Effect of Mg deficiency on the thermoelectric properties of $Mg_2(Si, Sn)$ solid solutions

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ABSTRACT

In this study, we analyze the change in the thermoelectric properties of a $Mg_x(Si, Sn)$ system upon varying nominal Mg content x (x = 1.8, 1.9, 2.1, 2.2, 2.3). Additional investigations are carried out to elucidate the mechanism through which Mg-deficient conditions induce point defects, such as Mg vacancies and anion anti-site defects, and determine the influence of these defects on the thermoelectric properties of a $Mg_x(Si, Sn)$ system. We find that Mg deficiency can induce reduction of band gap through multiple point defects as well as phase separation of crystal structures. Temperature-dependent measurements of the Seebeck coefficient and the Hall coefficient indicate that Mg deficiency induces p-type behavior; this is confirmed by an analysis of the thermoelectric transport properties by using a single parabolic band model at low temperature. The p-type conduction in the Mg-deficient system suggests that Mg vacancies are the predominant defects. However, the

efficiency of p-type doping is two to three orders of magnitude lower (~10^{18} cm^{-3}) than expected when considering only Mg vacancies as the origin of charge carriers. Density functional theory calculations suggest that the anion anti-site defect on the Mg site is attributable for the low measured carrier concentration and low doping efficiency. Moreover, the energy band structure of the Mg-deficient Mg_x(Si, Sn) system is shown to undergo significant deformation and allow the formation of an impurity band at the X point due to the Mg-deficient conditions, enabling the system to have a relatively anion-rich condition. Furthermore, Mg deficiency minimizes the thermal conductivity to 1–1.5 W/m·K at room temperature owing to an early bipolar contribution and separated structural phases. This study provides the Mg deficiency as a new control parameter that can be utilized to enhance the p-type thermoelectric performance of Mg silicides.

Keywords: Thermoelectrics, Silicides, Phase separation, Point defect, Impurity state.

1. Introduction

Thermoelectric (TE) materials serve as fundamental building blocks for TE devices, which are solid-state heat engines that directly convert heat to electricity. The efficiency of a TE material is typically evaluated on the basis of its figure of merit, $zT = S^2T/(\kappa\rho)$ [1], where S is the Seebeck coefficient, T is the absolute temperature, κ is the thermal conductivity, and ρ is the electrical resistivity. A zT of ~ 1.5 is equivalent to an energy conversion efficiency of ~10% [1,2]. Recently, several TE materials have achieved a zT of ≥ 1 or ≥ 2, *e.g.,* in Bi-Te-based alloys [3,4], PbTe [5,6], Skutterudite[7,8], and Zintl phase materials[9,10]. However, these materials contain hazardous or expensive heavy-metal elements. Because these materials increase the production and power generation cost, research has recently been underway to reduce the power generation cost from a techno-economic perspective [11]. Si-based TE materials can be used to create nontoxic, lightweight, and affordable TE devices [12,13]. Mg silicide compounds exhibiting n-type behavior and high TE performance (zT ~ 1 or zT > 1) have been developed through strategies such as the partial substitution of Si by Sn and a

convergence of conduction bands [14] and iso-valent substitution of C on a Si site of Mg_2Si by Sb doping [15] and Ge on an anion site of $Mg_2(Si,Sn)$ by Bi doping [16]. To ensure the high stability and long lifetime of TE devices under repeated thermal stress, it is desirable to use n- and p-type materials with similar mechanical properties. Thus, p-type Mg silicides with the requisite *zT* values must be developed to match those of n-type materials. Although the theoretically estimated *zT* values of p-type Mg_2Si systems are as high as ~0.8, which are comparable to those of their n-type counterparts [17], the highest value experimentally achieved so far is 0.5 for Li-doped $Mg_2(Si,Sn)$ [18] and ~0.3 for Ag, Ga co-doped $Mg_2(Si,Sn)$ [19]. This low performance is due to insufficient doping efficiency and a low carrier concentration of $< 10^{20}$ cm^{-3} [20]. To achieve an optimal carrier concentration of $\geq 5\times10^{20}$ cm^{-3} [17], Mg vacancy defects can play an important role as acceptors in the $Mg_2(Si,Sn)$ system [21], thus improving the p-type performance. Mg deficiency and Mg excess are widely accepted as common sources of Mg vacancies and interstitials, respectively [22,23]. Interestingly, calculations of the defect-formation energy in a ternary $Mg_2(Si,Sn)$ system indicate that p-type behavior can be enhanced when the Si:Sn ratios is low and Mg-deficient conditions are utilized [17]. Thus, the first consideration in any strategy for increasing the *zT* of p-type Mg silicides is the accurate control of the Mg content of the host system. Because the Mg content easily reduces during the annealing/sintering process owing to the high vapor pressure of Mg, the Mg content of $Mg_2(Si,Sn)$ can be typically adjusted by adding excess Mg or controlling the partial pressure of Mg via the evaporation of additional Mg during the annealing process [24,25]. Thus far, studies on the effect of Mg content variation on transport properties have mainly focused on n-type Mg silicides. Several studies have demonstrated the control of Mg vacancies in Mg_2Sn by varying the pressure of an Ar atmosphere during synthesis [26] and by inducing Mg vacancies in Mg_2Sn via B-doping [27]. Another study has shown that the undesirable Mg vacancies in the lattice play a negative role in reducing electron concentration although reducing the lattice thermal conductivity [28]. These studies have helped elucidate the role of defects induced in binary Mg_2Si, Mg_2Sn, and ternary $Mg_2(Si,Sn)$. However, they have only focused on n-type properties and exploited point defects as scattering centers. The effects of variation of the Mg content on p-type $Mg_x(Si,Sn)$ and the reason for the deformation of the electronic band structure although Mg vacancies can serve as holes in

the system have not yet been elucidated. Furthermore, previous studies did not consider the possibility and effect of the secondary phase of the host system although Mg silicide can easily unmix, usually in the form of a host matrix and a secondary phase, owing to the existence of a miscibility gap at a wide range of Si:Sn ratios [29].

In this study, we hypothesize that a Mg vacancy could behave as an effective acceptor in Mg silicides, which has not been considered in previous n-type studies. We thus examine the possibility of utilizing Mg vacancies for developing high-performance p-type Mg silicides by investigating the effect of the Mg content of a $Mg_2(Si,Sn)$ system by varying the initial Mg content. We first conduct a systematic investigation of the effect of Mg content on the crystal structure and TE properties of $Mg_x(Si,Sn)$ solid solutions (x = 1.8, 1.9, 2.1, 2.2, 2.3) and suggest an approach for improving p-type TE properties using the strategy of point defect control. X-ray diffraction and Rietveld refinement results provide evidence of the existence of a secondary phase in a solid solution system. The electronic band structure is determined using density functional theory (DFT) calculations, revealing the possible types of multiple defects and non-rigid band-like behavior by employing the Korringa–Kon–Rostoker (KKR) method with coherent potential approximation (CPA) and support of the Bloch spectral function (BSF) calculation with local density approximation (LDA). The transport property analysis conducted using the single parabolic band (SPB) model and considering acoustic phonon and alloy scattering provides clues regarding the deformation of the electronic band structure and non-rigid band-like behavior.

2. Material and methods

2.1. Material synthesis

Mechanical alloying and cold pressing followed by annealing were conducted to synthesize a series of $Mg_2(Si,Sn)$ samples. Mg chips (99.98%; Sigma-Aldrich), Si granules (99.999%; Alfa Aesar), and Sn shots were used as starting materials (99.999%; Alfa Aesar). To vary the Mg content, the starting materials were combined in specific ratios with different nominal Mg contents of $Mg_xSi_{0.4}Sn_{0.6}$ (x = 2.3, 2.2, 2.1, 1.9, 1.8). Next, the samples wher ball-milled in a planetary ball mill (Pulverisette 7, Fritsch) with a ball-to-powder ratio of 30:1 at

500 rpm for 6 h with 7 mL of n-hexane (~100 wt% of powder) to prevent the particles from sticking to the wall of the ball mill cup [30,31]. The initial Mg content was chosen based on our empirical investigation, to be x = 2.3, which showed a near-stoichiometric end composition ($Mg_2Si_{0.4}Sn_{0.6}$) while samples with x < 2.3 were Mg deficient. The lowest Mg content was chosen to be x = 1.8 because it corresponds to the composition where phase separation (discussed below) starts to appear. The sample mixture was then pressed for 10 min under a load of 6 tons using a manual cold press (PTJ-15, MTI), sealed in a quartz tube under high vacuum (~10^{-6} Torr), and allowed to diffuse for 22 h at 973 K to obtain a stable phase. Next, the heat-treated compound was pulverized in an agate mortar and repressed for 10 min under a load of 6 tons. Next, the as-obtained pellets were sintered in a sealed quartz tube at 973 K for 4 h under a vacuum. We found that this two-step process is essential to obtain a stable phase in an ambient atmosphere. Ball milling and pulverization were conducted in an Ar-filled glove box wherein O_2 and H_2O concentration were < 0.1ppm.

2.2. Crystal structure and composition

The bulk crystal structure was determined through powder X-ray diffraction (XRD) in the θ–2θ scan mode (D/MAX-2500-PC, Rigaku) using a Cu-Kα beam source at 1.5418 Å. Lattice constants were calculated by referring to the *hkl* planes of Mg_2Si and Mg_2Sn. The phase ratio of $Mg_2(Si,Sn)$ was estimated via Rietveld refinement using the open software MAUD by applying the R_{wp} < 15% criterion based on the XRD pattern (see Table 1) [32]. The crystal structure of $Mg_2(Si,Sn)$ were constructed by Free software, VESTA, with a refined .cif file from Crystallographic Open Database (COD) (Fig. 1b). Moreover, the composition was quantified Through inductively coupled plasma (ICP)-optical emission spectroscopy (OES) (Spectro, Arcos FHM22). For ICP-OES, the samples were dissolved in HCl, and a 0.001 ppm standard solution of each element was used. ICP-OES provides information about the elemental composition of the samples, while Rietveld refinement results reveal the atomic occupancies of each element through fitting parameters. The combination of these two techniques enables cross-verification of the results, leading to a more reliable assessment of the chemical composition than either alone. It is important to consider that the ICP-OES result indicates the remnants of Si

and secondary phases. To overcome this, the Mg occupancy from the Rietveld refinement was set as a fixed value and used to infer the number of other anions, including the remnants of Si. This inferred value was then cross-checked with the ICP-OES result to obtain a reasonable composition. Furthermore, the morphology and elemental distribution were analyzed through FE-SEM analysis (HITACHI, SU6600) at an accelerating voltage of 15 kV. The surface of all samples chemically polished to obtain cleaner images using a 0.01 μm alcohol-based diamond suspension.

2.3. Transport properties

The TE properties of the samples were determined using a custom liquid nitrogen cryostat (JANIS Cryostat, Lake Shore Cryotronics Inc.) with a rectangular bar-shaped geometry (1.5 × 1.5 × 7 mm). Two custom T-type thermocouples were attached to the surface of each sample to determine the temperature difference and Seebeck voltage. Two additional copper electrodes were attached to opposite surfaces to record the Hall resistance and Nernst voltage in a magnetic field. The Seebeck coefficient (S), the Nernst coefficient (N), and the thermal conductivity (κ) were measured under steady-state conditions using a 120 Ω resistive heater (SGD1.5/120, OMEGA Engineering Inc.). The electrical resistivity (ρ), and Hall resistivity were recorded using the four-wire method. To minimize the electrical and thermal contact resistances, the majority of the electrodes were attached via spot welding, which takes advantage of the rapid release of charge at the instant of electrical contact. Convective and radiative heat losses were minimized during the measurements using a high vacuum ($<10^{-6}$ Torr) and gold-plated radiation shield. Finally, the Seebeck noise from the copper electrode between each sample point was eliminated using a reference junction on the same temperature heat sink, which canceled the Seebeck voltage of the copper wire. Measurement errors, including geometrical, random, and systematic errors, were analyzed (detailed in Supplementary Materials). The geometric error in our measurements, with a dimensional scale of a few millimeters, was approximately 2%, accounting for the typical uncertainty of the micrometer (0.02 mm). The random error was attributed to equipment noise from the nanovoltmeter and AC bridge. The largest error was ≤ 1.5%, while most errors were ≤ 0.3%. Systematic errors

for each parameter were determined by comparing data measured by our cryostat with those measured by ZEM-3 (ZEM-3, ULVAC) and LFA (LFA 467 HyperFlash, NETZSCH), both of which are accepted in the field as standard measurement instruments for TE properties. For comparison, standard materials with well-known TE properties were employed. The resistance measurement had a systematic error of 10%, the Seebeck coefficient measurement had a systematic error of 12%, and the thermal conductivity measurement had a systematic error of 7%.

2.4. Electronic structure calculations

Electronic structure calculations were performed using the DFT and the KKR method. The CPA [33,34] was used to simulate the effects of Si-Sn alloying and the presence of point defects, which were randomly distributed in the crystalline material. The experimental crystal structure with a lattice parameter (a) of 6.604 Å and a Si:Sn ratio of 3:7 was used because the overall experimental composition of the sample with high Mg deficiency (x = 1.9 and 1.8) could be similar to that ratio (Table 1). A regular k-point mesh was used in the calculations, with 1500 k-points for the self-consistent cycle and 10^5 k-points for the BSF calculations (number of points given in the irreducible part of the Brillouin zone). The crystal potential was constructed in the framework of the LDA using the Vosko, Wilk, and Nussair [35] formula for the exchange-correlation part, and full-potential full-relativistic calculations were performed. The position of E_F was obtained using the Lloyd formula [33]. To describe the band gap more accurately, it is necessary to adopt advanced methods such as the semi-local exchange-correlation potentials that go beyond the standard LDA or generalized gradient approximation (GGA) treatments of exchange-correlation effects. Unfortunately, no such methods are currently available in conjunction with the KKR-CPA method, which allows us to calculate the electronic structure in the presence of multiple defects and Si-Sn alloying effects. Due to this limitation, we employed the LDA in this study.

3. Results and discussion

3.1. Phase separation due to Mg deficiency

Table 1 lists the nominal and measured compositions. Mg was lost during the synthesis at a fraction of 2–10 at. %. The Mg loss increased when the starting Mg content was increased. The XRD results of all samples, except the sample with the highest Mg deficiency (x = 1.8), indicate the formation of a solid solution of $Mg_2(Si,Sn)$. This is indicated by the location of the XRD peaks between those of the references Mg_2Si and Mg_2Sn peaks. In contrast, the x = 1.8 sample has two distinct peaks, indicating unmixed phases (Fig. 1a). An asymmetric (skewed to the left) main XRD peak is observed between 23° and 23.5° in Fig. 1b, as well as an additional shoulder on the left-hand side of this peak in higher-Mg-deficient systems indicate the presence of a Sn-rich $Mg_2(Si,Sn)$ phase in the matrix [25,29]. In principle XRD peak broadening could be due to microstrain in the crystallites and the different sizes of the individual crystallites. However, as visible in the Scherrer equation, these two factors cause the peak shape to remain symmetrical. Hence, the asymmetric shape of the XRD peaks, which could not be distinguished separately, predominantly indicated a mixed phase [29]. Rietveld refinement revealed that the crystal structure might comprise at least two dominant phases. The peak shift toward a lower 2θ value along the Mg deficiency axis indicates an enlargement of the lattice constant (Fig. 1d), suggesting that ternary $Mg_2(Si,Sn)$ contains more Sn [27,36]. As shown in Table 1, the higher the Mg deficiency, the higher the Sn content in the secondary phase, as indicated by the shoulder peak. While all samples show some amount of the Sn-rich secondary phase, we find that this amount increases drastically at $x < 1.8$, indicating a threshold beyond which unmixing is much more relevant. This agrees with the previous investigation, wherein the Mg loss leads to clear phase separation owing to the miscibility gap in the Mg silicide system [25,37]. As shown in Table 1, the highly Mg-deficient samples (x=1.8, 1.9) contain remnant anions in their composition. This remnant Si was confirmed by investigating the elemental distribution through scanning electron microscopy (SEM)/energy-dispersive X-ray spectroscopy (EDS) mapping (Fig. 2 and S3–S6). In addition, a higher content of Sn was observed in the vicinity of the Si islands, suggesting that a Sn-rich phase and Si as a single element coexist. This is supported by the SEM/EDS image shown in Fig. 2, which reveals higher Sn content in the area around the Si islands, where remnants of Si are possibly mixed with the Sn-rich

phase. Conversely, the sample with the highest Mg content (x = 2.3) exhibited a relatively homogeneous distribution (Fig S6). Moreover, the Si islands had no discernible effect on the XRD patterns owing to their highly localized distribution.

3.2. Transport properties in Mg-deficient systems

For all samples, the electrical resistivity decreased with increasing temperature, which is typical behavior of intrinsic semiconductors (Fig. 3a) [38]. However, the resistivity decreased (Fig. 3a) and the carrier concentration increased (Fig. 4b) with increasing Mg deficiency, suggesting that Mg deficiency induces a doping effect. The temperature-dependent Seebeck coefficient indicates that Mg deficiency suppresses the p–n sign transition of the carrier type in the system (Fig. 3b). Given that the sample with the highest excess of Mg (x = 2.3) exhibited a relatively pure intrinsic behavior at 300 K with an n-type Seebeck coefficient [39], it was deduced that Mg deficiency led to the generation of holes in the system and enhancement of the power factor by more than an order of magnitude in relation to that of the less Mg-deficient system (Fig. 3c). Because the electrical TE properties vary with Mg deficiency, the systems can be divided into three categories: stoichiometric (x = 2.3), less deficient (x = 2.2, 2.1), and more deficient (x = 1.9, 1.8) systems. Samples with similar deficiencies show similar behavior presumably because the difference in the total deficiency is not very large. For the measured transport data, an influence of the secondary phase cannot be typically ruled out; however, one can assume that the transport is dominated by the matrix phase, with the secondary phases mainly affecting scattering rates of electrons and phonons [40]. This is supported by the observation that the Seebeck coefficient at low temperatures is within a factor of three for all samples, while the electrical resistivity differs by orders of magnitude.

The temperature had a different effect on the dominant carrier type depending on the degree of Mg deficiency (Fig. 4a). The Hall coefficient drops to zero (inset of Fig. 4a) for the samples with p-n transitions. The Seebeck coefficient sign changed because of a higher mobility of the electrons compared to the holes and the thermal excitation of electron-hole pairs. Essentially, faster electrons overcompensate the initially dominant

holes with increasing thermal excitation, with the degree of compensation (and the temperature of sign change) depending on the initial hole concentration because of the formation of defects (Mg vacancies) [18,39,41,42]. The Hall coefficient is relatively constant for low temperatures in the temperature window where |S| increases, *i.e.*, where transport is still hole dominated. The carrier concentration at 100 K increased as the Mg content decreased (Fig. 4b). The samples with excess Mg (x = 2.3, 2.2, and 2.1) had comparable carrier concentrations. In contrast, the carrier concentration increased slightly when Mg deficiency was relatively high (x = 1.9, 1.8). Mg vacancies (V_{Mg}) are a source of p-type conduction in $Mg_2(Si,Sn)$ systems [41,42]; hence, it is inferred that V_{Mg} contributes significantly to the carrier concentration. To achieve the optimal p-type TE performance suggested by DFT calculations, the carrier concentration must be in a mid-range of 10^{20} cm^{-3} [43,44]. If V_{Mg} can be completely ionized in the unit cell, resulting in two holes per V_{Mg} [41,45], the carrier concentration calculated using the lattice constant via XRD is likely to be on the order of 10^{20} cm^{-3} (Fig. 4b, and detailed in Supplementary Materials). However, the observed contribution was two to three orders of magnitude lower than that expected for the fully ionized case. Also, the $10^{17–18}$ cm^{-3} range corresponds to the carrier concentration of intrinsic n- and p-type Mg silicides [18,39]. The low doping efficiency indicates that additional compensatory factors were present in the system. The ternary $Mg_2(Si,Sn)$ system with a Si:Sn ratio of 3:7 had a negligible p-type conduction probability owing to the presence of a favorable donor, such as interstitial Mg (I_{Mg}), and a relatively high defect-formation energy of V_{Mg}, even under Mg-deficient conditions [17,46]. In previous studies, p-type conduction was eventually observed for ternary $Mg_2(Si,Sn)$ with a Si:Sn ratio of 2:8 under Mg-deficient conditions [17,45]. Theoretical and experimental data suggest that p-type conduction is favorable at a higher Sn content of the $Mg_2(Si,Sn)$ systems [17,44]. Thus, the charge compensation factor must be considered, which is likely the result of defects in the undoped system. Such possible defects include acceptors such as V_{Mg} and donors such as I_{Mg}, as well as the anti-site of an anion on the Mg site (X_{Mg}, *X: Si, Sn*). The calculation of the band structure with three possible defects indicates the charge compensation as the dominant factor. Fig. 5(a) shows the calculated electronic band structure represented in terms of the BSF of $Mg_2Si_{0.3}Sn_{0.7}$, which is the approximate composition of the main phase from the Rietveld

refinement (Table 1). The spectral functions were plotted on a logarithmic scale, where the high intensity of the BSF (black region) represents the position of the band center. In contrast, the color scale shows the band-smearing effect due to scattered and disordered electrons, where the bands gained a finite bandwidth. The stronger the electron scattering, the more smeared the bands and the larger the bandwidth. As discussed in previous studies, local-density-type exchange-correlation functionals tend to underestimate the value of the bandgap, particularly for Sn-rich materials [47,48], in which even a band overlap was observed. This explains why a bandgap close to zero is observed in the investigated samples. For undoped $Mg_2Si_{0.3}Sn_{0.7}$, the Fermi level was located at the valence band maximum (VBM) (Fig. 5a). When the material becomes Mg-deficient due to the formation of V_{Mg}, as illustrated in Fig. 5(b), the Fermi level moves down into the valence band, proving that V_{Mg} can act as a strong acceptor, delivering two holes per vacancy. The shape of the spectral functions did not change significantly, confirming that V_{Mg} behaves as a rigid band dopant, leading only to a shift in the Fermi level with a slightly strengthened band-smearing effect. As already mentioned, if V_{Mg} were the only defect in the material, the carrier concentration would reach 10^{20} cm^{-3} at V_{Mg} concentrations of the order of 1%, contrary to the experimental observations herein. The most likely compensatory factors for V_{Mg} were I_{Mg} and Sn_{Mg}. Fig. 5(c)–(e) illustrates the Fermi level shift in the Mg-deficient system toward the bandgap as a result of additional Sn_{Mg}. This charge compensation effect was accompanied by the non-rigid band-like behavior of Sn_{Mg}, leading to a stronger band-smearing effect and the formation of additional impurity states in the Brillouin zone. The Sn_{Mg} impurity states had a large spectral weight at the X point, growing in k-space with increasing defect concentration (Fig. 5c, d). Owing to the shortcomings of LDA in estimating the bandgap, whether these extra impurity states are, in reality, located parallel to the VBM rather than in the gap cannot be confirmed. The charge donor effect of Sn_{Mg} is much weaker than that of the anti-site defect, which follows the rigid band model. Because of the formation of the additional "cloud" of electronic states of the original bands, the Fermi level slowly shifted toward the VBM; thus, even 5% Sn_{Mg} was insufficient to compensate for 2% V_{Mg} defects. A large amount of Sn_{Mg} (approximately 8% of Sn_{Mg}) was required to compensate for 2% of V_{Mg} (Fig. 5e). Owing to the high Mg deficiency of the present system, the amount of formed I_{Mg} is expected to be much less. Nevertheless,

I_{Mg} atoms are considered an additional source of compensation in the present system, as illustrated in Fig. 5(f). However, I_{Mg} could not effectively compensate for V_{Mg}. The Fermi level remained within the valence band. Thus, we propose that Mg deficiency can induce p-type doping and phase separation, but at the expense of the doping efficiency (*i.e.*, inducing low doping efficiency) owing to charge compensation between V_{Mg} and Sn_{Mg} [29,49].

The application of an appropriate band model can enhance understanding of the impact of Mg deficiency on TE properties. The transport properties in the $Mg_2(Si,Sn)$ samples exhibit in some temperature range the behavior of non-degenerate semiconductors. As shown in Fig. 3(b), the temperature-dependent Seebeck coefficient reveals two distinct regimes in the system: (1) the extrinsic regime and (2) the intrinsic regime, with the latter beginning at 150 K for the sample with the lowest hole concentration (x=2.3) and at 300 K for the samples with the highest Mg deficiency. The intrinsic regime of the transport properties can be identified by the simplified S-ln(σ) plot suggested by G. H. Jonker [50,51]:

$$S = \frac{k_B}{e}\left(b - \ln\sigma\right), \tag{1}$$

where b is the value related with effective mass m^* and carrier mobility μ, such that $b \approx (m^*)^{3/2}\mu$. According to Eq. (1), we can infer that for intrinsic conduction a linear relation between S and log of σ with a slope of $-k_B/e$ is expected. Fig. 3(d) shows that such behavior is observed in all our samples, confirming the presence of an intrinsic transport regime in the temperature range under consideration. In contrast, the SPB model can be employed in cases where S increases with temperature, *i.e.*, below 200 K for most samples as seen in Fig. 3b. By using the SPB model at low temperatures, we can better understand how the transport properties change with Mg deficiency.

Below 200 K, the dominant electron scattering mechanism can be identified by calculating the scattering parameter using galvanomagnetic and thermomagnetic measurements [52–54] within the non-degenerate and parabolic band model [55]. The resulting values of the scattering parameter, r, for the Mg-deficient samples are found to be close to zero (Fig. S2), indicating that the primary scattering sources for the charge carriers are acoustic phonons and alloy scattering (r = 0) below 200 K [18]. Thus, we analyzed other transport properties

using the SPB model with the assumption that the dominant scattering factors are acoustic phonons and alloy scattering [45,56]. The transport data based on the SPB model when r = 0 are described below [18] and the results of the calculations using Eqs. 2–5 are listed in Table 2.

$$\alpha = \pm \frac{k_B}{e}\left[\eta - \frac{2F_1(\eta)}{F_0(\eta)}\right], \tag{2}$$

$$F_i(\eta) = \int_0^\infty \frac{x^i}{1+\exp(x-\eta)}\,dx, \tag{3}$$

$$\eta = \frac{E_F}{k_B T}, \tag{4}$$

$$L = \left(\frac{k_B}{T}\right)^2 \left[\frac{3F_2(\eta)}{F_0(\eta)} - \left(\frac{2F_1(\eta)}{F_0(\eta)}\right)^2\right], \tag{5}$$

where η is the reduced Fermi level and h is the Planck's constant. The η of the samples with higher Mg deficiency (x = 1.8, 1.9) has a positive value, indicating that transport could be conducted inside the band, whereas the η of the relatively homogeneous samples (x = 1.9, 2.1, 2.2) has a negative value, indicating that the Fermi level should be on the band gap. In contrast, the previously studied Li-doped $Mg_2(Si,Sn)$ system has an η value of $\geq$ 2.3, indicating efficient doping [18]. The η indicates that the developed systems are minimally affected by defects or impurities, which may be due to compensatory defects. It is also inferred that the change in η may follow the volume fraction of the secondary phase (Tables 1 and 2), indicating that p-type transport behavior may also be strongly affected by the secondary phase. These negative η values are also in good agreement with the electrical transport properties at low temperatures (Figs. 3 a and b). At relatively high temperatures, near room temperature (~300 K), the Seebeck coefficient shows that the transport property is not governed by a SPB, and minority carriers must be taken into account. This effect could be presented by the almost zero bandgap of the Mg-deficient $Mg_2(Si,Sn)$ system (Fig. 5). Thus, our system, which can have an impurity band at the X point, thereby reducing the band gap, can induce an early bipolar effect. However, the electrical TE properties of the Mg-deficient system did not match those of the two-band model, which showed a large deviation between the experimental and fitting data at 400 K [57]. Hence, the transport properties may be

strongly affected by the secondary phase or other unknown reasons, at least in terms of the electrical properties. The transport properties observed in the investigated samples may originate from the multi-phase and non-rigid band behavior. Considering the carrier concentration of $\leq 10^{17}$ cm^{-3} and the possible defects in the system, we inferred that the multiple defects caused by the probability of a higher-order perturbation lead to the distortion of the band structure [58–60] as the phase inhomogeneity increases, where Mg deficiency in the system (Fig. 1c) or an anion on the Mg site causes the electronic band structure to become non-rigid like a band (Fig. 5f).

3.3. Thermal conductivity and early bipolar contribution

The lattice thermal conductivity was determined by combining the Wiedemann–Franz law, $\kappa_e = L\sigma T$, and the Lorentz number from Eq. (5). Owing to the low carrier concentration, all samples had negligible electrical charge contributions of ≤ 0.5% of the total thermal conductivity (Fig. 6a). This indicated that phonons are responsible for most of the thermal energy transfer [55]. Regardless of the electrical contribution, the thermal conductivity was 40%–50% lower than that of the Li-doped Mg_2(Si, Sn) system [18,56] and other Mg_2(Si, Sn) systems, including the intrinsic system [39]. The low thermal conductivity could be a result of both alloy scattering and additional scattering due to the phase separation caused by Mg deficiency, granular morphology, and presence of Si impurities, which might exert energy-filtering effects and impart of interfacial resistance (Fig. 2 and S3–S6) [61–63]. It is observed that thermal conductivity generally reduces with increasing Mg deficiency. Given that the measured densities of all samples are ≥ 96% of the theoretical densities (Table S2), the reduction of thermal conductivity with increasing Mg deficiency could be attributed to the enhanced degree of phase separation and the increased number of intrinsic defects. To confirm the effect of Mg deficiency on thermal conductivity, the Klemens-Callaway model was considered [64,65]. The lattice thermal conductivity can be expressed as follows:

$$\kappa_L = \frac{1}{3}\int_0^{\omega_{\max}} C_p(\omega) v_g(\omega)^2 \tau(\omega) d\omega, \quad (6)$$

where, ω is the phonon frequency, C_P is the heat capacity, v_g is the group velocity, and τ is the relaxation time.

With an assumption that deviations of C_P and v_g are negligible between the samples, the effect of τ with varying degree of Mg deficiency on the lattice thermal conductivity can be considered. τ can be expressed by Matthiessen's rule, $\tau_{total}^{-1} = \sum_i \tau_i^{-1}$, where i represents a type of scattering mechanism. In our samples, boundary scattering, Umklapp scattering, and point defect scattering can be considered. Assuming that τ of boundary scattering and Umklapp scattering are comparable between the samples at a given temperature, the scattering rate for point defect scattering can be expressed as below [65]:

$$\tau_{PD}^{-1} = \frac{V_0 \Gamma \omega^4}{4\pi v_p^2(\omega) v_g(\omega)}, \quad (7)$$

where V_0 is the volume per atom, v_p is the phase velocity, and Γ is the scattering parameter. Γ is affected by the mass difference between each elemental site, which also includes the case in which an atomic vacancy exists [65]. Because the atomic vacancies in our system are largely determined by Mg deficiency, we can conclude that the lattice thermal conductivity is a function of the degree of Mg deficiency at a given temperature. The inset of Fig. 6(a) shows that there is a strong correlation between Mg deficiency and lattice thermal conductivity, suggesting the dominant contribution of point defect scattering to thermal conductivity reduction in the Mg deficient systems.

Temperature-dependent thermal conductivity typically increases exponentially above 500 K because of the bipolar effect induced by the thermal excitation of the $Mg_2(Si,Sn)$ system in the intrinsic regime [36,39]. However, the thermal conductivity of the Mg-deficient system increased slightly over the entire temperature range (even below 100 K), whereas the excess Mg system with no lattice elongation in its crystalline structure exhibited a temperature-dependent reduction of thermal conductivity. This is because excess Mg did not affect the lattice as the composition was relatively stoichiometric. Because of the effects of Mg deficiency on the lattice constant and band structure, an early bipolar contribution to the thermal conductivity was induced, which could be attributed to the reduced bandgap [66] caused by the formation of multiple point defects V_{Mg} and Sn_{Mg}.

3.4. Dimensionless figure-of-merit, zT

The temperature dependence of zT (Fig. 6b) varied with the Mg content. The second most Mg-deficient $Mg_2(Si,Sn)$ sample had the largest zT value among the intrinsic level systems. The results indicate that controlling Mg content, as a factor governing both electronic band structure and phase separation, can effectively improve TE performance. Mg deficiency can lower thermal conductivity by causing increased phonon scattering and altering the electronic band structure. However, it may result in charge compensation due to multiple defects.

4. Conclusions

Changes and trends in the TE properties of Mg-deficient $Mg_2(Si,Sn)$ solid solutions were investigated. Mg deficiency can induce unmixing and the formation of a second phase which has a higher Sn content than the main phase. Mg deficiency also causes p-type conduction in the material system owing to the formation of charged defects such as V_{Mg}. However, we observed that Mg deficiency allows inefficient doping, probably because of the formation of compensating defects such as X_{Mg}. Non-rigid band-like deformation and possible defects due to Mg deficiency were confirmed via DFT-based electronic band structure calculations. All Mg-deficient samples were p-type at low temperatures with a carrier concentration range of 10^{18} cm^{-3}, while they showed mixed conduction at higher temperatures. Moreover, the additional impurity electronic states around the X point could be responsible for the early bipolar contribution to the thermal conductivity, despite the fact that the deformed lattice resulted in the thermal conductivity that was approximately half that of a previously studied system. Because the Mg content of the $Mg_2(Si,Sn)$ system could affect the impurity state in the band structure and induce an extremely low thermal conductivity of 1–1.5 W/m·K, the Mg content should be carefully controlled to maximize the doping efficiency and phonon scattering in the $Mg_2(Si,Sn)$ system. As a future work, searching for a more efficient dopant in the Mg-deficient $Mg_2(Si,Sn)$ system could effectively enhance p-type TE properties.

Author Contributions

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Conflicts of Interest

There are no conflicts to declare.

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References

[1] J. Mao, G. Chen, Z. Ren, Thermoelectric cooling materials, Nat. Mater. 20 (2021) 454–461. https://doi.org/10.1038/s41563-020-00852-w.

[2] F. Tohidi, S. Ghazanfari Holagh, A. Chitsaz, Thermoelectric Generators: A comprehensive review of characteristics and applications, Appl. Therm. Eng. 201 (2022) 117793. https://doi.org/10.1016/j.applthermaleng.2021.117793.

[3] H. Mamur, M.A. Üstüner, H. Korucu, M.R.A. Bhuiyan, A review of the performance evaluation of thermoelectric nanostructure materials $Bi_{2-x}Sb_xTe_3$ ($0.20 \leq X \leq 1.80$), Clean. Chem. Eng. 6 (2023) 100101. https://doi.org/10.1016/j.clce.2023.100101.

[4] Y. Saberi, S.A. Sajjadi, A comprehensive review on the effects of doping process on the thermoelectric properties of Bi_2Te_3 based alloys, J. Alloys Compd. 904 (2022) 163918. https://doi.org/10.1016/j.jallcom.2022.163918.

[5] B. Jia, Y. Huang, Y. Wang, Y. Zhou, X. Zhao, S. Ning, X. Xu, P. Lin, Z. Chen, B. Jiang, J. He, Realizing high thermoelectric performance in non-nanostructured n-type PbTe, Energy Environ. Sci. (2022) 1920–1929. https://doi.org/10.1039/d1ee03883d.

[6] M. Wu, H. Cui, S. Cai, S. Hao, Y. Liu, T.P. Bailey, Y. Zhang, Z. Chen, Y. Luo, C. Uher, C. Wolverton, V.P. Dravid, Y. Yu, Z. Luo, Z. Zou, Q. Yan, M.G. Kanatzidis, Weak Electron–Phonon Coupling and Enhanced Thermoelectric Performance in n-type PbTe–Cu_2Se via Dynamic Phase Conversion, Adv. Energy Mater. 13 (2023) 2203325. https://doi.org/10.1002/aenm.202203325.

[7] Y. Jiang, L. Na, H. Ma, HPHT synthesis and enhanced thermoelectric transport properties of double-doped $Co_4Sb_{11}Te_xSn_{1-x}$ skutterudites, J. Alloys Compd. 894 (2022) 4–10. https://doi.org/10.1016/j.jallcom.2021.162426.

[8] B. Wang, H. Jin, W. Yi, J. Chen, J. Li, Y. Zhao, J. Li, Ni substitution improves the high-temperature thermoelectric performance of electronegative element Se-filled skutterudite $Se_{0.05}Ni_xCo_{4-x}Sb_{12}$, J. Alloys Compd. 909 (2022) 164733. https://doi.org/10.1016/j.jallcom.2022.164733.

[9] Y. Wang, X. Zhang, Y. Wang, N. Liu, Y. Liu, Q. Lu, High thermoelectric performance of nanostructured Mg_3Sb_2 on synergistic Te-doping and Mg/Y interstitial, J. Mater. Sci. 57 (2022) 3183–3192. https://doi.org/10.1007/s10853-021-06797-y.

[10] J. Li, S. Zhang, K. Han, B. Sun, L. Cao, Large improvement in thermoelectric performance of pressure-tuned Mg_3Sb_2, RSC Adv. 12 (2022) 1149–1156. https://doi.org/10.1039/d1ra08930g.

[11] Y. Zhou, X. Liu, B. Jia, T. Ding, D. Mao, T. Wang, G.W. Ho, J. He, Physics-guided co-designing

flexible thermoelectrics with techno-economic sustainability for low-grade heat harvesting, Sci. Adv. 9 (2023) 1–11. https://doi.org/10.1126/sciadv.adf5701.

[12] R. Freer, D. Ekren, T. Ghosh, K. Biswas, P. Qiu, S. Wan, L. Chen, S. Han, C. Fu, T. Zhu, A.K.M. Ashiquzzaman Shawon, A. Zevalkink, K. Imasato, G.J. Snyder, M. Ozen, K. Saglik, U. Aydemir, R. Cardoso-Gil, E. Svanidze, R. Funahashi, A. V Powell, S. Mukherjee, S. Tippireddy, P. Vaqueiro, F. Gascoin, T. Kyratsi, P. Sauerschnig, T. Mori, Key properties of inorganic thermoelectric materials—tables (version 1), J. Phys. Energy. 4 (2022) 022002. https://doi.org/10.1088/2515-7655/ac49dc.

[13] G.S. Polymeris, E. Hatzikraniotis, T. Kyratsi, Highly efficient Mg_2Si-based thermoelectric materials: A review on the micro- and nanostructure properties and the role of alloying, in: Thermoelectr. Energy Convers., Elsevier, 2021: pp. 429–466. https://doi.org/10.1016/B978-0-12-818535-3.00015-3.

[14] W. Liu, X. Tan, K. Yin, H. Liu, X. Tang, J. Shi, Q. Zhang, C. Uher, Convergence of conduction bands as a means of enhancing thermoelectric performance of n-type $Mg_2Si_{1-x}Sn_x$ solid solutions, Phys. Rev. Lett. 108 (2012) 1–5. https://doi.org/10.1103/PhysRevLett.108.166601.

[15] D. Shiojiri, T. Iida, H. Kakio, M. Yamaguchi, N. Hirayama, Y. Imai, Enhancement of thermoelectric performance of Mg_2Si via co-doping Sb and C by simultaneous tuning of electronic and thermal transport properties, J. Alloys Compd. 891 (2022) 161968. https://doi.org/10.1016/j.jallcom.2021.161968.

[16] J. Ju, K. Yin, M. Fang, H. Cai, H. Liu, Effect of Bi doping on the thermoelectric properties of $Mg_2Si_{0.3}Ge_{0.04}Sn_{0.66}$ compound, J. Mater. Res. Technol. 18 (2022) 3520–3525. https://doi.org/10.1016/j.jmrt.2022.04.043.

[17] B. Ryu, E.A. Choi, S. Park, J. Chung, J. de Boor, P. Ziolkowski, E. Müller, S.D. Park, Native point defects and low p-doping efficiency in $Mg_2(Si,Sn)$ solid solutions: A hybrid-density functional study, J. Alloys Compd. 853 (2021) 157145. https://doi.org/10.1016/j.jallcom.2020.157145.

[18] H. Kamila, P. Sahu, A. Sankhla, M. Yasseri, N.H. Pham, T. Dasgupta, E. Mueller, J. de Boor, Analyzing transport properties of p-type Mg_2Si-Mg_2Sn solid solutions: Optimization of thermoelectric performance and insight into the electronic band structure, J. Mater. Chem. A. 7 (2019) 1045–1054.

https://doi.org/10.1039/C8TA08920E.

[19] I. Assahsahi, B. Popescu, R. El Bouayadi, D. Zejli, M. Enculescu, A. Galatanu, Thermoelectric properties of p-type $Mg_2Si_{0.3}Sn_{0.7}$ doped with silver and gallium, J. Alloys Compd. 944 (2023) 169270. https://doi.org/10.1016/J.JALLCOM.2023.169270.

[20] H. Kamila, B. Ryu, S. Ayachi, A. Sankhla, E. Mueller, J. De Boor, Understanding the dopability of p-type Mg_2(Si,Sn) by relating hybrid-density functional calculation results to experimental data, J. Phys. Energy. 4 (2022). https://doi.org/10.1088/2515-7655/ac689d.

[21] Z. Huang, K. Hayashi, W. Saito, J. Pei, J.-F. Li, Y. Miyazaki, Enhanced thermoelectric performance of p-type Mg_2Sn single crystals via multi-scale defect engineering, J. Mater. Chem. A. 11 (2023) 2652–2660. https://doi.org/10.1039/D2TA08557G.

[22] K. Hayashi, Enhancement of thermoelectric performance of Mg_2Sn single crystals via lattice-defect engineering JSAP Review, JSAP Rev. (2022) 1–6. https://doi.org/doi.org/10.11470/oubutsu.91.5_271.

[23] M.Y. Toriyama, M.K. Brod, G.J. Snyder, Chemical Interpretation of Charged Point Defects in Semiconductors: A Case Study of Mg2Si, ChemNanoMat. 8 (2022). https://doi.org/10.1002/cnma.202200222.

[24] A. Sankhla, H. Kamila, H. Naithani, E. Mueller, J. de Boor, On the role of Mg content in Mg_2(Si,Sn): Assessing its impact on electronic transport and estimating the phase width by in situ characterization and modelling, Mater. Today Phys. 21 (2021) 100471. https://doi.org/10.1016/j.mtphys.2021.100471.

[25] M. Yasseri, K. Mitra, A. Sankhla, J. de Boor, E. Müller, Influence of Mg loss on the phase stability in Mg_2X (X = Si, Sn) and its correlation with coherency strain, Acta Mater. 208 (2021) 116737. https://doi.org/10.1016/j.actamat.2021.116737.

[26] Z. Huang, K. Hayashi, W. Saito, Y. Miyazaki, Realizing p-type Mg_2Sn Thermoelectrics via Ga-Doping and Point Defect Engineering , ACS Appl. Energy Mater. (2021). https://doi.org/10.1021/acsaem.1c02678.

[27] W. Saito, K. Hayashi, Z. Huang, K. Sugimoto, K. Ohoyama, N. Happo, M. Harada, K. Oikawa, Y.

Inamura, K. Hayashi, T. Miyazaki, Y. Miyazaki, Chemical-pressure-induced point defects enable low thermal conductivity for Mg_2Sn and Mg_2Si single crystals, ACS Appl. Energy Mater. 4 (2021) 5123–5131. https://doi.org/10.1021/acsaem.1c00670.

[28] G. Jiang, J. He, T. Zhu, C. Fu, X. Liu, L. Hu, X. Zhao, High performance $Mg_2(Si,Sn)$ solid solutions: A point defect chemistry approach to enhancing thermoelectric properties, Adv. Funct. Mater. 24 (2014) 3776–3781. https://doi.org/10.1002/adfm.201400123.

[29] M. Yasseri, A. Sankhla, H. Kamila, R. Orenstein, D.Y.N. Truong, N. Farahi, J. de Boor, E. Mueller, Solid solution formation in $Mg_2(Si,Sn)$ and shape of the miscibility gap, Acta Mater. 185 (2020) 80–88. https://doi.org/10.1016/j.actamat.2019.11.054.

[30] D. Kato, K. Iwasaki, M. Yoshino, T. Yamada, T. Nagasaki, Control of Mg content and carrier concentration via post annealing under different Mg partial pressures for Sb-doped Mg_2Si thermoelectric material, J. Solid State Chem. 258 (2018) 93–98. https://doi.org/10.1016/j.jssc.2017.10.003.

[31] M. Kubouchi, K. Hayashi, Y. Miyazaki, Quantitative analysis of interstitial Mg in Mg_2Si studied by single crystal X-ray diffraction, J. Alloys Compd. 617 (2014) 389–392. https://doi.org/10.1016/j.jallcom.2014.07.137.

[32] S.Y. Purwaningsih, N. Rosidah, M. Zainuri, T. Triwikantoro, S. Pratapa, D. Darminto, Comparation of X-ray diffraction pattern refinement using Rietica and MAUD of ZnO nanoparticles and nanorods, J. Phys. Conf. Ser. 1153 (2019). https://doi.org/10.1088/1742-6596/1153/1/012070.

[33] H. Ebert, The Munich SPR-KKR package, (2022).

[34] H. Ebert, D. Ködderitzsch, J. Minár, Calculating condensed matter properties using the KKR-Green's function method - Recent developments and applications, Reports Prog. Phys. 74 (2011). https://doi.org/10.1088/0034-4885/74/9/096501.

[35] P. Zwolenski, J. Tobola, S. Kaprzyk, A theoretical search for efficient dopants in Mg_2X (X = Si, Ge, Sn) thermoelectric materials, J. Electron. Mater. 40 (2011) 889–897. https://doi.org/10.1007/s11664-011-1624-y.

[36] W. Saito, K. Hayashi, J. Dong, J.F. Li, Y. Miyazaki, Control of the Thermoelectric Properties of Mg_2Sn Single Crystals via Point-Defect Engineering, Sci. Rep. 10 (2020) 1–9. https://doi.org/10.1038/s41598-020-58998-1.

[37] S. Tumminello, S. Ayachi, S.G. Fries, E. Müller, J. de Boor, Applications of thermodynamic calculations to practical TEG design: $Mg_2(Si_{0.3}Sn_{0.7})$/Cu interconnections, J. Mater. Chem. A. 9 (2021) 20436–20452. https://doi.org/10.1039/d1ta05289f.

[38] S. Wiliam, Electrons and holes in semiconductors with applications to transistor electronics, 7th ed., D. Van Nostrand Company, Inc., Princeton, New jersey, 1950.

[39] Y. Isoda, S. Tada, T. Nagai, H. Fujiu, Y. Shinohara, Thermoelectric properties of p-type $Mg_{2.00}Si_{0.25}Sn_{0.75}$ with Li and Ag double doping, J. Electron. Mater. 39 (2010) 1531–1535. https://doi.org/10.1007/s11664-010-1280-7.

[40] D.J. Bergman, O. Levy, Thermoelectric properties of a composite medium, J. Appl. Phys. 70 (1991) 6821–6833. https://doi.org/10.1063/1.349830.

[41] J. de Boor, T. Dasgupta, U. Saparamadu, E. Müller, Z.F. Ren, Recent progress in p-type thermoelectric magnesium silicide based solid solutions, Mater. Today Energy. 4 (2017) 105–121. https://doi.org/10.1016/j.mtener.2017.04.002.

[42] W. Liu, X. Tang, H. Li, J. Sharp, X. Zhou, C. Uher, Optimized thermoelectric properties of Sb-doped $Mg_{2(1+z)}Si_{0.5-y}Sn_{0.5}Sb_y$ through adjustment of the Mg content, Chem. Mater. 23 (2011) 5256–5263. https://doi.org/10.1021/cm202445d.

[43] J.H. Bahk, Z. Bian, A. Shakouri, Electron transport modeling and energy filtering for efficient thermoelectric $Mg_2Si_{1-x}Sn_x$ solid solutions, Phys. Rev. B - Condens. Matter Mater. Phys. 89 (2014) 1–13. https://doi.org/10.1103/PhysRevB.89.075204.

[44] P. Zwolenski, J. Tobola, S. Kaprzyk, KKR-CPA study of electronic structure and relative stability of Mg_2X (X = Si, Ge, Sn) thermoelectrics containing point defects, J. Alloys Compd. 627 (2015) 85–90. https://doi.org/10.1016/j.jallcom.2014.11.131.

[45] W. Liu, H. Chi, H. Sun, Q. Zhang, K. Yin, X. Tang, Q. Zhang, C. Uher, Advanced thermoelectrics governed by a single parabolic band: $Mg_2Si_{0.3}Sn_{0.7}$, a canonical example, Phys. Chem. Chem. Phys. 16 (2014) 6893–6897. https://doi.org/10.1039/c4cp00641k.

[46] X. Liu, L. Xi, W. Qiu, J. Yang, T. Zhu, X. Zhao, W. Zhang, Significant Roles of Intrinsic Point Defects in Mg_2X (X = Si, Ge, Sn) Thermoelectric Materials, Adv. Electron. Mater. 2 (2016) 1–10. https://doi.org/10.1002/aelm.201500284.

[47] J. Bourgeois, J. Tobola, B. Wiendlocha, L. Chaput, P. Zwolenski, D. Berthebaud, F. Gascoin, Q. Recour, H. Scherrer, Study of electron, phonon and crystal stability versus thermoelectric properties in Mg_2X (X = Si, Sn) compounds and their alloys, Funct. Mater. Lett. 6 (2013) 1–14. https://doi.org/10.1142/S1793604713400055.

[48] K. Kutorasinski, B. Wiendlocha, J. Tobola, S. Kaprzyk, Importance of relativistic effects in electronic structure and thermopower calculations for Mg_2Si, Mg_2Ge, and Mg_2Sn, Phys. Rev. B. 89 (2014) 1–8. https://doi.org/10.1103/PhysRevB.89.115205.

[49] L. Chen, G. Jiang, Y. Chen, Z. Du, X. Zhao, T. Zhu, J. He, T.M. Tritt, Miscibility gap and thermoelectric properties of ecofriendly $Mg_2Si_{1-x}Sn_x$ ($0.1 \leq x \leq 0.8$) solid solutions by flux method, J. Mater. Res. 26 (2011) 3038–3043. https://doi.org/10.1557/jmr.2011.385.

[50] G.H. Jonker, The application of combined conductivity and Seebeck-effect plot for the analysis of semiconductor properties, Philips Res. Reports. 23 (1968) 131–138.

[51] D.M. Rowe, G. Min, α-ln σ plot as a thermoelectric material performance indicator, J. Mater. Sci. Lett. 14 (1995) 617–619. https://doi.org/10.1007/BF00586157.

[52] H. Jin, J.P. Heremans, Optimization of the figure of merit in $Bi_{100-x}Sb_x/Al_2O_3$ nanocomposites, Phys. Rev. Mater. 2 (2018) 115401. https://doi.org/10.1103/PhysRevMaterials.2.115401.

[53] W. Zawadzki, Thermomagnetic effects in semiconductors, Phys. Status Solidi. 2 (1962) 385–410. https://doi.org/10.1002/pssb.19620020404.

[54] C.M. Crawford, E.A. Bensen, H.A. Vinton, E.S. Toberer, Efficacy of the Method of Four Coefficients to

Determine Charge-Carrier Scattering, Phys. Rev. Appl. 16 (2021) 1. https://doi.org/10.1103/PhysRevApplied.16.024004.

[55] S. Sunil Narayan, The Hall and Nernst effect in Bi and Bi-Sb alloys, RICE University, 1967.

[56] Q. Zhang, L. Cheng, W. Liu, Y. Zheng, X. Su, H. Chi, H. Liu, Y. Yan, X. Tang, C. Uher, Low effective mass and carrier concentration optimization for high performance p-type $Mg_{2(1-x)}Li_{2x}Si_{0.3}Sn_{0.7}$ solid solutions, Phys. Chem. Chem. Phys. 16 (2014) 23576–23583. https://doi.org/10.1039/c4cp03468f.

[57] H. Naithani, E. Müller, J. de Boor, Developing a two-parabolic band model for thermoelectric transport modelling using Mg_2Sn as an example, J. Phys. Energy. 4 (2022) 045002. https://doi.org/10.1088/2515-7655/ac7fb8.

[58] R.H. Parmenter, Symmetry Properties of the Energy Bands of the Zinc Blende Structure, Phys. Rev. 100 (1955) 573–579.

[59] G. Dresselhaus, Spin-Orbit Coupling Effects in Zinc Blende Structures, Phys. Rev. 100 (1955) 580–586.

[60] E.O. Kane, Band structure of indium antimonide, J. Phys. Chem. Solids. 1 (1957) 249–261. https://doi.org/http://dx.doi.org/10.1016/0022-3697(57)90013-6.

[61] B. Xu, T. Feng, M.T. Agne, L. Zhou, X. Ruan, G.J. Snyder, Y. Wu, Highly Porous Thermoelectric Nanocomposites with Low Thermal Conductivity and High Figure of Merit from Large-Scale Solution-Synthesized $Bi_2Te_{2.5}Se_{0.5}$ Hollow Nanostructures, Angew. Chemie Int. Ed. 56 (2017) 3546–3551. https://doi.org/10.1002/anie.201612041.

[62] B. Xu, T. Feng, Z. Li, S.T. Pantelides, Y. Wu, Constructing Highly Porous Thermoelectric Monoliths with High-Performance and Improved Portability from Solution-Synthesized Shape-Controlled Nanocrystals, Nano Lett. 18 (2018) 4034–4039. https://doi.org/10.1021/acs.nanolett.8b01691.

[63] H. Ning, G.D. Mastrorillo, S. Grasso, B. Du, T. Mori, C. Hu, Y. Xu, K. Simpson, G. Maizza, M.J. Reece, Enhanced thermoelectric performance of porous magnesium tin silicide prepared using pressure-less spark plasma sintering, J. Mater. Chem. A. 3 (2015) 17426–17432. https://doi.org/10.1039/C5TA03473F.

[64] J. Callaway, Model for lattice thermal conductivity at low temperatures, Phys. Rev. 113 (1959) 1046–

1051. https://doi.org/10.1103/PhysRev.113.1046.

[65] R. Gurunathan, R. Hanus, M. Dylla, A. Katre, G.J. Snyder, Analytical Models of Phonon-Point-Defect Scattering, Phys. Rev. Appl. 13 (2020) 1. https://doi.org/10.1103/PhysRevApplied.13.034011.

[66] W. Shockley, J. Bardeen, Energy bands and mobilities in monatomic semiconductors, Phys. Rev. 77 (1950) 407–408. https://doi.org/10.1103/PhysRev.77.407.