant degradation in the thermoelectric properties of the Li-doped Mg₂Si_{0.4}Sn_{0.6} samples, long term thermal stability must be tested before making a real device from this material.

Theoretical work on the Mg₂Si_{0.4}Sn_{0.6} material system is also needed in the future. For examples, the existence of the Bi interstitial atoms could be confirmed by calculating the formation energy of Bi atoms at different sites in the Mg₂Si_{0.4}Sn_{0.6} matrix. For the *p*-type Mg₂Si_{0.4}Sn_{0.6} material synthesized using Li₂CO₃ as the doping agent, theoretical calculations on the energy change of all possible reaction routes and the formation energy of Li at interstitial site or substitutional site could give a better explanation on the reaction and doping mechanism of Li₂CO₃.

More work is needed to make the $Mg_2Si_{0.4}Sn_{0.6}$ -based thermoelectric generators. The legs tend to break after the bonding experiment for both the 4-leg and the 8-leg modules. The designs and processing parameters need to be improved to solve this problem. A missing part in this work is the study of the insulation layer, which electrically isolates the thermoelectric generator from the heat source but thermally connect them together.

Overall, the results in this work have demonstrated that $Mg_2Si_{0.4}Sn_{0.6}$ is an excellent thermoelectric material for thermoelectric power generation. A pure $Mg_2Si_{0.4}Sn_{0.6}$ -based thermoelectric generator could be expected in the future for practical applications. BIBLIOGRAPHY

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