Eco-friendly high-performance silicide thermoelectric materials

Wei Liu¹, Kang Yin¹, Qingjie Zhang¹,*, Ctirad Uher²,*, and Xinfeng Tang¹, *

ABSTRACT

Silicide-based thermoelectrics are examples of cost-efficient and environmentally friendly new energy materials, which can be used for power-generation applications in the range of 500–800 K. We review the research focusing on the exploration of n-type Mg₂IV-based solid solutions (IV = Si, Ge and Sn) and summarize the most prominent discoveries achieved so far in their studies. Owing to their superior performance compared to other silicides, including p-type Mg₂IV, higher manganese silicides (HMS) are commonly considered as a suitable p-type material to be used in thermoelectric modules in conjunction with n-type Mg₂IV-based solid solutions for mid-temperature power-generation applications. We describe the strategies used to improve the thermal and electronic transport properties of n-type Mg₂IV-based solid solutions and mention some key features of HMS. We also point out the importance of mechanical properties and thermal stability of this family of materials and offer perspectives on the future research work to further improve their performance.

Keywords: silicides, band convergence, carrier doping, composition manipulation, mechanical properties, thermal stability

INTRODUCTION

Thermoelectric (TE) energy conversion, which can achieve the direct and reversible conversion between heat and electricity, provides for a wide range of applications in the area of waste-heat recovery, refrigeration and high-precision temperature control [1,2]. Hence, TE materials present an important alternative for the effective use of energy and, as such, have attracted much attention in the field of renewable energy technologies. The efficiency of TE energy conversion η is critically dependent on the dimensionless figure of merit ZT, defined as $ZT = S^2 \sigma T / \kappa$, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $T$ is the absolute temperature and $\kappa$ is the thermal conductivity. The term $S^2 \sigma$ is known as the power factor (PF), while the total thermal conductivity, $\kappa = \kappa_e + \kappa_l + \kappa_{\text{bi}}$, includes contributions from the electronic ($\kappa_e$), lattice ($\kappa_l$) and bipolar($\kappa_{\text{bi}}$) heat conduction [3]. In order to achieve high ZT and $\eta$, TE materials should possess high $S$ for large power output, high $\sigma$ for reduced Joule heat loss and low $\kappa$ for maintaining a large temperature gradient [4].

In the past two decades, several strategies have been explored to improve the PF and reduce the lattice thermal conductivity so that the ZT could be enhanced. Among them, concepts such as phonon-glass-electron-crystal [5–8], carrier doping [9–11], nanostructuring [12–17], modulation doping [18–21], electron-energy filtering [22–24], band-structure engineering [25–28], quantum confinement effects [29–31] and band convergence [32,33] were found particularly useful. The above strategies led to the development of several classes of thermoelectric materials with ZT values exceeding the previously difficult-to-attain value of unity. They include modified PbTe-based materials [34], SnTe-based materials [35–39], Bi₂Te₃-based materials [12,40], skutterudites [8,41], Mg₂IV (IV = Si, Ge and Sn)-based systems [33,42,43], half-Heusler alloys [44,45], Si₁₋ₓGeₓ alloys [20], clathrates [46] and Zintl phase materials [47], all with readily reproducible ZT > 1.0. Most recently, new physical concepts and synergistically applied strategies have resulted in the development of state-of-the-art materials having ZT > 1.5. Examples include superionic...
Cu$_2$Se [48], all-scale hierarchical structures based on PbTe [49], SnSe with its strongly anharmonic and anisotropic lattice bonding [9,50,51], as well as CoSb$_3$, having multiple electronic carrier pockets at the Fermi level [8,52]. From the practical-application aspects, TE materials should be thermally stable at their intended operational temperature, and should be synthesized from chemical elements that are cheap, earth-abundant and environmentally friendly. From this perspective, several aforementioned families of materials may not be attractive for large-scale applications, especially if they contain rather rare and expensive Te or environmentally objectionable and poisonous Pb.

Silicide-based TE materials, consisting of earth-abundant and non-toxic elements, have attracted sustained attention for their potential power-generation applications in the temperature range of 500–800 K. Among all semiconducting silicides, Mg$_2$IV-based materials and higher manganese silicides (HMS) are the most popular choices due to their promising n-type and p-type TE performance, respectively. Currently, the highest ZT values obtained with the n-type and p-type Mg$_2$IV-based materials near 800 K are about 1.5 and 0.7, respectively [53,54], while the highest ZT obtained with the p-type HMS is close to unity [55–57]. The charge-carrier concentration of most of these silicides can be tuned to the ideal level through appropriate doping, leading to significantly enhanced electronic properties and, hence, the ZTs. New synthesis methods promoting improved TE performance as well as simplified and more economically viable batch production, such as melt spinning [58], self-propagating high-temperature synthesis (SHS) [59] and ball milling [60] have proved very effective.

In Mg$_2$IV, the isovalent substitution of Si by Ge and/or Sn results in the formation of ternary and/or quaternary solid solutions, leading to remarkably reduced values of $\kappa_L$ and modified electronic transport [61]. Adjusting the Si/Ge/Sn ratio in Mg$_2$IV also modifies the electronic band structure of the material and, more specifically, gives rise to a convergence of the two nearby-lying conduction bands [33,62]. Consequently, the outstanding ZT values in n-type Mg$_2$IV are due to synergistic benefits arising from alloy scattering yielding a reduced $\kappa_L$, from optimized carrier doping promoting high values of $\sigma$ and from band convergence resulting in enhanced values of the Seebeck coefficient $S$.

In this review paper, n-type Mg$_2$IV-based materials were chosen as a representative family of silicides on which to illustrate the effectiveness of various strategies to optimize the TE performance. Specifically, this review paper summarizes the most prominent research results obtained so far with n-type Mg$_2$IV-based materials, and includes topics such as the synthesis method, the band-structure-engineering approach, the optimal carrier doping, as well as the more technologically relevant issues, such as the mechanical properties and the thermal stability. We also provide a brief account of the basic properties of HMS.

**SYNTHESIS OF Mg$_2$IV-BASED SOLID SOLUTIONS**

Mg$_2$IV (IV = Si, Ge and Sn)-based materials all crystallize in the antifluorite structure (cubic, space group Fm-3 m), where IV$^{4+}$ ions occupy the face-centered cubic sites and Mg$^{2+}$ ions fill in the center of tetrahedrons formed by IV$^{4+}$ ions [63]. Due to the same crystal structure and the very close lattice parameter, Mg$_2$Si, Mg$_2$Ge and Mg$_2$Sn can form solid solutions among each other. Continuous solid solutions exist in the entire composition range of the Mg$_2$Si$_{1-x}$Ge$_x$ system [64]. However, solid solutions have a limited composition range in the Mg$_2$Si$_{1-x}$Sn$_x$ and Mg$_2$Ge$_{1-y}$Sn$_y$ systems. In Mg$_2$Si$_{1-x}$Sn$_x$, solid solutions are believed to form only for $x < 0.4$ and $x > 0.6$, while, in Mg$_2$Ge$_{1-y}$Sn$_y$, the range of solid solubility is estimated to cover compositions with $y < 0.3$ and $y > 0.8$ [65,66]. Thus, the preparation of Sn-based solid solutions is rather difficult and is strongly dependent on the composition and temperature.

This section will focus on the preparation of Sn-based solid solutions, i.e. ternary Mg$_2$Si$_{1-x}$Sn$_x$ and Mg$_2$Ge$_{1-y}$Sn$_y$ as well as quaternary Mg$_2$Si$_{1-x}$Ge$_y$Sn$_z$, due to their excellent TE performance. These Sn-based solid solutions possess a superior TE performance to Mg$_2$Si$_{1-x}$Ge$_y$, which is due to some favorable features in the band structure and a greater mass contrast between Si and Sn than between Si and Ge, resulting in a lower lattice thermal conductivity [67]. Various synthesis processes to prepare bulk Mg$_2$IV-based materials have been developed since the 1950s, each with their own advantages and a scope of applications. Table 1 summarizes several typical synthesis methods used to prepare bulk Mg$_2$IV-based materials. In general, successful preparation of binary Mg$_2$IV should avoid phase non-uniformity in the final product due to insufficiently reacted constituent elements, while, in addition to this requirement, the fabrication of Sn-based ternary and quaternary solid solutions requires an appropriate annealing temperature and holding time to promote the formation of a solid solution between the binary components. Another challenge to obtaining ideal Mg$_2$IV-based
materials is the high vapor pressure and reactivity of elemental Mg at elevated temperatures, which may lead to non-stoichiometric compositions and the formation of MgO impurities in the material [68].

Melting methods, as the traditional approach, are often employed for the synthesis of Mg,IV-based materials. Yoshinaga et al. [69] have demonstrated that Mg$_2$Si single crystals could be derived from a stoichiometric melt of Mg$_2$Si using a vertical Bridgman method, with the initial Mg/Si ratio of 70/30. Other research groups reported the synthesis of polycrystalline Mg$_2$Si$_{1-x}$Sn$_x$ solid solutions by the melting method, followed by a long annealing treatment to achieve compositional homogeneity [42,70]. Although this method is very simple and the prepared Mg$_2$Si$_{1-x}$Sn$_x$ solid solutions possess excellent ZT values (ZT ≥ 1.1), there are some drawbacks that impede its wide application. First, it is rather difficult to obtain stoichiometric and high-purity Mg,IV-based materials by the melting method due to the inevitable and serious evaporation of Mg at high temperatures as well as the large difference in the melting point of the constituent elements (Mg: 923 K, Si: 1687 K, Ge: 1211 K and Sn: 505 K) [68,71]. Second, peritectic reactions upon cooling and the difficulty to precisely control the composition lead to poor reproducibility of the final product [72,73]. The effective way to mitigate these negative factors is to lower the synthesis temperature of the Mg,IV-based materials. To do so, Liu et al. [74] developed a two-step solid-state reaction method to synthesize Mg,IV-based materials between 873 and 973 K. Using this approach, the composition was controlled precisely, reproducibility was assured and very good TE properties were obtained in the ternary Mg$_2$Si$_{1-x}$Sn$_x$, and quaternary Mg$_2$Si$_{1–x–y}$Ge$_x$Sn$_y$, systems [75,76]. The relatively low reaction temperature as well as carefully carried-out mixing and grinding under an inert atmosphere were the key points to realize precise composition control and to avoid undesirable oxidation of Mg in Mg,IV-based materials. Thus, fabricated samples provided an ideal testing ground to investigate the influence of composition (i.e. x and y values), the content of Mg, as well as the optimal amount of Sb/Bi dopants on the TE performance [33,76–78]. An important modification of the synthesis process was made by Gao et al. [79], who sealed the mixture of Mg, Si and Sn powders under a liquid layer of B$_2$O$_3$ flux. The B$_2$O$_3$ flux method is quite simple (the B$_2$O$_3$ flux has a low melting point of 723 K) and does not require vacuum conditions during the synthesis, as the flux seals and protects the charge and suppresses evaporation of Mg. However, at the reaction temperatures, Mg reacts with B$_2$O$_3$ according to an equation 3Mg + B$_2$O$_3$ → 3MgO + 2B [80], and this causes difficulties in controlling the content of Mg. The technique is thus not suitable for the mass production. Subsequently, de Boor et al. [56] found out that the flux method was appropriate only for the Sn-rich Mg$_2$Si$_{1–x}$Sn$_x$ solid.

Table 1. Typical synthesis processes used to prepare bulk Mg,IV-based materials.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Material system</th>
<th>$ZT_{\text{max}}$</th>
<th>Advantages</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bridgman</td>
<td>Mg$_2$Si</td>
<td>–</td>
<td>Suitable for the growth of single crystals</td>
<td>[69]</td>
</tr>
<tr>
<td>ML+AN</td>
<td>Mg$_2$Si-Mg$_2$Sn</td>
<td>1.1</td>
<td>A simple direct synthesis method</td>
<td>[42]</td>
</tr>
<tr>
<td>ML+HP</td>
<td>Mg$_2$Si-Mg$_2$Sn</td>
<td>1.2</td>
<td></td>
<td>[70]</td>
</tr>
<tr>
<td>BFM+HP</td>
<td>Mg$_2$Si-Mg$_2$Sn</td>
<td>1.2</td>
<td>No need for vacuum protection during the</td>
<td>[79]</td>
</tr>
<tr>
<td>BFM+SPS</td>
<td>Mg$<em>2$Si$</em>{0.4}$Sn$_{0.6}$</td>
<td>1.5</td>
<td>synthetic reaction prior to sintering</td>
<td>[54]</td>
</tr>
<tr>
<td>SSR+SPS</td>
<td>Mg$_2$Si-Mg$_2$Sn</td>
<td>1.2</td>
<td>Precise control of the composition and of the</td>
<td>[74,85]</td>
</tr>
<tr>
<td>SSR+SPS</td>
<td>Mg$_2$Si-Mg$_2$Ge-Mg$_2$Sn</td>
<td>1.4</td>
<td>the Mg content</td>
<td>[76]</td>
</tr>
<tr>
<td>BM+HP</td>
<td>Mg$_2$Si-Mg$_2$Ge-Mg$_2$Sn</td>
<td>1.4</td>
<td>The synthetic reaction occurs at around</td>
<td>[84]</td>
</tr>
<tr>
<td>BM+HP</td>
<td>Mg$_2$Si</td>
<td>0.7</td>
<td>Room temperature and thus evaporation of Mg at</td>
<td>[83]</td>
</tr>
<tr>
<td>BM</td>
<td>Mg$_2$Si</td>
<td>–</td>
<td>elevated temperatures is avoided</td>
<td>[81]</td>
</tr>
<tr>
<td>BM+HP</td>
<td>Mg$_2$Si-Mg$_2$Sn</td>
<td>0.13</td>
<td></td>
<td>[82]</td>
</tr>
<tr>
<td>MS+SPS</td>
<td>Mg$<em>2$Si$</em>{0.4}$Sn$_{0.6}$</td>
<td>1.2</td>
<td>Rapid synthesis</td>
<td>[86]</td>
</tr>
<tr>
<td>MS+SPS</td>
<td>Mg$<em>2$Si$</em>{0.3}$Sn$_{0.7}$</td>
<td>1.3</td>
<td></td>
<td>[87]</td>
</tr>
<tr>
<td>SPS</td>
<td>Mg$_2$Si</td>
<td>0.65</td>
<td>Ultra-fast synthesis</td>
<td>[88]</td>
</tr>
<tr>
<td>SPS</td>
<td>Mg$_2$Si</td>
<td>–</td>
<td>Ultra-fast synthesis</td>
<td>[89]</td>
</tr>
</tbody>
</table>

ML, melting; AN, annealing; SSR, solid-state reaction; BM, ball milling; HP, hot pressing; BFM, B$_2$O$_3$ flux method; MS, melt spinning; SPS, spark plasma sintering; SHS, self-propagating high-temperature synthesis.
solutions, but definitely not for Mg2Si. The reason is a large volume expansion during the reaction, leading to the formation of Mg2Si and Si-rich Mg2Si1–xSnx, and the B2O3 flux seal is no longer effective. In order to avoid the loss of Mg and limit its oxidation at elevated temperatures, a ‘room-temperature’ approach based on ball milling has been employed. The first such study to prepare Mg2Si and Mg2Si1–xSnx was conducted by Schilz et al. [81] and Song et al. [82]. Recently, Bux et al. [83], as well as Mao et al. [84], reported on a successful ball-milling fabrication of Mg2Si and Mg2Si1–xSnx, without any obvious contamination or the presence of MgO impurities, resulting in excellent TE properties of the final hot-pressed ingots. Ball milling appears to be a very good method for preparing Mg2IV-based materials. However, further investigations aiming at batch synthesis of the material are still needed, and should include optimization of the milling parameters to prevent agglomeration of soft materials (Mg and Sn), minimization of adventitious contamination and a study of reliable reproduction of the TE properties of the final product.

Three very fast synthesis routes, namely melt spinning (MS) [86,87], SHS [88] and the one-step spark plasma sintering process [89], have also been developed and applied to the synthesis of Mg2IV-based materials, resulting in excellent TE properties. Zhang et al. [87] found out that the chief advantage of the MS process was the uniformity and homogeneity of the rapidly cooled material (thin and long ribbons subsequently powdereded), which provided an excellent pre-product prior to sintering, ultimately yielding a highly homogeneous composition of the sintered ingots and competitive TE performance. The other two fast synthesis methods turned out to be suitable for preparing Mg2Si, while attempts to synthesize Sn-rich solid solutions were not successful [88,89].

**Figure 1.** Schematic electronic band structures in the Mg2Si-Mg2Ge-Mg2Sn system. Heavy and light conduction bands are shown in red (C1) and blue (C2), respectively [33,67,84,92].

**BAND-STRUCTURE ENGINEERING APPROACH TO ENHANCE THE TE PERFORMANCE OF Mg2IV-BASED SOLID SOLUTIONS**

According to various reports, binary Mg2IV compounds have very similar band-structure characteristics: the edge of the conduction band is composed of a heavy conduction band (C1) and a light conduction band (C2) with a band offset of $E_0$. In Mg2Si and Mg2Ge, the lower-lying C1 band is mainly formed from the hybridized 3p orbital of Mg with s-orbital and d-$t_2g$ orbital of Si/Ge while, in contrast, in Mg2Sn, the lower-lying band is the C1 band composed of the hybridized Mg 3p orbital and the d-$t_2g$ orbital of Sn [42,84,90,91]. Therefore, it is feasible to realize an effective overlap (valley degeneracy) of C1 and C2 bands by selecting an appropriate composition of Mg2IV-based solid solutions, i.e. judiciously choosing the relative ratio of Si/Ge/Sn. As sketched in Fig. 1, adjusting the Sn content in the ternary Mg2Si1–xSnx and Mg2Ge1–ySn1–y solid solutions leads to a specific movement of C1 and C2 bands, with the band convergence predicted to occur in Mg2Si1–xSnx at Sn compositions near $x = 0.65–0.70$ [33,62] and in Mg2Ge1–ySn1–y at compositions around $y = 0.75–0.78$ [84].

Following upon the suggestions by Zaitsev et al. [42,90,93], Liu et al. [33] investigated in detail the influence of the Sn/Si ratio on the convergence of conduction bands in Mg2Si1–xSnx solid solutions via complementary band-structure calculations and experimental transport measurements. The results showed that the band offset $E_0$ between C1 and C2 decreased with the increasing content of Sn, and the two conduction bands coincided in energy at around $x = 0.7$, as depicted in Fig. 2a. Meanwhile, a significantly improved Seebeck coefficient was obtained as the content $x$ of Sn in Mg2Si1–xSnx increased, as shown in Fig. 2c. As compared to Mg2Si0.8Sn0.2 with its large value of $E_0$, the Seebeck coefficient of Mg2Si0.5Sn0.7 with the C1 and C2 bands converged was increased by 100% at room temperature and by 30% at 800 K. This enhancement was attributed to the increased density-of-states effective mass $m^*$ due to the crossover of the two conduction bands: $m^* = N_e^{2/3} m_0^*$, where $m^*$ and $N_e$ stand for the density-of-states effective mass of a single carrier pocket and the number of degenerate valleys, respectively. Convergence of the energy bands effectively increases $N_e$ and, hence, the density-of-states effective mass $m^*$, while it leaves the carrier mobility $\mu$ intact as the latter is proportional to $\mu \propto (m^*)^{-5/2}$. As highlighted in Fig. 2b, Mg2Si0.5Sn0.7 maintained a rather high value of $\mu$, although $m^*$ was large at this composition. As a consequence, Mg2Si0.5Sn0.7 achieved an
the coincidence of the band edges of the two conduction bands naturally leads to a single parabolic band (SPB) approximation, which is particularly convenient for an evaluation of the electronic transport properties [78,91,92,95]. Liu et al. [78] have demonstrated the predictive power of the SPB model in Bi-doped Mg$_2$Si$_{0.5}$Sn$_{0.7}$, where, using a room-temperature value of $m^*$, the predicted Seebeck coefficient agreed well with the experimental results in the whole temperature range.

Mao et al. [91] simulated the influence of a carrier distribution on the electronic transport by taking Mg$_2$Ge$_{0.25}$Sn$_{0.75}$ as a case study, and found out that $E_0$ should be as small as possible in order to achieve the optimal PF in the whole measured temperature range. Clearly, it would be preferable to have the two bands converged in the entire temperature range. However, the band gap is usually temperature-dependent, with its rate of change given by $dE/dT$ [42,67]. Assuming that $E_0$ is linearly dependent on the composition, and using experimental values of $E_0$ and $dE/dT$, Yin et al. [76] found that $E_0(T)$ at high temperatures was in the order of 10 meV, comparable to a value of thermal broadening in the Fermi distribution ($\sim 2k_BT$).

Recent investigations have indicated that, in the Mg$_2$Si$_{1-x}$Sn$_x$ system, the positive effect of band convergence on the electronic transport is universal. In Mg$_2$Ge$_{1-x}$Sn$_x$, the two conduction bands converged at around $y \approx 0.75$ [92]—a slight difference from the value $x \approx 0.7$ in Mg$_2$Si$_{1-x}$Sn$_x$ [33,62]. This is not surprising because the band structure of Mg$_2$Ge is very similar to that of Mg$_2$Si [67]. Studies of the conduction bands crossing in the Mg$_2$Si$_{0.68}$Sn$_{0.32}$-Mg$_2$Ge$_{0.22}$Sn$_{0.78}$-Sb$_{0.015}$ system have indicated that the PF would decrease when the actual sample composition was off the optimal band-crossing composition due to the fact that the carrier concentration was no longer optimal in both conduction bands [84].

Various studies confirmed that, in Mg$_2$IV-based solid solutions with converged conduction bands, excellent PF of 3.8–4.7 mW m$^{-1}$ K$^{-2}$ in the range of 300–800 K, which led to an outstanding ZT$_{max}$ of 1.3 at 750 K, and an average ZT of 0.9 between 300 and 800 K, as shown in Fig. 2d. It is noteworthy that the band convergence can be achieved for a wide range of carrier densities, as indicated in Fig. 3a, which is distinctly different from the band-resonant concept that requires the Fermi level to be pinned exactly to the resonant energy level [28,94].

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CARRIER DOPING AND OPTIMAL CARRIER CONCENTRATION IN Mg$_2$IV-BASED SOLID SOLUTIONS

Based on the classical transport theory, an increase in the electrical conductivity should lead to a decrease in the Seebeck coefficient. Taking into account that the overall thermal conductivity is also enhanced due to a larger electronic thermal conductivity, to optimize the thermoelectric figure of merit requires identifying the optimal carrier concentration. It turns out that the carrier concentrations for efficient thermoelectric conversion fall in the range of $10^{15}$–$10^{17}$ cm$^{-3}$, depending on the specific characteristics of TE materials [3]. Numerous reports on transport properties of n-type Mg$_2$Si$_{1-x}$Sn$_x$ solid
Figure 3. (a) Room-temperature Seebeck coefficient versus the carrier concentration in Mg$_2$Si$_{1-x}$Sn$_x$ solid solutions. (b) Variation of $ZT_{\text{max}}$ values with the room-temperature carrier concentration in Mg$_2$Si$_{1-x}$Sn$_x$ solid solutions [33]. Reprinted with permission from Ref. [33]. Copyright 2012, by the American Physical Society. (c) Relationship between the doping content of Sb or Bi and the electron density in Mg$_{2.16}$Si$_{0.84}$Sb$_{0.15}$, Mg$_{1.0}$(Sb/Bi)$_{1–z}$, [33,78]. (d) Relationship between the room-temperature carrier concentration and the actual Mg excess in Mg$_{2.16}$Si$_{0.84}$Sb$_{0.15}$, Mg$_{1.0}$(Sb/Bi)$_{1–z}$ [0 ≤ z ≤ 0.12] compounds. The inset shows the electron concentration dependence on a finer scale [77]. Reprinted with permission from Ref. [77]. Copyright by the American Chemical Society, 2011.

solutions show that, when the carrier concentration is increased from 10$^{18}$ cm$^{-3}$ to 10$^{20}$ cm$^{-3}$, the electrical conductivity increases by two orders of magnitude, while the Seebeck coefficient decreases only modestly (see Fig. 3a) and, consequently, the $PF$ can be 10 times larger. Studies at the Wuhan University of Technology [33,74,75,77,78,96–98] have shown that Sb or Bi doped into Mg$_2$Si$_{1-x}$Sn$_x$ in amounts of up to 4 at.% will increase the density of electrons from $\sim1.8 \times 10^{18}$ cm$^{-3}$ to $\sim3.2 \times 10^{20}$ cm$^{-3}$, leading, in turn, to a remarkably enhanced electrical conductivity and $PF$ in Mg$_2$Si$_{1-x}$Sn$_x$ solid solutions. Figure 3a–c illustrates the doping effect of Sb and Bi in Mg$_2$Si$_{0.6}$(Sb/Bi)$_{0.4}$ solid solutions, which documents the dominant role the carrier concentration plays in the TE performance of Mg$_2$Si$_{1-x}$Sn$_x$. Results from other research groups show a very similar trend across a spectrum of Mg$_2$IV-based materials. Carrying out systematic doping studies, an example of which is shown in Fig. 3b, Liu et al. [33] arrived at an optimal electron-density range of $1.6 \times 10^{20} \sim 2.5 \times 10^{20}$ cm$^{-3}$, applicable to Mg$_2$Si$_{1-x}$Sn$_x$ (0.2 ≤ x ≤ 0.8) solid solutions. Although the exact optimal electron concentration yielding the maximum $ZT_{\text{max}}$ was somewhat dispersed among different compositions of solid solutions, the general trend was consistent [70,84,92,99–101]. Synthesis routes, apart from having a major impact on the microstructure and homogeneity of the final product, also govern the type and density of native defects, which, in turn, influence the intrinsic carrier concentration of the resulting material [77,100]. Moreover, given that the Mg$_2$IV-based solid solutions are narrow-band-gap semiconductors ($E_g = 0.35–0.77$ eV), intrinsic carrier excitations become prominent at elevated temperatures (typically above 700 K), especially for samples having low carrier concentration [42,67,78]. Such intrinsic excitation processes are highly detrimental to the thermoelectric performance, as they cause not only a turnaround in the Seebeck coefficient, but also give rise to a progressively rising bipolar thermal-conductivity contribution. Given that one cannot arbitrarily increase the band gap, the only effective counter-measure to mitigate the influence of intrinsic excitations is to enhance the carrier concentration, i.e. to heavily dope the structure. This is one of the reasons why the optimal $ZT$ values in n-type Mg$_2$IV-based solid solutions are achieved at relatively high carrier concentrations [33].

Using first-principles calculations based on the density functional theory (DFT), Tani et al. [102] noted that the formation energy of Sb and Bi substituted on the sites of Si in Mg$_2$Si is negative under both Mg- and Si-rich limits, indicating that Sb and Bi impurities should have good solubility in the matrix. As both Bi and Sb atoms have one more valence electron than Si, such substitutions on the Si site should release one electron into the conduction band. Indeed, Sb and Bi are the most popular and effective n-type dopants in Mg$_2$IV-based materials. As shown in Fig. 3c, the effectiveness of Sb and Bi doping is close to 100% at low doping amounts [33,78]. Although Bi is comparably efficient as Sb in tuning the electron density, due to its much larger size, its solubility limit in Mg$_2$IV-based materials is much lower than that of Sb. Studies on Mg$_2$Si$_{1–x}$Sn$_x$ and Mg$_2$Si$_{0.6}$Sn$_{0.4}$Sb$_{0.1}$ have shown that the two matrices can accommodate Sb amounts of up to $x \approx 0.38$ [103,104], while Bux et al. [83] observed that the solubility limit of Bi in Mg$_2$Si was no more than about 1.3 at.% (with doping levels of Bi, up to 3.4 at.%, was found in ternary solid solutions of Mg$_2$Si$_{1–x}$Sn$_x$ (x = 0.6 and 0.7) [75,78]). This seems reasonable, since the difference in the ionic radii of Bi$^{3+}$ and Sn$^{4+}$ is much smaller than that between the radii of Bi$^{3+}$ and Si$^{4+}$. It should be mentioned that other elements, such as Ca, La and Al, have also been investigated and confirmed to be n-type dopants [99,105,106]; however, they were considerably less effective than Sb.

and Bi. The electron density of Mg₂IV-based materials doped with Ca, La and Al reached the upper limit of $1 \times 10^{20}$ cm$^{-3}$—not enough to achieve the optimal ZTs in n-type Mg₂IV-based compounds.

Besides doping, the TE performance of Mg₂IV-based compounds is also strongly related to the type and concentration of intrinsic defects in the crystal lattice. The significant loss of Mg during the synthesis often leads to a deficiency of Mg and the formation of Mg vacancies. Experimental results of Noslas et al. [103] and Dasgupta et al. [107] indicated that a high Sb-doping amount (over 5 at.%) gives rise to the formation of charged Mg vacancies, which tend to reduce the electron density and counteract the effect of Sb doping. This motivated the study of Mg stoichiometry and its deviations in Mg₂IV-based compounds, which also revealed the dependence on the synthesis process used in the fabrication of the material. More specifically, by varying the content of Mg in Sb-doped Mg$_2$Si$_{0.5}$Sn$_{0.5}$ solid solutions, it was found that a slight excess of Mg was a prerequisite for excellent electronic properties of n-type Mg₂IV-based materials [77]. Taking into account the experimentally determined loss of Mg of about 3 at.% in the adopted two-step solid-state reaction process followed by spark plasma sintering of ingots, a good control of Mg stoichiometry was achieved. As shown in Fig. 3d, the electron density of Mg$_{2(1+x)}$Si$_{0.49}$Sn$_{0.51}$Sb$_{0.01}$ would increase from $2.5 \times 10^{20}$ cm$^{-3}$ to $2.0 \times 10^{20}$ cm$^{-3}$ when the Mg content was varied from the Mg-deficient ($z = -0.02$) to the Mg-rich ($z = 0.07$) solid solutions. A similar trend was observed subsequently by Du et al. [100] and Jiang et al. [104].

Several groups have studied theoretically the native point defects in Mg₂IV and further clarification of the influence of Mg stoichiometry on the electronic transport properties was made [108–110]. It was shown that [108,110], among all intrinsic point defects in Mg-rich solid solutions, the energetically most favorable one is an interstitial Mg atom. Moreover, the results indicated that Mg interstitials shared electrons with the surrounding lattice-located Mg, modified the charge-density distribution and produced impurity-like energy levels below the conduction band minimum [108]. This finding well supported the experimental results that Mg interstitials formed as a consequence of Mg excess tend to enhance the electron density and shift the Fermi level upwards [77,100]. In the opposite case of an Mg-deficient structure, the dominant intrinsic defect in Mg₂IV should be an Mg vacancy, due to its very low formation energy [108,109]. Again, this result provided a viable explanation for the observed lower carrier concentration in Mg-deficient n-type Mg₂IV-based materials [77,103].

Although the formation of native defects in Mg₂IV-based materials is a challenging subject that may depend on many factors and clearly requires more detailed studies, the above early work serves as a useful guide for future studies.

Doping by Sb and Bi combined with manipulation of the native defects dominate the control of the charge-carrier concentration in n-type Mg₂IV-based materials and serve as a tuning knob to obtain the optimal carrier concentration that maximizes the PF. Such an approach was used in achieving, so far, the highest ZTs of 1.4–1.5 in n-type Mg₂IV-based solid solutions [111–113]. However, a significant factor in attaining such impressive ZT values was a reduction in the lattice thermal conductivity $\kappa_l$, the topic that will be reviewed in the next section.

**REDUCTION OF $\kappa_L$ IN Mg₂IV-BASED SOLID SOLUTIONS BY MANIPULATING THE COMPOSITION AND MICROSTRUCTURE**

To achieve high ZT values in TE materials, a reduction of the lattice thermal conductivity $\kappa_l$ is equally important as an enhancement in the PF. In Mg₂IV-based materials, two approaches have been generally adopted to reduce $\kappa_l$, i.e. making compositional manipulations, and tailoring and controlling the microstructure. In the following, we will review these two strategies.

In the early 1950s, Ioffe et al. [114] found out that forming solid solutions was an effective way to improve the TE performance of a material because the lattice thermal conductivity is dramatically diminished on account of strong alloy scattering. At the same time, the formation of solid solutions offers an opportunity to alter the band structure that might be beneficial for improving the PF. The fact that most of the state-of-the-art thermoelectric materials are some form of solid solutions (e.g. PbTe$_{1-x}$Se$_x$, Bi$_2$Te$_3$/Sb$_2$Te$_3$/Bi$_2$Se$_3$ alloys, Si$_{1-x}$Ge$_x$, and Zr$_{1-x}$Hf$_x$Si$_{1-y}$Sn$_y$) attests to the importance of Ioffe’s finding. In the 1960s, early pioneering studies on Mg₂IV-based solid solutions were carried out by Zaitsev et al. [61,67], who found that the $\kappa_l$ of Mg$_2$Si$_{1-x}$Ge$_x$, Mg$_2$Ge$_{1-x}$Sn$_x$, and Mg$_2$Si$_{1-y}$Sn$_y$ was strongly dependent on the composition and all three systems showed the lowest $\kappa_l$ at $x \approx 0.5$, as depicted in Fig. 4a. Taking the Mg$_2$Si$_{1-y}$Sn$_y$ solid solution as an example, the $\kappa_l$ at 300 K of its two end members, Mg$_2$Si and Mg$_2$Sn, was 7.9 Wm$^{-1}$K$^{-1}$ and 5.9 Wm$^{-1}$K$^{-1}$, respectively, while the lattice thermal conductivity of the ternary solid solutions with $0.4 \leq x \leq 0.7$ was reduced down to $\sim 2.0$ Wm$^{-1}$K$^{-1}$, representing...
a decrease of about 75% compared to the value of Mg$_2$Si. In addition, Mg$_2$Si$_{1-x}$Sn$_x$ possessed the lowest $\kappa_L$ among the three solid solutions and, thus, appeared as a very promising candidate for obtaining good TE performance. The reason for its appeal was the largest mass fluctuation (Si vs. Sn) and the lattice parameter discrepancy between Mg$_2$Si and Mg$_2$Sn. It should be pointed out that, since there are miscibility gaps in the phase diagram of Mg$_2$Ge$_{1-x}$Sn$_x$ and Mg$_2$Si$_{1-x}$Sn$_x$ solid solutions [65,66], whether any phase segregation plays a role in lowering $\kappa_L$ of solid solutions within and near the miscibility gap remains an open question.

So far, most investigations have focused on Mg$_2$Si$_{1-x}$Sn$_x$, Mg$_2$Ge$_{1-x}$Sn$_x$ and Mg$_2$Si$_{1-x}$Ge$_x$ ternary systems, in that order, with only few studies of quaternary Mg$_2$Si$_{1-x-y}$Ge$_y$Sn$_x$ and quintuple Mg$_2$Si$_{1-x-y}$Ge$_y$Sn$_x$P$_2$ systems, as the latter possess too complex phase diagrams. Owing to low values of $\kappa_L$ (2–2.5 Wm$^{-1}$K$^{-1}$) that have the origin in enhanced alloy phonon scattering, excellent TE properties have been achieved in Mg$_2$Si$_{0.4}$Sn$_{0.6}$, Mg$_2$Si$_{0.4}$Sn$_{0.6}$ and Mg$_2$Si$_{0.4}$Sn$_{0.6}$ solid solutions [33,42]. Recently, Khan et al. [112,113,118] investigated a series of Sb- and Bi-doped Mg$_2$Si$_{0.55}$Sn$_{0.45}$Ge$_{0.05}$ solid solutions, and obtained a high $ZT$ value of 1.4 at 800 K in Mg$_2$Si$_{0.45}$Sn$_{0.55}$Ge$_{0.05}$Bi$_{0.05}$ with $z = 0.02$. The outstanding $ZT$ value was attributed to the very low $\kappa_L$ achieved via composition manipulation, with the room-temperature $\kappa_L$ diminished by 78% compared to $\kappa_L$ of Mg$_2$Si$_{1-x}$Bi$_x$ with $z = 0.02$. Zhang et al. [119] showed that substituting Ge in the lattice of Mg$_2$Si$_{0.4}$Sn$_{0.6}$ was beneficial for suppressing the bipolar transport in the temperature range up to 800 K, resulting in a reduced $\kappa$. Yin et al. [76] demonstrated, in their recent work, that the dependence of the $\kappa_L$ of Mg$_2$Si$_{1-x-y}$Ge$_y$Sn$_x$ on sample composition can be described by the Adachi’s model. For the frequently studied composition of Mg$_2$Si$_{0.4}$Sn$_{0.6}$ displaying the band convergence, Ge substitutions on sites of Sn could further enhance mass and strain field driven phonon scattering and thus even more effectively reduce $\kappa_L$, especially in the range of 600–800 K. Specifically, at 700 K, the $\kappa_L$ of Mg$_2$Ge$_{0.05}$Sn$_{0.95}$ was reduced by 18% compared to that of Mg$_2$Ge$_{0.05}$Sn$_{0.95}$, apart from tuning the Si/Ge/Sn ratio and doping on the anion site, introducing intrinsic point defects on the Mg site (e.g. Mg interstitials or Mg vacancies) also plays an important role in reducing the $\kappa_L$ and thus enhancing the figure of merit in Mg$_2$IV-based solid solutions. Figure 4b shows a remarkable reduction in the lattice thermal conductivity of Mg$_2$Si$_{0.4}$Sn$_{0.6}$, achieved by Jiang et al. [104] due to a high Sb-doping level and the formation of intrinsic point defects. The sample with $x = 0.11$ had a lower $\kappa_L$ at high temperatures compared to that of the sample with $x = 0.12$, because it contained more Mg interstitials in the crystal lattice. Scattering parameter calculations indicated that the mass difference between Mg and Mg vacancy dominated over the difference between Sb and Sn, pointing out a significant role Mg vacancies played in reducing $\kappa_L$. Over 15% reduction in $\kappa_L$ at room temperature was observed in samples with a large Sb-doping content ($x > 0.11$) and an increased density of Mg vacancies, as compared to the sample with $x = 0.02$. In general, compositional variations on the Mg site are promising ways of reducing $\kappa_L$, although not as effective as substitutions on the anion site where the amount of dopant as well as the mass and size difference of the ions is much greater.

Microstructure modification is another important way one might accomplish a reduction in the $\kappa_L$ of Mg$_2$IV-based solid solutions. The approach may be divided into two categories. A second-phase structure can be introduced as a result of peritectic reactions according to the phase diagram or via phase segregation in addition, non-equilibrium preparation methods, such as ball milling followed by rapid sintering, can be utilized to obtain a fine-structured material.

Making use of the peritectic reaction at 1130 K and the miscibility gap in the pseudo-binary phase diagram of Mg$_2$Si-Mg$_2$Sn, Zhang et al. [99] fabricated a unique composite material Mg$_{2-x}$La$_x$Sn$_{0.55}$Sn$_{0.45}$ ($0 \leq x \leq 0.015$), in which Si-rich bulk grains were in-situ coated by thin layers of a Sn-rich material, and the Sn-rich grain boundary phase was selectively doped with La. The thickness

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**Figure 4.** (a) Relationship between the lattice thermal conductivity ($\kappa_L$) at room temperature and the composition of Mg$_2$IV-based pseudo-binary solid solutions [67]. Adapted with permission of Taylor & Francis Group LLC via the Copyright Clearance Center. (b) Temperature dependence of $\kappa_L$ in Mg$_2$Si$_{0.55}$Sn$_{0.45}$-Sb$_x$, ($x = 0.02, 0.11, 0.12, 0.27$ and $0.38$). The dashed line indicates the theoretical minimum $\kappa_L$, estimated using the Cahill’s model [104]. Reprinted with permission from Ref. [104]. Copyright by WILEY-VCH, Weinheim, 2014.
of the Sn-rich layer was in the range of hundreds of nanometers, while the size of the bulk grains was $\sim 10 \ \mu \text{m}$. A low $\kappa_L$ of $\sim 2.3 \ \text{Wm}^{-1}\text{K}^{-1}$ was obtained in the undoped sample at room temperature, and the $\sigma/\kappa$ ratio was increased by a factor of 17 after doping with 0.5 at.% of La. Recently, Yin et al. [120] demonstrated the formation of in-situ nanostructures with different compositions and distribution patterns can be achieved in solid solutions of $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$ via quenching the powder prepared by a solid-state reaction at different peritectic reaction temperatures (e.g. 837 K, 900 K and 1130 K). Nano-sized Si-rich agglomerates were observed when quenching at 900 K, while homogeneously distributed Sn-rich nano-particles of uniform size were present after quenching at 1130 K. Only the uniformly dispersed Sn-rich in-situ formed precipitates of nanometer-scale may significantly enhance the boundary scattering of phonons and, indeed, a 10% decrease in $\kappa_L$ in the range of 300–600 K was observed compared to samples containing Si-rich agglomerates. Thus, quenching at peritectic temperatures is an effective approach to design the desired in-situ nanostructures.

Besides peritectic reactions, phase segregation is the other possible route of forming unique microstructures, utilizing the miscibility gap in $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$ ($0.4 \leq x \leq 0.6$) and $\text{Mg}_2\text{Ge}_{1-x}\text{Sn}_x$ ($0.3 \leq x \leq 0.8$). As reported by Liu et al. [98], a significant number of nano-sized Sn-rich phases were observed to precipitate out of the matrix of the $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$ system. The lattice thermal conductivity of the prepared $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$ was even smaller than that of $\text{Mg}_2\text{Si}_{0.5}\text{Sn}_{0.5}$ (the greatest disorder between Si and Sn), which was attributed to the enhanced phonon scattering by nanostructures.

The use of non-equilibrium preparation techniques is another important approach to manipulate the microstructure of $\text{Mg}_2\text{IV}$-based solid solutions. Wang et al. [121] studied theoretically the correlation between $\kappa_L$ and the size of nanoparticles in $\text{Mg}_2\text{IV}$-based solid solutions, and found that a fraction of 3.4% of nanoparticles could potentially lead to a reduction in $\kappa_L$ of $\sim 60\%$ at 300 K and $\sim 40\%$ at 800 K, with an optimal particle size of a few nanometers. Recently, Bellanger et al. [122] prepared nanostructured $\text{Mg}_2\text{Si}_{0.4}\text{Sn}_{0.6}$ solid solutions composed of grains with the size below 200 nm and finely distributed Sn-rich nanoparticles by mechanical alloying combined with spark plasma sintering. Thus, prepared samples showed an ultra-low room-temperature thermal conductivity of less than 1.2 $\text{Wm}^{-1}\text{K}^{-1}$. A semi-quantitative model was developed to capture the different contributions to phonon-scattering processes arising from the nano/microstructural parameters and it was suggested that the most efficient way to decrease $\kappa$ was to prepare samples with a small grain size instead of nanoparticles [122]. However, the major drawback following such a suggestion would be appreciable grain growth under the thermal load.

Although $\kappa_L$ could be reduced through the formation of intrinsic point defects and by introducing nanostructures in the matrix, alloying, i.e. substituting Ge and/or Sn on the Si site, is still the most effective approach. To consider power-generation applications of $\text{Mg}_2\text{IV}$-based solid solutions, apart from excellent TE properties, they must be mechanically robust and thermally stable at the intended operational regime, too. Before we discuss the mechanical properties and the thermal stability of $n$-type $\text{Mg}_2\text{IV}$-based solid solutions, we will briefly introduce some fundamental issues pertaining to $p$-type HMS.

**HMS as Effective $p$-Type Materials**

Efficient operation of a thermoelectric module requires having both $n$- and $p$-type thermoelectric elements. $p$-type HMS are superior to $p$-type $\text{Mg}_2\text{IV}$-based materials on account of their relatively higher $ZT$ values as well as more robust mechanical properties. Hence, $p$-type HMS are good choices to combine with efficient $n$-type $\text{Mg}_2\text{IV}$-based materials for the construction of TE modules. Here, we summarize key issues relevant to properties of $p$-type HMS, more detailed discussion can be found in two recent publications [55,56].

HMS, exemplified by $\text{MnSi}_{1+0.5}$ with $\delta = 0.01–0.05$, represent a series of Nowotny chimney-ladder phases, consisting of a square-arranged Mn sublattice and a ‘ladder’ sublattice of pairs of Si atoms forming two coupled helices inside the chimney [123–126]. Early studies of HMS were conducted on single crystalline specimens grown by the Czochralski and the Bridgman methods [127–129], which contained intermetallic layered precipitates of MnSi. Later on, attempting to prepare polycrystalline HMS materials with stoichiometric composition and without the undesirable MnSi precipitates, different synthesis routes, such as ball milling, induction melting, arc melting, solid-state reaction, melt spinning and thermal explosion, have been employed [130–134]. Recently, Girard et al. [135] have reported that high-purity MnSi-free single crystals of HMS could be synthesized by the chemical vapor transport method. However, the MnSi phase would precipitate from the HMS during the consolidation process due to the unstable nature of MnSi at high temperatures. Compared to the growth of single crystals, the preparation of polycrystalline HMS has
Figure 5. (a) Room-temperature fracture toughness of \(Mg_{2.16}Si_0.3Sn_{0.7}Sb_{0.02}\) with dispersed 0.8 at.% of SiC nanoparticles (SiC\(_p\)) and 0.8 at.% of SiC nanowires (SiC\(_w\)). (b) Crack propagation in \(Mg_{2.16}Si_0.3Sn_{0.7}Sb_{0.02}\) containing 0.8 at.% of SiC nanoparticles [146]. Reprinted with permission. Copyright by Elsevier, 2017.

The microstructure.

**IMPROVED MECHANICAL PROPERTIES AND THERMAL STABILITY IN Mg\(_2\)IV-BASED SOLID SOLUTIONS IN RELATION TO HMS**

Mg\(_2\)IV-based compounds are fragile and require delicate handling during sintering and cutting/polishing processes in order to avoid cracks in the bulk ingots. Gelbstein et al. [144] and Gao et al. [111] showed that Mg\(_2\)Si\(_{1-x}\)Sn\(_x\) solid solutions possess a reasonable Vickers hardness of 3.07–3.54 GPa at room temperature, but a rather inferior fracture toughness (\(~0.99\) MPam\(^{-1/2}\)), compression strength (\(~492 \pm 80\) MPa) and flexural strength (\(~79 \pm 10\) MPa). For comparison, HMs, the most promising \(p\)-type silicide with excellent mechanical properties, has its fracture toughness of 1.63 MPam\(^{-1/2}\), compression strength of 1083 ± 150 MPa and flexural strength of 178 ± 10 MPa—considerably higher values than those of Mg\(_2\)Si\(_{1-x}\)Sn\(_x\) [144]. Thus, it is very challenging to fabricate TE devices from Mg\(_2\)IV-based solid solutions due to their poor mechanical properties. Only after significant improvements in the mechanical properties of Mg\(_2\)IV-based solid solutions are made can one seriously contemplate fabrication of thermoelectric modules based on these materials. Current efforts to improve the mechanical properties of Mg\(_2\)IV-based solid solutions focus on strengthening the structure by introducing SiC additives to the matrix [145,146]. This is often done during the ball-milling stage of fabrication that is followed by spark plasma sintering to consolidate the material [147–149]. Schmidt et al. [145] have shown recently that incorporating 1–2 vol.% of SiC nanoparticles into Mg\(_2\)Si would improve the fracture toughness by about 33%. Although a significant improvement over the pristine Mg\(_2\)Si has been achieved, it is still not competitive with the HMS-based material. Inspired by this work, Yin et al. [146] introduced some SiC nanoparticles and nanowires into the Mg\(_2\)Si\(_0.3\)Sn\(_0.7\) matrix and evaluated the TE performance of their composite samples. Owing to excellent mechanical properties of SiC (the flexural strength of 640 MPa and the fracture toughness of 3.8 MPam\(^{1/2}\) at room temperature), the compression strength, the flexural strength, the Vickers hardness and the fracture toughness of their SiC-loaded Mg\(_2\)Si\(_0.3\)Sn\(_0.7\) samples were dramatically improved. As shown in Fig. 5a, with the addition of merely 0.8 at.% SiC nanowires, the fracture toughness of Mg\(_2\)Si\(_0.3\)Sn\(_0.7\) was enhanced by about 50% and reached \(~1.35\) MPam\(^{1/2}\) —close to the value characteristic of HMS. In addition, the ability to deflect crack propagation in the structure of SiC/Mg\(_2\)Si\(_0.3\)Sn\(_0.7\), depicted in Fig. 5b, served as an example of the toughening mechanism giving rise to enhanced mechanical properties. Equally importantly, a small amount of additives had negligible influence on the TE performance of Mg\(_2\)Si\(_0.3\)Sn\(_0.7\), documented by a peak ZT of 1.20 at 750 K. Since relatively little work has been done on optimizing mechanical properties of Mg\(_2\)IV-based materials, there is still a great prospect for further improvements by exploring potentially better additives and optimizing their size and dispersion in the matrix. With judiciously chosen additives, one might benefit from a simultaneous improvement in both the mechanical and TE properties, as shown recently by Zheng et al. [116].

Thermal stability is yet another important issue regarding commercialization of Mg\(_2\)IV-based...
solid solutions. Recently, first steps in this direction were taken by Bourgeois et al. [150] and Skomedal et al. [151], who studied the thermal stability of Mg$_2$Si$_{1-x}$Sn$_x$ ($x = 0.25$ and $0.6$) between 300 and 673 K. Their results demonstrated that the solid solutions start to decompose and oxidize when the temperature exceeds 630 K. By the way, the decomposition rate of the powders seems much faster than that of the bulk ingots. In their subsequent work, Skomedal et al. [152] found the evidence for high-temperature oxidation of Mg$_2$Si$_{1-x}$Sn$_x$. The solid solutions exhibited breakaway oxidation in the range of 703–773 K, and the onset temperature of the breakaway region decreased with the increasing Sn content. The breakaway process was described by a combination of the formation of a non-protective MgO layer and the presence of Sn-rich liquid at the interface between the oxide and Mg-depleted Mg$_2$Sn. In order to prevent oxidation, researchers applied vacuum packaging or protective coatings (such as Al$_2$O$_3$ and YSZ) [151,153]. However, Yin et al. [154] pointed out that vacuum packaging may not be the best approach when dealing with Mg$_2$IV-based materials, as Mg evaporation is a very serious problem under vacuum conditions, magnified by the formation of β-SnSb in Sb-doped Mg$_2$Si$_{0.7}$Sn$_{0.3}$.

As shown in Fig. 6, composition deterioration under vacuum would reduce the carrier concentration and lower the electrical conductivity and ZT values of Mg$_2$Si$_{0.3}$Sn$_{0.7}$. Applying BN coatings turned out to be a good strategy to solve the problems with Mg evaporation and oxidation. Mg$_2$Si$_{0.3}$Sn$_{0.7}$ with a protective BN coating could operate in air and below 773 K for long periods of time (720 h) with no detectable deterioration in the TE performance. However, after a longer service at 823 K, phase segregation had occurred, numerous pores were observed in the material and the TE performance was seriously degraded. Very recently, Zhang et al. [155] demonstrated an improved oxidation resistance in Mg$_2$Si$_{0.4}$Sn$_{0.6}$ by depositing an atomic layer of Al$_2$O$_3$. As a result, the TE performance remained stable upon a thermal treatment at 823 K and under the flow of an Ar gas for 12 h. As we have found out (unpublished), particularly great caution has to be exercised with solid solutions having compositions within or near the miscibility gap in Mg$_2$Si$_{1-x}$Sn$_x$, i.e. for Sn contents $0.4 \leq x \leq 0.6$, where phase separation is inevitable after a prolonged exposure (e.g. 1–3 weeks) at even modest temperatures of 570 K. Thus, it is essential to choose right compositions situated in the miscible region of the phase diagram (Mg$_2$Si$_{0.3}$Sn$_{0.7}$ seems to be ideal) to minimize problems with the stability of the structure. Protective coatings (e.g. Al$_2$O$_3$, YSZ ceramics, and BN or so) are clearly beneficial but the way they are applied (magnetron sputtering, chemical vapor deposition, etc.) should be tested for their effectiveness.

**OUTLOOK AND SUMMARY**

This article provides a review of the most important research advancements regarding thermoelectric properties of n-type Mg$_2$IV-based materials and p-type HMS, including the challenging issues related to the material’s synthesis, band-structure engineering, optimization of the carrier concentration, reduction of the lattice thermal conductivity, as well as the importance of mechanical properties and the thermal stability of the structure. The particularly prominent points related to these issues are briefly summarized below:

(i) The difficulty in preparing Mg$_2$IV-based materials is caused by the high vapor pressure and oxidation of Mg at elevated temperatures. Thus, the solid-state reaction process or ball-milling method exemplified by their much-reduced reaction actions are highly beneficial for the precise control of composition and phase structure.
(ii) In Mg$_2$IV-based materials, the conduction band convergence greatly increases the density-of-states effective mass, leading to a much enhanced Seebeck coefficient with no detrimental effect on the electrical conductivity. The band convergence is realized through adjusting the Si/Ge/Sn ratio.

(iii) Sb and Bi are the best n-type dopants in Mg$_2$IV-based materials, while Mg interstitials, forming as a consequence of the excess of Mg, also behave as electron donors. Combining Sb/Bi doping with a slight Mg excess is a very effective route of adjusting and tuning the electron density and thus optimizing the PF.

(iv) Compositional adjustments applied synergistically with nanostructuring result in a reduction of the lattice thermal conductivity. However, the most effective suppression of the lattice thermal conductivity is accomplished by alloying binary Mg$_2$IV compounds to form solid solutions. Care should be taken to avoid compositions corresponding to immiscible regions of the phase diagram that result in unstable solid solutions readily decomposing upon a prolonged exposure to elevated temperatures. Protective coatings are highly recommended to enhance the operational life time of Mg$_2$IV-based solid solutions, particularly when operated in air.

(v) Modest amounts of SiC added to the Mg$_2$IV matrix can effectively enhance the mechanical properties of the material. Other additives and their amount, size and dispersion in the matrix should be explored with the aim of benefitting both the thermoelectric and mechanical properties.

While possessing promising thermoelectric properties with ZT$s$ reaching values of 1.4 near 800 K, being lightweight, environmentally friendly, composed of inexpensive and readily available chemicals, further improvements in the TE performance of n-type Mg$_2$IV-based solid solutions are needed to make them viable for large-scale industrial applications, such as converting waste industrial heat into electricity. Improvements in the TE performance should go hand in hand with making the material mechanically more robust and improving its thermal stability under operational conditions at elevated temperatures. This is important in order to provide a good match with the mechanically more robust HMS that might serve as p-type legs of silicide-based modules. Other essential research concerns searching for stable and reliable electrode materials and their bonding with the TE elements, the suppression of diffusion at interfaces and the minimization of the contact resistance. These are challenging tasks but well worth tackling by the international thermoelectric community.

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