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Efficient Thermoelectric Materials Based on Solid Solutions of Mg$_2$X Compounds (X = Si, Ge, Sn)

Vladimir K. Zaitsev, Grigoriy N. Isachenko and Alexander T. Burkov

Abstract

The silicides have obvious attractive characteristics that make them promising materials as thermoelectric energy converters. The constituting elements are abundant and have low price, many of compounds have good high temperature stability. Therefore, considerable efforts have been made, especially in the past 10 years, in order to develop efficient silicide-based thermoelectric materials. These efforts have culminated in creation of Mg$_2$(Si-Sn) n-type thermoelectric alloys with proven maximum thermoelectric figure of merit $ZT$ of 1.3. This success is based on combination of two approaches to maximize the thermoelectric performance: the band structure engineering and the alloying. In this chapter, we review data on crystal and electronic structure as well as on the thermoelectric properties of Mg$_2$X compounds and their solid solutions.

Keywords: silicides, magnesium silicide, thermoelectricity, figure of merit

1. Introduction

Among the large family of silicon-based compounds, semiconducting silicides have received particular interest as thermoelectric materials because they are potentially cheap and mostly stable materials. Comparatively, low charge carriers’ mobility in these semiconductors is compensated by high electron state density, i.e. high effective mass of charge carriers. Therefore, silicides were the main focus of thermoelectric research community since the 1950s [1]. Investigations of these materials were especially active during the past 10 years. The most important results have been achieved for Mg$_2$X (X = Si, Sn, Ge)-based alloys. Based on the Zaitsev et al. [2] work, n-type Mg$_2$(Si-Sn) solid solutions with thermoelectric figure of merit...
$ZT = \frac{S^2\sigma}{\kappa} \quad (S$ is thermopower or Seebeck coefficient; $\sigma$ is electrical conductivity; $\kappa$ is thermal conductivity, and $T$ is absolute temperature) up to 1.3 were obtained by several research groups [3–7]. Many researchers believe that there is possibility for further improvement. Now considerable efforts are directed to the development of a matching p-type material.

Already in the 1960s, it was shown that Mg$_2$X compounds (X = Si, Ge, Sn) and their solid solutions are promising compounds for thermoelectric energy conversion [8, 9]. Very high values of $ZT$ are reported in Refs. [10, 11]. However, later the interest to these compounds has been almost vanished until the last decade. A new wave of research activity on Mg$_2$X compounds was initiated by information about high figure of merit achieved in Mg$_2$Si-Mg$_2$Sn solid solutions and growing interest to environment-friendly materials for thermoelectric energy conversion.

The maximum conversion efficiency of thermoelectric generator $\eta$ is determined by dimensionless figure of merit $ZT$ [12]:

$$\eta = \frac{T_H - T_C}{T_H} \frac{\sqrt{ZT + 1} - 1}{\sqrt{ZT + 1} + \frac{T_C}{T_H}},$$

where $T_H$ and $T_C$ are temperatures at hot and at cold junctions of thermoelectric generator thermopile. $ZT$ is the dimensionless figure of merit, averaged over working temperature range $\Delta T = T_H - T_C$. The semiconductor physics theory gives the following estimate for parameter $Z$ [13]:

$$Z_{\text{max}} = \frac{3}{m^*} \frac{(m^*)^2 \mu}{\kappa_{\text{lat}}},$$

where $m^*$ is the effective mass of electron state density (DOS), $\mu$ is the free charge carriers’ mobility, and $\kappa_{\text{lat}}$ is the lattice thermal conductivity. One can see that a good thermoelectric material will have heavy effective mass, high charge carriers’ mobility, and low lattice thermal conductivity. However, in fact coefficients determining $Z$ are strongly interdependent. Thermoelectric materials with high DOS typically have low mobility. Introducing a disorder to suppress the thermal conductivity usually leads to decrease of charge carriers’ mobility. This is the reason of slow progress in the development of efficient thermoelectrics.

The unique characteristics of an electronic band structure of Mg$_2$X compounds make possible to explore the combination of two approaches to optimize the thermoelectric performance of such materials: the band structure engineering and the alloying [2, 5]. The combination allows to simultaneously maximize electronic parameters, characterized by power factor $S^2\sigma$, and to minimize lattice thermal conductivity, yielding high values of parameter $Z$. 

Thermoelectrics for Power Generation - A Look at Trends in the Technology
In this chapter, we summarize the present state of the knowledge on the crystal and electronic structure of Mg$_2$X compounds and their alloys, and review experimental data on thermoelectric properties of compounds.

2. Properties of Mg$_2$X compounds

2.1. Physical properties and crystal structure of Mg$_2$X

The basic properties of Mg$_2$X compounds are shown in Table 1. Melting temperature and energy gap, $E_g$, are typical for so-called middle temperature range thermoelectrics ($600 < T < 1200$ K). The materials, especially Mg$_2$Si, have very low density, $d$. Therefore, the ratio $\frac{ZT}{d}$ for Mg$_2$Si is the highest among commercial thermoelectrics. This is advantage for applications, where weight is a significant factor. High ZT in Mg$_2$Si can be related to high electron ($\mu_e$) and low hole ($\mu_h$) mobility. Their values at room temperature are shown in Table 1. Mg$_2$Ge has the highest electron mobility, but the electron to hole mobility ratio is lower in comparison to that for Mg$_2$Si. Mg$_2$Sn has the highest effective mass of DOS. It should be noted that among Mg$_2$X compounds, Mg$_2$Sn has the highest hole mobility with small difference between election and hole mobility. This suggests that p-type thermoelectrics based on Mg$_2$X alloys should contain a large fraction of Mg$_2$Sn.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting temperature, $T_m$ (K)</th>
<th>Lattice constant, $a$ (Å)</th>
<th>Density, $d$ (g cm$^{-3}$)</th>
<th>Bandgap $E_g$ (0 K) (eV)</th>
<th>Mobility (300 K)</th>
<th>Lattice thermal conductivity $\kappa_{lat}$ (300 K) (W m$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
</table>

Table 1. Some parameters of Mg$_2$X compounds.

Phase diagrams for the systems of magnesium and carbon groups of elements are well known [14]. Each phase diagram contains only one chemical compound of Mg$_2$X-type and two eutectic points. Mg$_2$X compounds crystallize with cubic, CaF$_2$-type, structure (space group Fm$\bar{3}$m) [16, 20]. In Mg$_2$X structure, the fluorine atom is replaced by the magnesium atom and the calcium atom is replaced by X atom (Figure 1). Each atom of the X group is surrounded by eight magnesium atoms in a regular cube. The bond in all these compounds is covalent [18]. Lattice parameters of compounds are presented in Table 1.
2.2. Energy spectra of current carriers in Mg$_2$X

Fundamental parameters of the electronic structure of the Mg$_2$X compound can be obtained from optical and electronic transport property measurements on high quality single crystals. Comprehensive review of transport properties and electronic energy structure for Mg$_2$X compounds is given in Ref. [21]. Based on the analysis of optical and electronic transport data, supplemented by results of band structure calculations, the band structure of Mg$_2$X compounds was proposed [16, 22–27]. Figure 2 shows schematically the most important characteristic of this band structure near to Fermi energy. The valence band of the compounds is similar to the valence band of Si and Ge. It consists of two degenerate bands ($V_1$, $V_2$) with different effective masses ($m_{V1}^*$ and $m_{V2}^*$) and a third band ($V_3$) split below the other two bands by gap $E_2$ due to spin-orbital interaction. The maximums of valence bands are located at Γ-point of a Brillouin zone. The conduction band consists of two subbands $C_L$ and $C_H$ of light ($m_{C_L}^*$) and heavy ($m_{C_H}^*$) electrons with their minimums located at X-point of a Brillouin zone. These subbands are separated by energy gap $E_1 = E_{C_L}(X) - E_{C_H}(X)$. There is a third conduction band $C$ with minimum at Γ-point, separated by gap $E_0$ from the top of valence bands. However, $E_0$ is considerably larger than indirect band gap $E_{ij}$; therefore, $C$ band has no direct effect on thermoelectric properties of Mg$_2$X compounds. Theoretical calculations confirmed this structure except for the fact that these calculations did not take into account spin-orbital interaction [16, 25–27]. Location of conduction band minimum at the X-point is favorable for thermoelectric performance of a material. In this case, the effective mass of DOS is six times heavier than inertial mass.
Because of that n-type Mg₂Si has high electrical conductivity and high thermopower. On the other hand, the valence band structure does not have such favorable thermoelectric features. The maximum of the valence band is at Γ-point; thus, the inertial mass and effective mass of DOS are not different. The valence band has three subbands, one of which split due to spin-orbital interaction [28]. This splitting extends with the increasing atom mass.

![Figure 2. Schematic band structure of Mg₂X. For Mg₂Si and Mg₂Ge light electron band (C₃) lies below heavy electron band (C₁), as shown in the picture. In the case of Mg₂Sn the heavy electron band C₁ is below the light electron band C₃.](image)

Parameters of band structure for Mg₂Sn, Mg₂Ge, and Mg₂Si are presented in Table 2. The values of indirect band gap \( E_g \) determined from electrical conductivity temperature dependence \( (E_g^T) \) and from optical data \( (E_g^0) \) are in good agreement. \( E_1 \) and \( E_2 \) are gaps between the conduction and valence subbands, respectively. \( E_0 \) is a direct band gap value. According to definition of \( E_0 \), it is positive for Mg₂Ge and Mg₂Si, where the low-lying conduction band has smaller effective mass. The opposite situation is in Mg₂Sn, where \( E_1 \) is negative. The effective mass of conduction band \( m_{CL}^* \) is shown for a low-lying subband, i.e. \( m_{CL}^* \) for Mg₂Ge and Mg₂Si, while \( m_{CH}^* \) — in the case of Mg₂Sn. The temperature coefficient of a band gap is shown in the last column.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( E_g^T ), eV</th>
<th>( E_g^0 ), eV</th>
<th>( E_1 ), eV</th>
<th>( E_0 ), eV</th>
<th>( E_2 ), eV</th>
<th>( \frac{m_{CL}^*}{m_0} )</th>
<th>( \frac{m_{CH}^*}{m_0} )</th>
<th>( \frac{dE_g}{dT} \times 10^4 ) (eV K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg₂Sn</td>
<td>0.36 [18]</td>
<td>0.35 [23]</td>
<td>−0.16 [23]</td>
<td>0.48 [22]</td>
<td>1.2 [23]</td>
<td>1.3 [23]</td>
<td>−3.2 [23]</td>
<td></td>
</tr>
<tr>
<td>Mg₂Ge</td>
<td>0.74 [18]</td>
<td>0.57 [24]</td>
<td>0.58 [24]</td>
<td>1.80 [29]</td>
<td>0.20 [22]</td>
<td>0.18 [30]</td>
<td>0.31 [30]</td>
<td>−1.8 [24]</td>
</tr>
<tr>
<td>Mg₂Si</td>
<td>0.77 [18]</td>
<td>0.78 [22]</td>
<td>0.4 [22]</td>
<td>0.03 [22]</td>
<td>0.45 [31]</td>
<td>0.9 [31]</td>
<td>−6 [18]</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Parameters of Mg₂X band structure (presented in Figure 3).
2.3. Thermal conductivity of Mg\(_2\)X compounds

Figure 3 shows temperature dependencies of reciprocal thermal conductivity of pure Mg\(_2\)X compounds. One can see that reciprocal thermal conductivity can be described satisfactory by a linear law and residual reciprocal thermal conductivity is zero within experimental uncertainty. The most probable reason for observed difference in data of different authors is dependence of reciprocal thermal conductivity on deviation from stoichiometry.

3. Solid solutions of Mg\(_2\)X compounds

3.1. Mg\(_2\)X-based solid solutions

As one can see from Table 1, Mg\(_2\)X compounds have relatively high thermal conductivity, which should be decreased to make these compounds practically useful thermoelectrics. However, decreasing in thermal conductivity should not lead to a considerable decrease of charge carriers’ mobility. Thermal conductivity can be reduced by selective scattering of phonons and electrons by point defects through forming solid solutions (alloys) between these isostructural compounds.

There is a continuous series of solid solutions in the system Mg\(_2\)Si-Mg\(_2\)Ge [9]. Phase diagrams of Mg\(_2\)Si-Mg\(_2\)Sn and Mg\(_2\)Ge-Mg\(_2\)Sn have wide peritectic region in the middle composition range [15, 33]. Until recently, it was commonly accepted that solid solutions exist only at compositions \(x < 0.4\) and \(x > 0.6\) for the Mg\(_2\)Si\(_{1-x}\)Sn\(_x\) system, and at \(x < 0.3\), \(x > 0.5\) for the Mg\(_2\)Ge\(_{1-x}\)Sn\(_x\) system. However, it has been demonstrated that solid solutions of any composition can be produced avoiding liquid stage by mechanical alloying.

Figure 4 shows dependences of lattice parameter (\(a\)) on alloys composition (\(x\)). In Ref. [33], it was shown that \(a(x)\) dependence follows to Vegard’s law for the whole composition range of the Mg\(_2\)Si-Mg\(_2\)Sn system.
Figure 4. Lattice parameter $a$ vs. solid solution composition $x$ dependences: 1—$\text{Mg}_2\text{Sn}_{1-x}\text{Ge}_x$ [15]; 2—$\text{Mg}_2\text{Si}_{1-x}\text{Ge}_x$ [9]; 3—$\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$ [33]; 4—Vegard’s law.

3.2. Thermal conductivity of $\text{Mg}_2X$ solid solutions

Figure 5 shows the experimental values of lattice thermal conductivity of $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$ [34], $\text{Mg}_2\text{Ge}_{1-x}\text{Sn}_x$ [34], $\text{Mg}_2\text{Si}_{1-x}\text{Ge}_x$ [35] alloys, and the results of calculations according to procedure, described in Refs. [34, 36]. In alloys, thermal conductivity sharply decreases with the addition of a small amount of second compound, while it has a weak dependence on the composition in the middle composition range $0.2 < x < 0.8$. One can see that the lowest thermal conductivity can be achieved in the system $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$ due to the maximum mass difference between the compounds. Consequently, this system is the most favorable from the point of view of thermoelectric energy conversion.

Figure 5. Lattice thermal conductivity of alloys at room temperature: 1—$\text{Mg}_2\text{Si}_{1-x}\text{Ge}_x$, 2—$\text{Mg}_2\text{Ge}_{1-x}\text{Sn}_x$, 3—$\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$. Symbols: experiment 1—[35]; 2, 3—[34]; lines—calculation [35].
3.3. Dependency of energy gap on solid solution composition

Besides lower thermal conductivity, the solid solutions of Mg_X provide opportunity to further enhancement of thermoelectric properties by electronic band structure engineering. Figure 6 shows dependences of energy gap of Mg_X alloys vs. composition [9, 15, 37–40]. From the study of the Mg_Si-Mg_Ge system [9]—one can conclude that energy gap is practically independent of alloy composition.

The situation is very different in other two alloy systems. The Mg_Ge-Mg_Sn system was studied by Busch et al. [15]. Notwithstanding the very narrow band gaps of Mg_Sn and Mg_Ge, it can be concluded that band gap dependence on solid solution composition is nonlinear. Our results of the band gap study of Mg_Ge_x_Sn_1-x solid solutions confirm this behavior. The situation is the same in the Mg_Si-Mg_Ge system [37–40]. Zaitsev et al. [37] proposed that there is band inversion in Mg_Si_1-x_Sn_x solid solutions. It means that in Mg_Si and Mg_Sn conduction bands C_L and C_H change their positions. Band inversion hypothesis was confirmed theoretically. Fedorov et al. [38] showed that the lowest conduction bands of Mg_Si and Mg_Ge are formed by Si or Ge states, whereas that of Mg_Sn was formed by Mg states. Figure 7 shows schematically dependence of relative positions of heavy electrons and light electrons conduction bands, as well as, the top of the valence band on the Mg_Si_1-x_Sn_x alloy composition. The lower panel explains the occurrence of kink on dependence of the band gap on composition at the inversion point. According to calculation in Ref. [5], composition dependence on light electron subband position in Mg_Si_1-x_Sn_x is nonlinear, while corresponding dependence of position of heavy electron subband is linear. Therefore, actual dependence of band gap on composition is more complex. Nevertheless, the scheme shown in Figure 7 illustrates correctly the essential physics. At the composition value, corresponding to band inversion point, the minima of heavy and light electrons subbands have equal energy. From the point of view of thermoelectricity, such situation is favorable, because DOS increases without decreasing in electron mobility. Such
degeneration of subbands occurs at certain composition and certain temperature, so this favorable situation is very limited.

![Figure 7. Schematic dependence of relative positions of heavy and light electron conduction subbands as well as the top of the valence band on the composition of the Mg$_2$Si$_{1-x}$Sn$_x$ alloy (the upper panel). Explanation of origin of kink on band gap dependence (the lower panel).](image)

Calculations show that the most favorable situation realizes when heavy electrons subband lays higher [41]. Another advantage of this situation is the absence of interband scattering [40].

3.4. Synthesis technology and doping

There are several methods to produce Mg$_2$X compounds. One of them is direct co-melting [8, 10]. This method has some limitation due to the large difference in melting temperature of components and high magnesium vapor pressure. It is necessary to pay a special attention to magnesium losses due to evaporation and segregation of the components (especially for Mg$_2$Sn).

Another way to produce these compounds is through a solid-state reaction. Mg$_2$X compounds have negative heat of formation, i.e. the formation reaction is exothermic [42–45]. However, oxide films on Mg particles prevent the reaction. Therefore, it is necessary to pay attention to the purity of components and avoid oxidization during mixing. Alternative manufacturing route has been developed for magnesium silicide derivatives [46]. Elemental powders were mixed in stoichiometric proportions, cold pressed into cylindrical preforms and heated in an oxygen-free environment to initiate the exothermic reaction. Reaction products were addi-
tionally heat treated for homogenization. Dense sinters can be produced by hot uniaxial pressing of the obtained powders under moderate temperature and pressure conditions.

Several advantages were identified in the proposed technology: relatively short time of synthesis, possibility of in-situ or ex-situ doping and grain size control.

Single crystals of Mg$_2$X compounds can be easily produced by any methods of directed crystallization.

It is hard to produce homogeneous solid solutions via a liquid phase through co-melting of the components. One of the problems is related to large difference in masses of magnesium, silicon, germanium, and tin atoms. Without stirring, segregation by specific weight occurs. The other problem relates to phase diagrams of solid solutions, which have large difference in liquidus and solidus curves in a wide range of compositions [33]. Therefore, compositional segregation occurs during crystallization as well. In order to homogenize alloys, a long-term annealing is necessary. The necessary homogenization annealing time is determined by diffusion processes, which depend on temperature and crystallite size. Temperature cannot be high due to magnesium evaporation. In order to shorten the annealing time, hot pressing can be utilized. Ingots of alloys are crushed into powder and then powder is pressed in a vacuum. The finer grain size the less time for homogenization is needed [47]. Annealing is not required for the samples produced from nanosize particles.

Recently, mechanical alloying in the ball mill followed by spark plasma sintering (SPS) has become the most popular preparation technique for this solid solution.

As mentioned above, the figure of merit Z is function of free charge carriers’ concentration. Optimal concentration yielding maximum $ZT$ value is equal to about $10^{19}$ to $10^{20}$ cm$^{-3}$. Theoretical and experimental investigations of a doping impurity effect in Mg$_2$Si for a wide range of impurity elements (B, Al, N, P, Sb, Bi, Cu, Ag, Au) were made by Tani and Kido [48, 49]. As, P, Sb, Bi, Al, and N were suggested as n-type dopants whereas Ga is suggested as p-type dopant. For In, Ag, Cu, and Au, the doping effect, i.e. a resulting conduction type, depends on the site in lattice where a doping atom will occupy. Actually, Ag-doped samples show p-type of conductivity. In Mg$_2$Sn-rich solid solutions, impurities Na, Li, Ga, Ag and at low concentration Al and In act as p-type dopants [50–53].

4. Thermoelectric properties of Mg$_2$X and its alloys

4.1. Mg$_2$X composites

As it was already mentioned that the new wave of research activity on Mg$_2$X-based thermoelectrics was initiated by work of Zaitsev et al., who demonstrated stable Mg$_2$(Si-Sn) alloys with a maximum $ZT$ value of about 1.1 at 800 K [2]. A systematic study of Mg$_2$Si thermoelectric properties was performed by Tani et al. They found $(ZT)_{max}$ for Mg$_2$Si, doped with 2 at% of bismuth of about 0.86 at 820 K with samples, fabricated by SPS [54]. However, such large $(ZT)_{max}$ has been not supported by independent researchers [55]. Sb and P-doped Mg$_2$Si was
investigated from 300 up to 900 K with the Sb content of up to 2% [56] and the P content up to 3% [57]. The samples were prepared from high-purity powder components by SPS. The maximum $ZT = 0.56$ was obtained at 860 K for sample with 2% of Sb due to the lowest thermal conductivity.

Samples of Mg$_2$Si, undoped and doped with Bi and Ag, were grown by a vertical Bridgman method [58, 59]. The n-type Bi-doped samples have a maximum $ZT$ of 0.65 at 840 K, while Ag-doped samples are of p-type (below 650 K) and show a maximum $ZT$ of 0.1 at 570 K.

A comprehensive study of a doping mechanism, i.e. location of dopants in Mg$_2$Si was undertaken by Farahi et al. [60]. Samples of Sb- and Bi-doped Mg$_2$Si were prepared via two-stage annealing of powder mixtures of individual components at 823 K for 3.5 days and at 873 K for 5 days, followed by hot pressing. It was shown that part of dopants replaces Si, while the rest forms, Mg$_3$Sb$_2$ and Mg$_3$Bi$_2$, found between the grains of doped Mg$_2$Si particles. As doping of Sb and Bi only partly led to Si substitution, experimentally determined charge carriers’ concentration was lower than originally expected.

Using a technique of incremental milling, phase pure Mg$_2$Si was produced within a few hours with negligible oxygen contamination [61]. In this technique, to prevent agglomeration of ductile Mg during ball milling, Mg is added to Si + doped mixture by small portions followed a comparatively short milling period until the stoichiometric amount of Mg is attained. More effective Bi doping is achieved with higher mobility values at lower concentrations of dopant compared to previous work. A peak $ZT$ value of about 0.7 is achieved at 775 K using an optimum doping level with only 0.15% of Bi, which is an order of magnitude lower than that mentioned in Ref. [54].

Temperature dependences of the figure of merit $ZT$ of Mg$_2$Si samples doped with different dopants are shown in Figure 8.

![Figure 8](image-url)
4.2. Figure of merit of n-type Mg,X-based solid solutions

Analysis of transport properties and band structure features has shown that the MgSi-MgSn system is the most promising for development of efficient n-type thermoelectrics. Figure 9 shows the effect of high band degeneracy on $ZT$. Temperature dependences of $ZT$ are shown for n-type Mg$_{2}$Si$_{0.4}$Sn$_{0.6}$ (left) and Mg$_{2}$Si$_{0.6}$Sn$_{0.4}$ (right) alloys. $C_{L}$ and $C_{H}$ subbands of the conduction band are close to each other in the Mg$_{2}$Si$_{0.4}$Sn$_{0.6}$ alloy, as the result it has higher $ZT$ at lower temperatures. In Mg$_{2}$Si$_{0.6}$Sn$_{0.4}$ subbands $C_{L}$ and $C_{H}$ are separated by a narrow gap; therefore, at low temperatures $C_{H}$ subband gives no contribution to electronic transport. Therefore, $ZT$ of Mg$_{2}$Si$_{0.4}$Sn$_{0.6}$ at low temperatures is smaller in comparison with $ZT$ of Mg$_{2}$Si$_{0.6}$Sn$_{0.4}$. However, at higher temperatures, the $C_{H}$ subband in this alloy gives increasing contribution to electrical conductivity and thermopower, which gives rise to enhanced $ZT$ values. Although both solid solutions have high maximum $ZT$ values close to 1.2, the average value ($ZT_{av}$) of Mg$_{2}$Si$_{0.4}$Sn$_{0.6}$ in the temperature range of 400–850 K, is higher (about 0.83 and 0.78, respectively). This study revealed the best compositions of n-type solid solutions and allowed reproducible synthesis of thermoelectrics with $ZT_{av} = 1.2$ and higher [2, 5]. Comparison of obtained results with the data for the state-of-the-art thermoelectrics revealed that these materials are among the best thermoelectrics of n-type in the temperature range of 600–870 K.

Figure 9. Figure of merit $ZT$ temperature dependences of alloys Mg$_{2}$Si$_{0.4}$Sn$_{0.6}$ (right) and Mg$_{2}$Si$_{0.6}$Sn$_{0.4}$ (left). $n$, $10^{20}$ cm$^{-3}$: (right) 1—3.17; 2—3.30; 3—3.83; 4—4.54. $n$, $10^{20}$ cm$^{-3}$: (left) 1—2.31; 2—2.52; 3—2.99; 4—3.10.

Several approaches have been used in order to maximize the figure of merit, including optimization of alloy composition and doping level, various types of nanostructuring. The nanostructuring is currently considered as the most promising and universal approach to enhance the thermoelectric performance. There are a number of technological approaches for producing different kinds of nanostructured materials. Most important among them are nanocrystalline materials, materials with nanoprecipitates of second phase and materials with...
nanoinclusions of foreign substance. All these approaches were applied with different degree of success to Mg\textsubscript{2}X compounds and related alloys.

Effects of nanostructuring on Mg\textsubscript{2}Si were theoretically modeled and systematically analyzed in Ref. [62]. It was shown that nanostructuring limits the energy-dependent phonon mean free path in Mg\textsubscript{2}Si, which results in significant reduction (50\%) in lattice thermal conductivity. However, it was also concluded that nanostructuring in both p-type and n-type Mg\textsubscript{2}Si increases significantly charge carrier scattering and leads to unfavorable reduction in electrical conductivity. A decrease in charge carriers’ mobility of nanostructured Mg\textsubscript{2}Si strongly affects the power factor, resulting in only minor enhancement in the overall figure of merit. In the case of nanostructured n-type Mg\textsubscript{2}Si, an optimal doping concentration of 8.1 \times 10^{19} \text{ cm}^{-3} was estimated for achieving \textit{ZT} of 0.83 at 850 K, which is less than 10\% improvement in comparison with the maximum \textit{ZT} of bulk Mg\textsubscript{2}Si. On the other hand, in the case of nanostructured p-type Mg\textsubscript{2}Si, a maximum \textit{ZT} of 0.90 at 850 K was predicted, which is nearly 37\% improvement over the maximum \textit{ZT} of bulk Mg\textsubscript{2}Si. The predicted optimum dopant concentration for p-type Mg\textsubscript{2}Si was equal to 4.3 \times 10^{20} \text{ cm}^{-3}. In practice, inherent challenge for p-type Mg\textsubscript{2}Si is a charge carriers’ compensation effect that limits the maximum charge carriers’ concentration by value 10^{18} \text{ cm}^{-3}.

A higher effect of nanostructuring on the efficiency of n-Mg\textsubscript{2}Si and n-Mg\textsubscript{2}Si\textsubscript{0.8}Sn\textsubscript{0.2} alloys was predicted in another theoretical work [63]. It was shown that relatively higher depression of lattice thermal conductivity compared to decrease in electrical conductivity due to grain boundary scattering can lead to 10 and 15\% increase of \textit{ZT} at 850 K in nanostructured materials based on Mg\textsubscript{2}Si and Mg\textsubscript{2}Si\textsubscript{0.8}Sn\textsubscript{0.2}, respectively. A nanostructured alloy is more favorable for increase in the figure of merit than bulk Mg\textsubscript{2}Si.

The presence of nanoinclusions is considered as an alternative approach to achieve nanoscale effects. Theoretical estimate of additional scattering on nanoinclusions of Mg\textsubscript{2}Si and Mg\textsubscript{2}Ge in the n-Mg\textsubscript{2}Si\textsubscript{0.4}Sn\textsubscript{0.6} matrix predicted a considerable increase in the figure of merit [64]. A small concentration of nanoparticles (about 3.4\%) can lead to 60\% reduction of thermal conductivity at 300 K and to 40\% at 800 K with the optimal particle size of a few nanometers. The best value of \textit{ZT} 1.9 at 800 K is predicted for Mg\textsubscript{2}Si or Mg\textsubscript{2}Ge nanoparticles in Mg\textsubscript{2}Si\textsubscript{0.4}Sn\textsubscript{0.6}, which is considerably higher than the best experimental value for these alloys.

Various material synthesis technologies and alloy compositions were used in experiments in order to increase the figure of merit. Combination of induction melting, melt spinning (MS), and spark plasma sintering (SPS) methods were used to produce n-type Mg\textsubscript{2}Si\textsubscript{0.4}Sn\textsubscript{0.6} alloys doped with Bi [6]. Multiple localized nanostructures within the matrix containing nanoscale precipitates and mesoscale grains were formed, resulting in a remarkable decrease of lattice thermal conductivity, particularly for the samples with nanoscale precipitates having a size of 10–20 nm. Meanwhile, electrical resistivity was reduced and the Seebeck coefficient was increased by Bi-doping, causing improved electrical performance. Figure of merit \textit{ZT} was significantly improved and the maximum value reaches 1.20 at 573 K for the Mg\textsubscript{2}Si\textsubscript{0.4}Sn\textsubscript{0.6}+3\% Bi sample, which is higher than that of nondoped samples. In comparison to samples of a similar composition, prepared by a conventional procedure, these samples have very low thermal conductivity, larger thermopower, and lower electrical conductivity.
Another way to increase the $ZT$ value is use of quasi-quaternary alloys Mg-Si-Mg-Sn-Mg-Ge. Although theoretical calculation did not predict noticeable influence of Ge on the lattice thermal conductivity of Mg-Si-Mg-Sn [65], it was demonstrated experimentally that $ZT$ can be increased up to 1.4 in Bi-doped Mg$_{0.7}$Si$_{0.3}$Sn$_{0.7}$Ge$_{y}$ ($x = 0.4$ and $y = 0.05$) alloys [3, 66]. Alloys were prepared by solid-state synthesis and sintering via hot pressing. Transmission electron microscopy (TEM) confirmed the coexistence of phases with different stoichiometry and yielded nanofeatures of the Mg$_{0.7}$Si$_{0.3}$Sn$_{0.7}$Ge$_{y}$ phase. Thermoelectric properties of these materials were affected by different stoichiometry and the Sn-rich phase is believed to play a crucial role. High figure of merit could be attributed to a relatively high power factor that is related to contribution of the Sn-rich phase as well as low thermal conductivity that originates from nanostructuring.

Homogeneous alloys Mg$_{0.3}$Si$_{0.7}$Sn$_{0.7}$ were successfully prepared by nonequilibrium synthesis (melt spinning) followed by hot pressing and a plasma-assisted sintering (MS-PAS) technique [7]. Microstructure homogenization promotes charge carrier transport and effectively enhances the power factor. As a result, the MS-PAS sample achieved the highest figure of merit $ZT$ of 1.30 at 750 K. However, the Mg$_{0.3}$Si$_{0.7}$Sn$_{0.7}$ alloy is intrinsically unstable at higher temperatures and tends to decompose into various Si-rich and Sn-rich phases even following the modest annealing at 773 K for 2 h.

The influence of grain size on thermoelectric properties of Mg$_{0.3}$Si$_{0.7}$Sn$_{0.7}$ doped with Sb was investigated using samples prepared by hot-pressing synthesized powders with grain sizes in the range from 100 to below 70 nm [67]. Contrary to expectation, no significant reduction of thermal conductivity in nanograin samples was found. $ZT$ showed very weak dependence on grain’s size with maximum values of about 0.8–0.9 at 900 K.

The best $ZT$ results for n-type of Mg-Si-based thermoelectrics are summarized in Figure 10.

4.3. Figure of merit of p-type Mg$_{2}$X solid solutions

To realize high performance of n-type Mg$_{2}$X-based alloys in practical applications, one needs to have a matching p-type material, preferably of the same base material. Therefore, considerable efforts have been made to the development of p-type Mg$_{2}$X-based alloys. However, progress with this development has been not so impressive as with n-type materials. At present, the maximum $ZT$ of p-type Mg$_{2}$X-based alloys is about 0.5. There are several reasons for this. The high $ZT$ of the n-type Mg$_{2}$(Si-Sn) alloys is connected in part with high valley degeneracy of the conduction band that increases in alloys due to the band inversion effect. The valley degeneracy effect is absent for the valence band, since the top of this band is located at the Γ-point of the Brillouin zone. Furthermore, hole mobility is lower than the electron mobility in all Mg$_{2}$X compounds; hence, the onset of intrinsic conduction gives a negative impact on thermoelectric performance at lower temperatures in comparison with n-type alloys. The difference between hole and electron mobility is smallest in Mg$_{2}$Sn, where the electron-to-hole mobility ratio is about 1.5. Therefore, one can expect that the most efficient p-type alloy will contain a large fraction of Mg$_{2}$Sn.
Figure 10. The best figure of merit of the Mg$_2$Si-Mg$_2$Sn alloy. 1—Mg$_2$Si$_{0.4}$Sn$_{0.6}$+Sb \([2]\); 2—Mg$_2$Si$_{0.3}$Sn$_{0.7}$+0.6\% Sb \([5]\); 3—Mg$_2$Si$_{0.4}$Sn$_{0.6}$+1\% Bi \([6]\); 4—Mg$_2$Si$_{0.3}$Sn$_{0.7}$Ge$_{0.05}$Bi$_{0.02}$ \([3]\); 5—Mg$_2$(Si$_{0.3}$Sn$_{0.7}$)$_{0.98}$Sb$_{0.02}$ \([7]\).

There are several potential p-type dopants for Mg$_2$X compounds. The most effective impurities for Mg$_2$Sn-rich alloys are Ga and Li. Both of these dopants provide hole concentrations higher than $10^{20}$ cm$^{-3}$. Our study shows that these impurities yield one hole per dopant atom up to 2.5\% Ga and 1.5\% Li. Alloy Mg$_2$Si$_{0.3}$Sn$_{0.7}$ doped with these impurities has a maximum $ZT$ of up to 0.45 at 650 K \([4, 68]\).

Experimental and theoretical studies of effects related to Ga doping of the Mg$_2$Si compound and the Mg$_2$Si$_{0.6}$Ge$_{0.4}$ alloy by measurements of electrical resistivity, thermopower, Hall coefficient, and thermal conductivity, supplemented by electronic band structure calculations, have shown that p-type materials with the maximum $ZT$ value of 0.36 at 625 K can be obtained for Mg$_2$Si$_{0.6}$Ge$_{0.4}$:Ga (0.8\%) \([69]\).

Another p-type dopant is silver. The maximum figure of merit $ZT$ of 0.38 was achieved at 675 K for Mg$_{1.98}$Ag$_{0.02}$Si$_{0.4}$Sn$_{0.6}$ \([70]\). It was found that the solubility of Ag in Mg$_2$Si$_{0.3}$Sn$_{0.7}$ is about 2\%. Oversaturated Ag doping in Mg$_2$Si$_{0.3}$Sn$_{0.7}$ is unfavorable for the improvement of thermoelectric properties.

Investigation on the effect of Li doping on electrical and thermal transport properties of Mg$_2$Si$_{0.3}$Sn$_{0.7}$ alloys indicated that Li is an efficient dopant occupying Mg sites. Theoretical calculations as well as experiments indicate that Li doping preserves high hole mobility. While overall thermal conductivity increases with an increase in the Li content (due to enhanced electrical conductivity) at low to mid-range temperatures, the beneficial effect of Li doping is shifting the onset of bipolar conductivity to higher temperatures and thus extending the regime, where thermal conductivity benefits from Umklapp phonon scattering. As a consequence, thermoelectric performance is significantly improved with the figure of merit $ZT$...
reaching a value of 0.50 at around 750 K at the Li doping level of 0.07 [71]. Figure 11 summarizes ZT temperature dependences for the best p-type Mg$_2$X-based alloys.

Figure 11. The figure of merit for the state-of-the-art p-type Mg$_2$Si-Mg$_2$Sn alloys. 1—Mg$_2$(Si$_{0.3}$Sn$_{0.7}$)$_{0.985}$Ga$_{0.015}$ [4]; 2—Mg$_2$Si$_{0.6}$Ge$_{0.4}$+0.8% Ga [69]; 3—Mg$_{1.98}$Ge$_{0.4}$Sn$_{0.6}$Ag$_{0.02}$ [70]; 4—Mg$_{1.86}$Si$_{0.3}$Sn$_{0.7}$Li$_{0.14}$ [71]; 5—Mg$_{1.99}$Si$_{0.3}$Sn$_{0.7}$Li$_{0.01}$ [68].

Known attempts to use nanostructuring have not yielded positive results for p-doped Mg$_2$X-based alloys. Another practically important problem with p-type alloys containing a large fraction of Mg$_2$Sb is their intrinsic instability.

5. Conclusion

The last decade comprehensive study of Mg$_2$X and Mg$_2$X-based alloys has yielded rather impressive results. Mg$_2$X-based n-type alloys are sufficiently stable at a temperature up to about 800 K and have maximum figure of merit close to 1.5. The combination of high-thermo-electric performance with low cost of raw elemental materials places these materials among the best thermoelectrics for temperature range from 300 to 800 K. However, there are still many problems to be solved in order to bring these alloys to the application stage. The most important problem is the failure to develop a matching p-type thermoelectric material. The best ZT value for p-type Mg$_2$X-based alloys does not exceed 0.5. Moreover, the p-type alloys are not sufficiently stable. Another problem is the absence of technology for making stable, high quality electrical contacts with the alloys. However, this problem certainly can be solved with adequate efforts and resources.
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