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Efficient Thermoelectric Materials Based on Solid Solutions of Mg₂X Compounds (X = Si, Ge, Sn)

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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 Mg₂(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 Mg₂X 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 Mg₂X (X = Si, Sn, Ge)-based alloys. Based on the Zaitsev et al. [2] work, n-type Mg₂(Si-Sn) solid solutions with thermoelectric figure of merit

$ZT = \frac{S^2\sigma}{\kappa}T$ (S is thermopower or Seebeck coefficient; σ is electrical conductivity; κ 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_2X 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_2X compounds was initiated by information about high figure of merit achieved in Mg_2Si-Mg_2Sn solid solutions and growing interest to environment-friendly materials for thermoelectric energy conversion.

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

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

where T_H and T_C are temperatures at hot and at cold junctions of thermoelectric generator thermopile. $\overline{ZT}$ 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]:

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

where m^* is the effective mass of electron state density (DOS), μ is the free charge carriers' mobility, and κ_{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_2X 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.

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 (μ_n) and low hole (μ_p) 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.

Compo-und	Melting temperature, T_m	Lattice constant, a	Density, d	Bandgap E_g (0 K)	Mobility (300 K)		Lattice thermal conductivity κ_{lat} (300K)
					μ_n	μ_p	
	(K)	(Å)	(g cm^{-3})	(eV)	(cm^2 V^{-1}·s^{-1})		(W m^{-1} K^{-1})
Mg$_2$Si	1375 [14]	6.338 [15]	1.88 [18]	0.77 [18]	405	65	7.9 [19]
Mg$_2$Ge	1388 [14]	6.3849 [16]	3.09 [18]	0.74 [18]	530	110	6.6 [19]
Mg$_2$Sn	1051 [14]	6.765 [17]	3.59 [18]	0.35 [18]	320	260	5.9 [19]

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 Fm3m) [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**.
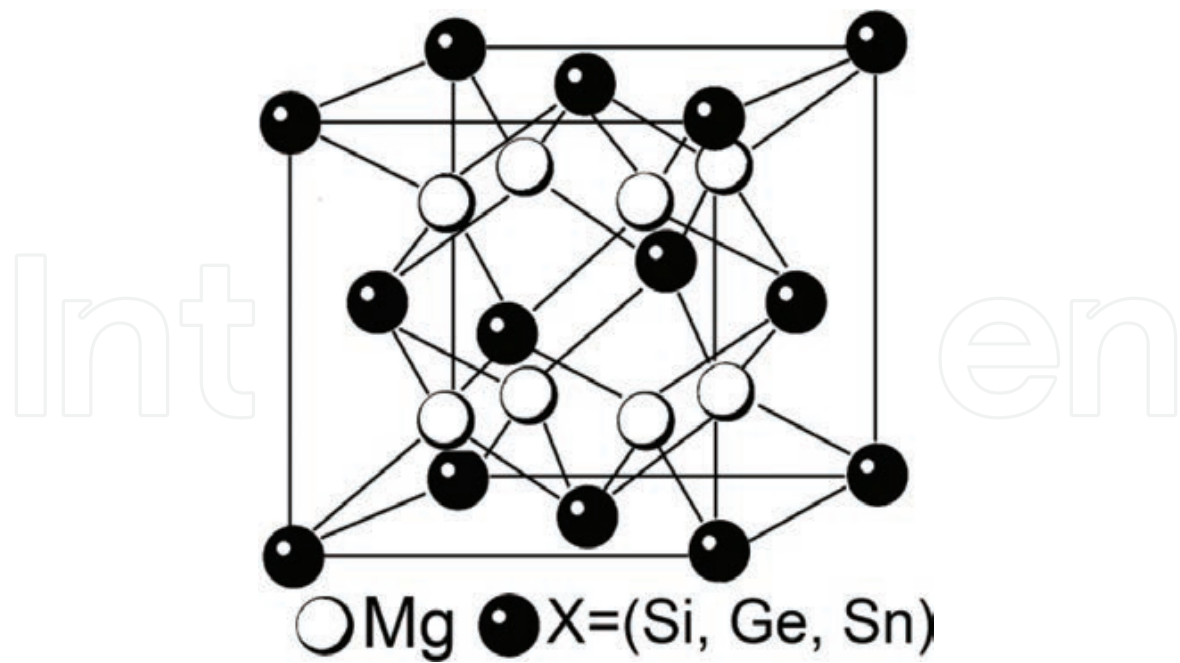
Figure 1. Mg₂X crystal structure.

2.2. Energy spectra of current carriers in Mg₂X

Fundamental parameters of the electronic structure of the Mg₂X 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 Mg₂X 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 Mg₂X 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 ($m_{V_1}^*$ and $m_{V_2}^*$)and a third band (V_3) split below the two other 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 $E_1 = E_{C_H}(X) - E_{C_L}(X)$. 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_g; therefore, C band has no direct effect on thermoelectric properties of Mg₂X 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 perform-ance of a material. In this case, the effective mass of DOS is six times heavier than inertial mass.

Because of that n-type Mg$_2$Si 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 valance 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.
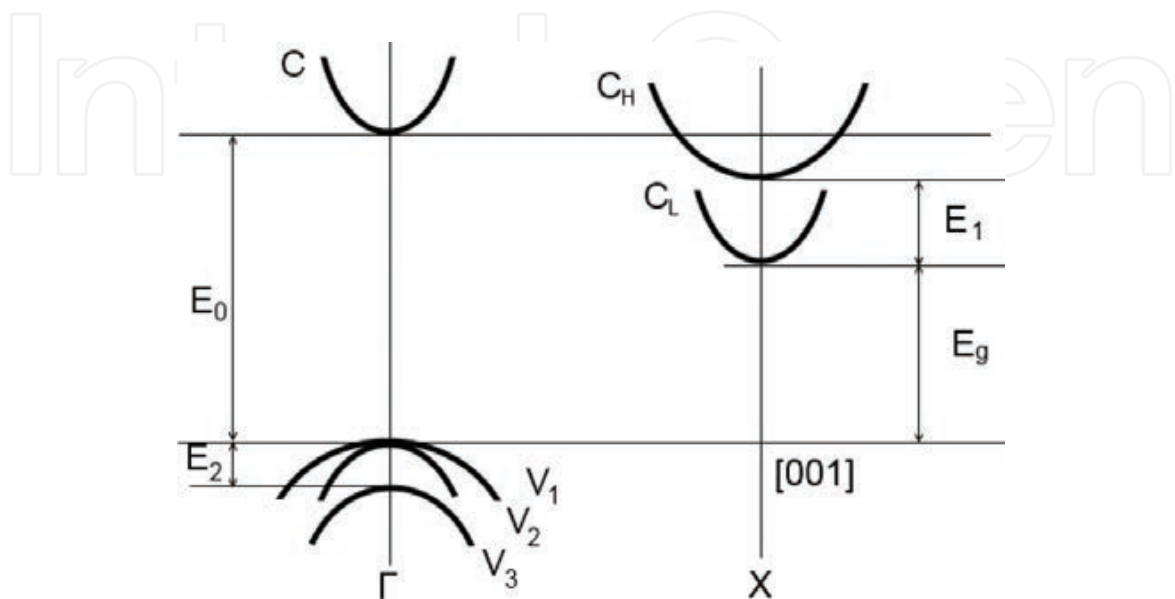

Figure 2. Schematic band structure of Mg$_2$X. For Mg$_2$Si and Mg$_2$Ge light electron band (C$_L$) lies below heavy electron band (C$_H$), as shown in the picture. In the case of Mg$_2$Sn the heavy electron band C$_H$ is below the light electron band C$_L$.

Parameters of band structure for Mg$_2$Sn, Mg$_2$Ge, and Mg$_2$Si 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_1, it is positive for Mg$_2$Ge and Mg$_2$Si, where the low-lying conduction band has smaller effective mass. The opposite situation is in Mg$_2$Sn, where E_1 is negative. The effective mass of conduction band (m_C^*) is shown for a low-lying subband, i.e. $m_{C_L}^*$ for Mg$_2$Ge and Mg$_2$Si, while $m_{C_H}^*$ —in the case of Mg$_2$Sn. The temperature coefficient of a band gap is shown in the last column.

Compound	E_g^T, eV	E_g^0, eV	E_1, eV	E_0, eV	E_2, eV	$\dfrac{m_C^*}{m_0}$	$\dfrac{m_{V_1 V_2}^*}{m_0}$	$\dfrac{dE_g}{dT} \times 10^4$, (eV K^{-1})
Mg$_2$Sn	0.36 [18]	0.35 [23]	−0.16 [23]		0.48 [22]	1.2 [23]	1.3 [23]	−3.2 [23]
Mg$_2$Ge	0.74 [18]	0.57 [24]	0.58 [24]	1.80 [29]	0.20 [22]	0.18 [30]	0.31 [30]	−1.8 [24]
Mg$_2$Si	0.77 [18]	0.78 [22]	0.4 [22]		0.03 [22]	0.45 [31]	0.9 [31]	−6 [18]

Table 2. Parameters of Mg$_2$X band structure (presented in **Figure 3**).

2.3. Thermal conductivity of Mg_2X compounds

Figure 3 shows temperature dependencies of reciprocal thermal conductivity of pure Mg_2X 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.
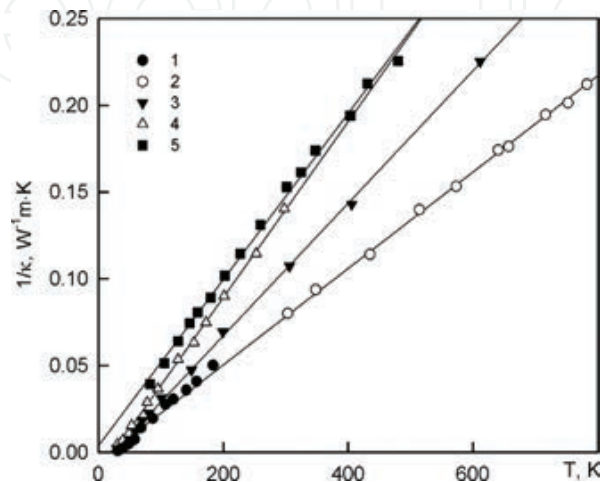

Figure 3. Temperature dependence of reciprocal thermal conductivity of pure Mg_2X compounds: 1, 2—Mg_2Si [19, 21]; 3 —Mg_2Ge[19]; 4, 5—Mg_2Sn[19, 32].

3. Solid solutions of Mg_2X compounds

3.1. Mg_2X-based solid solutions

As one can see from **Table 1**, Mg_2X 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_2Si-Mg_2Ge [9]. Phase diagrams of Mg_2Si-Mg_2Sn and Mg_2Ge-Mg_2Sn 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 $Mg_2Si_{1-x}Sn_x$ system, and at $x < 0.3$, $x > 0.5$ for the $Mg_2Ge_{1-x}Sn_x$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_2Si-Mg_2Sn system.
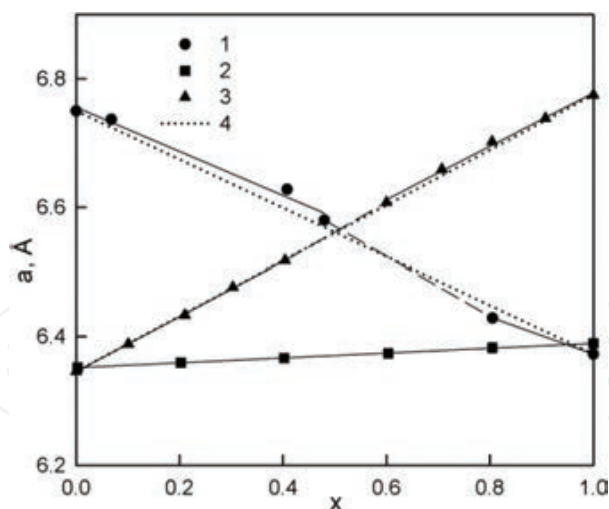
Figure 4. Lattice parameter a vs. solid solution composition x dependences: 1—$Mg_2Sn_{1-x}Ge_x$ [15]; 2—$Mg_2Si_{1-x}Ge_x$ [9]; 3—$Mg_2Si_{1-x}Sn_x$ [33]; 4—Vegard's law.

3.2. Thermal conductivity of Mg₂X solid solutions

Figure 5 shows the experimental values of lattice thermal conductivity of $Mg_2Si_{1-x}Sn_x$ [34], $Mg_2Ge_{1-x}Sn_x$[34], $Mg_2Si_{1-x}Ge_x$ [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 $Mg_2Si_{1-x}Sn_x$ 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.
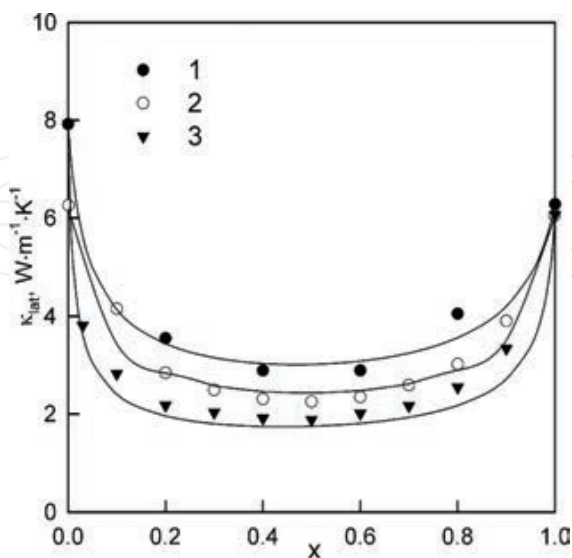

Figure 5. Lattice thermal conductivity of alloys at room temperature: 1–$Mg_2Si_{1-x}Ge_x$, 2–$Mg_2Ge_{1-x}Sn_x$, 3–$Mg_2Si_{1-x}Sn_x$. Symbols: experiment 1–[35]; 2, 3–[34]; lines–calculation [35].

3.3. Dependency of energy gap on solid solution composition

Besides lower thermal conductivity, the solid solutions of Mg_2X provide opportunity to further enhancement of thermoelectric properties by electronic band structure engineering. **Figure 6** shows dependences of energy gap of Mg_2X alloys vs. composition [9, 15, 37–40]. From the study of the Mg_2Si-Mg_2Ge system [9]—one can conclude that energy gap is practically independent of alloy composition.
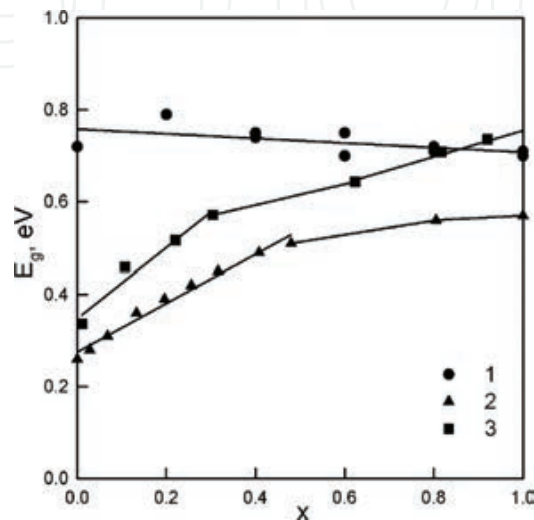

Figure 6. Energy gap E_g of alloys as a function of composition x. 1—$Mg_2Si_{1-x}Ge_x$ [9]; 2—$Mg_2Sn_{1-x}Ge_x$ [15]; 3—$Mg_2Si_{1-x}Sn_x$ [37].

The situation is very different in other two alloy systems. The Mg_2Ge-Mg_2Sn system was studied by Busch et al. [15]. Notwithstanding the very narrow band gaps of Mg_2Sn and Mg_2Ge, it can be concluded that band gap dependence on solid solution composition is nonlinear. Our results of the band gap study of $Mg_2Ge_{1-x}Sn_x$ solid solutions confirm this behavior. The situation is the same in the Mg_2Si-Mg_2Sn system [37–40]. Zaitsev et al. [37] proposed that there is band inversion in $Mg_2Si_{1-x}Sn_x$ solid solutions. It means that in Mg_2Si and Mg_2Sn 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_2Si and Mg_2Ge are formed by Si or Ge states, whereas that of Mg_2Sn 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 $Mg_2Si_{1-x}Sn_x$ 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 $Mg_2Si_{1-x}Sn_x$ 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.
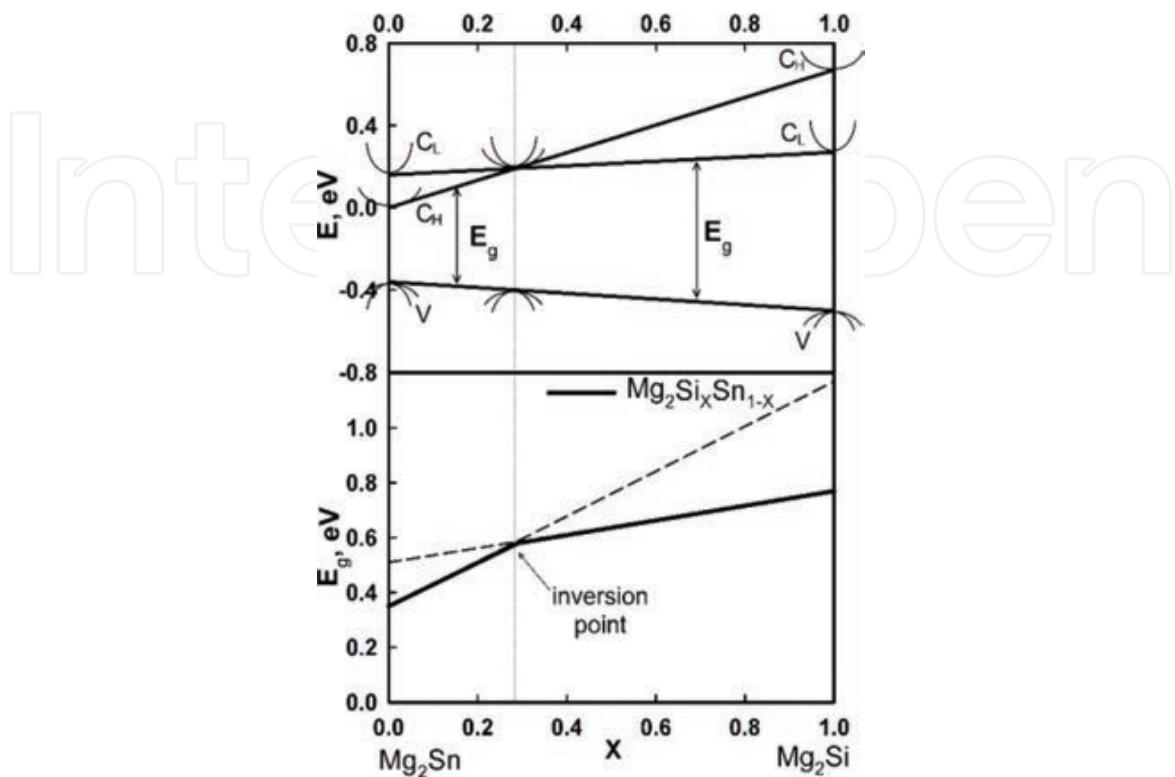

Figure 7. Schematic dependence of relative positions of heavy and light electron conduction subbands as well as the top of the valence band on the composition of the Mg₂Si₁₋ₓSnₓ alloy (the upper panel). Explanation of origin of kink on band gap dependence (the lower panel).

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 Mg₂X 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 Mg₂Sn).

Another way to produce these compounds is through a solid-state reaction. Mg₂X 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_2X 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_2Si 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_2Sn-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_2X and its alloys

4.1. Mg_2X composites

As it was already mentioned that the new wave of research activity on Mg_2X-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_2Si thermoelectric properties was performed by Tani et.al. They found $(ZT)_{max}$ for Mg_2Si, 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_2Si 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**.
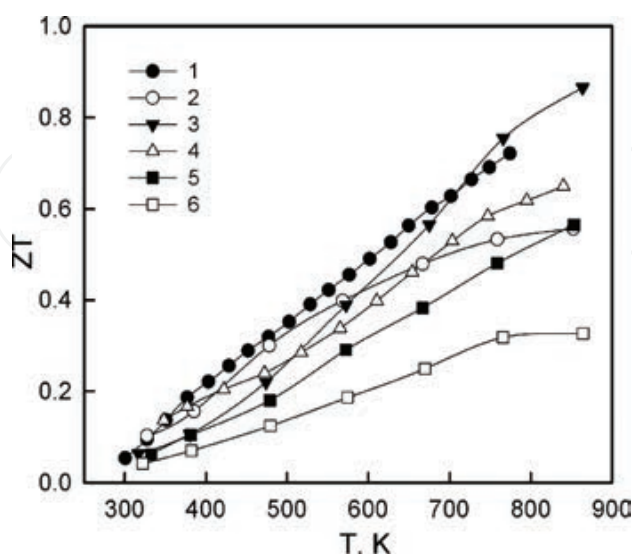

Figure 8. Figure of merit ZT temperature dependences of Mg$_2$Si. 1—Mg$_2$Si+0.15% Bi [61]; 2—Mg$_2$Si+0.5% Sb [58]; 3—Mg$_2$Si+2% Sb [54]; 4—Mg$_2$Si+1% Bi [59]; 5—Mg$_2$Si+2% Sb [56]; 6—Mg$_2$Si+3% P [57].

4.2. Figure of merit of n-type Mg₂X-based solid solutions

Analysis of transport properties and band structure features has shown that the Mg_2Si-Mg_2Sn 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 $Mg_2Si_{0.4}Sn_{0.6}$ (left) and $Mg_2Si_{0.6}Sn_{0.4}$ (right) alloys. C_L and C_H subbands of the conduction band are close to each other in the $Mg_2Si_{0.4}Sn_{0.6}$ alloy, as the result it has higher ZT at lower temperatures. In $Mg_2Si_{0.6}Sn_{0.4}$, 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 $Mg_2Si_{0.6}Sn_{0.4}$ at low temperatures is smaller in comparison with ZT of $Mg_2Si_{0.6}Sn_{0.4}$. 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 $Mg_2Si_{0.4}Sn_{0.6}$, 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 $ZT_{max} \approx 1.2$ 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.
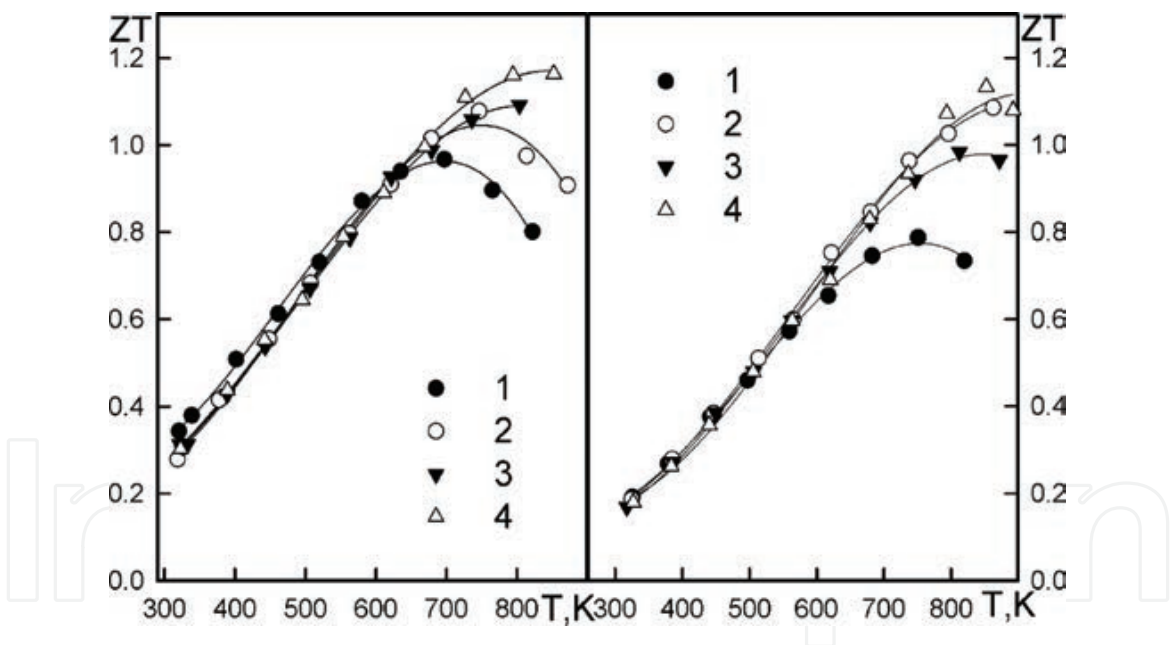

Figure 9. Figure of merit ZT temperature dependences of alloys $Mg_2Si_{0.6}Sn_{0.4}$ (right) and $Mg_2Si_{0.4}Sn_{0.6}$ (left). n, $10^{20}\,cm^{-3}$: (right) 1—3.17; 2—3.30; 3—3.83; 4—4.54. n, $10^{20}\,cm^{-3}$: (left) 1—2.31; 2—2.52; 3—2.99; 4—3.10.

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$_2$X compounds and related alloys.

Effects of nanostructuring on Mg$_2$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$_2$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$_2$Si increases significantly charge carrier scattering and leads to unfavorable reduction in electrical conductivity. A decrease in charge carriers' mobility of nanostructured Mg$_2$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$_2$Si, an optimal doping concentration of 8.1×10^{19} cm^{-3} was estimated for achieving ZT of 0.83 at 850 K, which is less than 10% improvement in comparison with the maximum ZT of bulk Mg$_2$Si. On the other hand, in the case of nanostructured p-type Mg$_2$Si, a maximum ZT of 0.90 at 850 K was predicted, which is nearly 37% improvement over the maximum ZT of bulk Mg$_2$Si. The predicted optimum dopant concentration for p-type Mg$_2$Si was equal to 4.3×10^{20} cm^3. In practice, inherent challenge for p-type Mg$_2$Si is a charge carriers' compensation effect that limits the maximum charge carriers' concentration by value 10^{18} cm^{-3}.

A higher effect of nanostructuring on the efficiency of n-Mg$_2$Si and n-Mg$_2$Si$_{0.8}$Sn$_{0.2}$ 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 ZT at 850 K in nanostructured materials based on Mg$_2$Si and Mg$_2$Si$_{0.8}$Sn$_{0.2}$, respectively. A nanostructured alloy is more favorable for increase in the figure of merit than bulk Mg$_2$Si.

The presence of nanoinclusions is considered as an alternative approach to achieve nanoscale effects. Theoretical estimate of additional scattering on nanoinclusions of Mg$_2$Si and Mg$_2$Ge in the n-Mg$_2$Si$_{0.4}$Sn$_{0.6}$ 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 ZT 1.9 at 800 K is predicted for Mg$_2$Si or Mg$_2$Ge nanoparticles in Mg$_2$Si$_{0.4}$Sn$_{0.6}$, 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$_2$Si$_{0.4}$Sn$_{0.6}$ 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 ZT was significantly improved and the maximum value reaches 1.20 at 573 K for the Mg$_2$Si$_{0.4}$Sn$_{0.6}$+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_2Si-Mg_2Sn-Mg_2Ge. Although theoretical calculation did not predict noticeable influence of Ge on the lattice thermal conductivity of Mg_2Si-Mg_2Sn [65], it was demonstrated experimentally that ZT can be increased up to 1.4 in Bi-doped $Mg_2Si_{1-x-y}Sn_xGe_y$ ($x = 0.4$ 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 $Mg_2Si_{1-x-y}Sn_xGe_y$ 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 $Mg_2Si_{0.3}Sn_{0.7}$ 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 $Mg_2Si_{0.3}Sn_{0.7}$ 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 $Mg_2Si_{0.8}Sn_{0.2}$ 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 nanograined 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_2Si-based thermoelectrics are summarized in **Figure 10**.

4.3. Figure of merit of p-type Mg_2X solid solutions

To realize high performance of n-type Mg_2X-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_2X-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_2X-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_2X 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_2Sn, 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_2Sn.
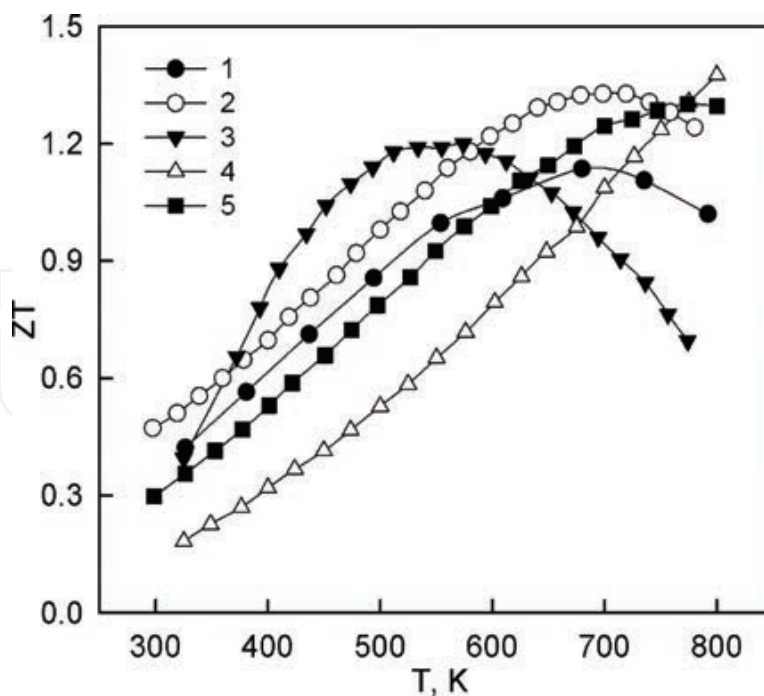
Figure 10. The best figure of merit of the Mg$_2$Si-Mg$_2$Sn alloy. 1—Mg$_2$Si$_{0.4}$Sn$_{0.6}$+Sb [2]; 2—Mg$_2$Si$_{0.3}$Sn$_{0.7}$+0.6% Sb [5]; 3—Mg$_2$Si$_{0.4}$Sn$_{0.6}$+1% Bi [6]; 4—Mg$_2$Si$_{0.53}$Sn$_{0.4}$Ge$_{0.05}$Bi$_{0.02}$ [3]; 5—Mg$_2$(Si$_{0.3}$Sn$_{0.7}$)$_{0.98}$Sb$_{0.02}$ [7].

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$_{0.4}$Sn$_{0.6}$ is about 2%. Oversaturated Ag doping in Mg$_2$Si$_{0.4}$Sn$_{0.6}$ 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_2X-based alloys.
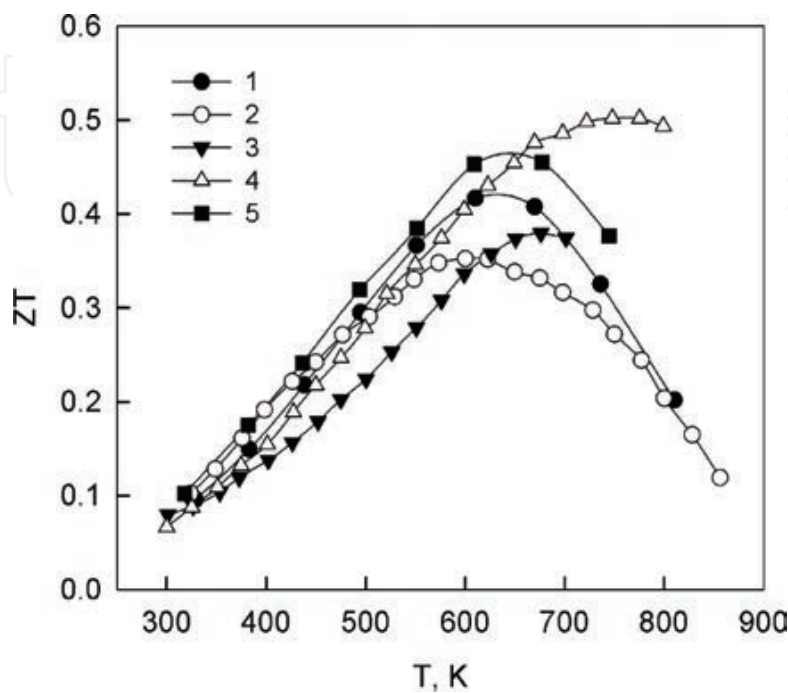

Figure 11. The figure of merit for the state-of-the-art p-type Mg_2Si-Mg_2Sn alloys. $1—Mg_2(Si_{0.3}Sn_{0.7})_{0.985}Ga_{0.015}$ [4]; $2—Mg_2Si_{0.6}Ge_{0.4}+0.8\%$ Ga [69]; $3—Mg_{1.98}Ge_{0.4}Sn_{0.6}Ag_{0.02}$ [70]; $4—Mg_{1.86}Si_{0.3}Sn_{0.7}Li_{0.14}$ [71]; $5—Mg_{1.99}Si_{0.3}Sn_{0.7}Li_{0.01}$ [68].

Known attempts to use nanostructuring have not yielded positive results for p-doped Mg_2X-based alloys. Another practically important problem with p-type alloys containing a large fraction of Mg_2Sb is their intrinsic instability.

5. Conclusion

The last decade comprehensive study of Mg_2X and Mg_2X-based alloys has yielded rather impressive results. Mg_2X-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_2X-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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References

[1] Nikitin E.: Investigation on temperature dependencies of electrical conductivity and thermopower of silicides. Zhurnal Tekhnicheskoj Fiziki. 1958;28:23–25.

[2] Zaitsev VK, Fedorov MI, Gurieva EA, Eremin IS, Konstantinov PP, Samunin AY, Vedernikov MM.: Highly effective Mg$_2$Si$_{1-x}$Sn$_x$ thermoelectrics. Physical Review B. 2006;74(4):45207. DOI: 10.1103/PhysRevB.74.045207

[3] Khan A, Vlachos N, Kyratsi T.: High thermoelectric figure of merit of Mg$_2$Si$_{0.55}$Sn$_{0.4}$Ge$_{0.05}$ materials doped with Bi and Sb. Scripta Materialia. 2013;69(8):606–609. DOI: 10.1016/j.scriptamat.2013.07.008

[4] Fedorov MI, Zaitsev VK, Isachenko GN.: High effective thermoelectrics based on the Mg$_2$Si-Mg$_2$Sn solid solution. Solid State Phenomena. 2011;170:286–292. DOI: 10.4028/www.scientific.net/SSP.170.286

[5] Liu W, Tan X, Yin K, Liu H, Tang X, Shi J, Zhang Q, Uher C.: Convergence of conduction bands as a means of enhancing thermoelectric performance of n-type Mg$_2$Si$_{1-x}$Sn$_x$ solid solutions. Physical Review Letters. 2012;108(16):166601. DOI: 10.1103/PhysRevLett.108.166601

[6] Zhang X, Liu H, Lu Q, Zhang J, Zhang F.: Enhanced thermoelectric performance of Mg$_2$Si$_{0.4}$Sn$_{0.6}$ solid solutions by in nanostructures and minute Bi-doping. Applied Physics Letters. 2013;103(6):063901. DOI: 10.1063/1.4816971

[7] Zhang Q, Zheng Y, Su X, Yin K, Tang X, Uher C.: Enhanced power factor of Mg$_2$Si$_{0.3}$Sn$_{0.7}$ synthesized by a non-equilibrium rapid solidification method. Scripta Materialia. 2015;96:1–4. DOI: 10.1016/j.scriptamat.2014.09.009

[8] Nikitin EN, Bazanov VG, Tarasov VI.: The thermoelectric properties of solid solution Mg$_2$Si-Mg$_2$Sn. Soviet Physics of Solid State. 1961;3(12):2648–2651.

[9] Labotz RJ, Mason DR, O'Kane DF.: The thermoelectric properties of mixed crystals Mg$_2$Ge$_x$Si$_{1-x}$. Journal of the Electrochemical Society. 1963;110(2):127–134.

[10] Nicolau MC. Material for direct thermoelectric energy conversion with a high figure of merit. In: Proceedings of International Conference on Thermoelectric Energy Conversion; Arlington, Texas. 1976. p. 59.

[11] Noda Y, Kon H, Furukawa Y, Nishida IA, Masumoto K.: Temperature dependence of thermoelectric properties of $Mg_2Si_{0.6}Ge_{0.4}$. Materials Transactions, JIM. 1992;33(9):851–855.

[12] Ioffe AF. Semiconductor Thermoelements and Thermoelectric Cooling. London: Infosearch; 1957. 184 p.

[13] Chasmar RP, Stratton R.: The thermoelectric figure of merit and its relation to thermoelectric generators. Journal of Electronics and Control. 1959;7(1):52–72. DOI: 10.1080/00207215908937186

[14] Baker H, editor. ASM Handbook, Volume 03 – Alloy Phase Diagrams. USA: ASM International; 1992. 512 p.

[15] Busch G, Winkler U.: Electrical conductivity of intermetallic solid solutions. Helvetica Physica Acta. 1953;26(5):578–583.

[16] Grosch GH, Range KJ.: Studies on AB2-type intermetallic compounds. I. Mg_2Ge and Mg_2Sn: single-crystal structure refinement and ab inito calculations. Journal of Alloys and Compounds. 1996;235(2):250255.

[17] Zintl E, Kaiser H.: On the ability of elements to bind negative ions. Zeitschrift für anorganische und allgemeine Chemie. 1933;211(1/2):113–131.

[18] Winkler U.: Electrical properties of intermetallic compounds Mg_2Si, Mg_2Ge, Mg_2Sn and Mg_2P. Helvetica Physica Acta. 1955;28(7):633–666.

[19] Martin JJ.: Thermal conductivity of Mg_2Si, Mg_2Ge and Mg_2Sn. Journal of Physics and Chemistry of Solids. 1972;33(5):1139–1148.

[20] Sacklowski A.: X-ray investigations of some alloys. Annalen der Physik. 1925;382(11): 241–272.

[21] Zaitsev VK, Fedorov MI, Eremin IS, Gurieva EA.: Thermoelectrics on the base of solid solutions of Mg_2B^{IV} compounds (B^{IV}=Si, Ge, Sn). In: D.M. Rowe, editor. CRC Handbook of Thermoelectrics: Macro to Nano. New York: CRC Press; 2006. p. 29-1-29-11.

[22] Koenig P, Lynch DW, Danielson GC.: Infrared absorption in magnesium silicide and magnesium germanide. Journal of Physics and Chemistry of Solids. 1961;20(1/21961): 122–126.

[23] Lipson HG, Kahan A.: Infrared absorption of Mg_2Sn. Physical Review. 1964;133A: 800–810.

[24] Lott LA, Lynch DW.: Infrared absorption in Mg_2Ge. Physical Review. 1966;141(2):681–686.

[25] Au-Yang MY, Cohen ML.: Electronic structure and optical properties of Mg$_2$Si, Mg$_2$Ge and Mg$_2$Sn. Physical Review. 1969;178(3):1358–1364.

[26] Baranek P, Schamps J, Noiret I.: Ab initio studies of electronic structure, phonon modes, and elastic properties of Mg$_2$Si. Journal of Physical Chemistry B. 1997;101(45):9147–9152.

[27] Arnaud B, Alouani M.: Electron-hole excitations in Mg$_2$Si and Mg$_2$Ge compounds. Physical Review B. 2001;64(3):033202.

[28] Kutorasinski K, Wiendlocha B, Tobola J, Kaprzyk S. Importance of relativistic effects in electronic structure and thermopower calculations for Mg$_2$Si, Mg$_2$Ge, and Mg$_2$Sn. Physical Review B. 2014;89(11):115205. DOI: 10.1103/PhysRevB.89.115205

[29] Mead CA.: Photothresholds in Mg$_2$Ge. Journal of Applied Physics. 1964;35(8):2460–2462. DOI: 10.1063/1.1702881

[30] Redin RD, Morris RG, Danielson GC.: Semiconducting properties of Mg$_2$Ge single crystals. Physical Review. 1958;109(6):1916–1920. DOI: 10.1103/PhysRev.109.1916

[31] Morris RG, Redin RD, Danielson GC.: Semiconducting properties of Mg$_2$Si single crystals. Physical Review. 1958;109(6):1909–1915. DOI: 10.1103/PhysRev.109.1909

[32] Zaitsev VK, Nikitin EN.: Electrical properties, thermal conductivity and forbidden-band width of Mg$_2$Sn at high temperatures. Soviet Physics of Solid State. 1970;12:289–292.

[33] Nikitin EN, Tkalenko EN, Zaitsev VK, Zaslavskii AI, Kuznetsov AK.: Investigation of phase diagram and of some properties of Mg$_2$Si-Mg$_2$Sn solid solutions. Neorg. Mater. 1968;4(11):1902–1906.

[34] Zaitsev VK, Tkalenko EN, Nikitin EN.: Lattice thermal conductivity of Mg$_2$Si-Mg$_2$Sn, Mg$_2$Ge-Mg$_2$Sn and Mg$_2$Si-Mg$_2$Ge solid solutions. Soviet Physics of Solid State. 1969;11:221–224.

[35] Labotz RJ, Mason DR.: The thermal conductivities of Mg$_2$Si and Mg$_2$Ge. Journal of the Electrochemical Society. 1963;110(2):120–126.

[36] Fedorov MI, Zaitsev VK.: Optimization of thermoelectric parameters in some silicide based materials. In: Proceedings of XIX International Conference on Thermoelectrics (ICT 2000); Cardiff, UK, 2000. p. 17.

[37] Zaitsev VK, Nikitin EN, Tkalenko EN.: Width of forbidden band in solid solutions Mg$_2$Si-Mg$_2$Sn. Soviet Physics of Solid State. 1969;11:3000.

[38] Fedorov M.I., Gurieva E.A., Eremin I.S., Konstantinov P.P., Samunin A.Yu, Zaitsev V.K., Sano S., Rauscher L. Kinetic properties of solid solutions Mg$_2$Si$_{1-x-y}$Sn$_x$Ge$_y$, Proceedings of VIII European Workshop on thermoelectrics, Poland, Krakow, September 15–17, 2004, p.75.

[39] Fedorov MI, Zaitsev VK, Eremin IS, Gurieva EA, Burkov AT, Konstantinov PP, Vedernikov MV, Samunin AYu, Isachenko GN.: Kinetic properties of p-type $Mg_2Si_{0.4}Sn_{0.6}$ solid solutions. In: Proceedings of Twenty-Second International Conference on Thermoelectrics, ICT'03; IEEE; 2003. p. 134.

[40] Fedorov MI, Pshenay-Severin DA, Zaitsev VK, Sano S, Vedernikov MV.: Features of conduction mechanism in n-type $Mg_2Si_{1-x}Sn_x$ solid solutions. In: Proceedings of Twenty-Second International Conference on Thermoelectrics, ICT'03; IEEE; 2003, p. 142.

[41] Pshenay-Severin DA and Fedorov MI.: Effect of the band structure on the thermoelectric properties of a semiconductor. Physics of the Solid State. 2007;49(9):1633–1637. DOI: 10.1134/S1063783407090053

[42] Clark CR, Wright C, Suryanarayana C, Baburaj EG, Froes FH.: Synthesis of Mg_2X (X = Si, Ge, or Sn) intermetallics by mechanical alloying. Materials Letters. 1997;33(1-2):71–75.

[43] Xiaoping Niu, Li Lu.: Formation of magnesium silicide by mechanical alloying. Advanced Performance Materials. 1997;4(3):275–283.

[44] Riffel M, Schilz J.: Influence of production parameters on the thermoelectric properties of Mg_2Si. In: Proceedings of 16th International Conference on Thermoelectrics, ICT'97; 1997. p. 283.

[45] Schilz J, Muller E, Kaysser WA, Langer G, Lugscheider E, Schiller G, Henue R.: Graded thermoelectric materials by plasma spray forming. In: Shiota I, Miyamoto Y, editors. Functionally Graded Materials 1996. Netherlands: Elsevier Science B.V.; 1997. p. 563–568.

[46] Godlewska E, Mars K, Zawadzka K.: Alternative route for the preparation of $CoSb_3$ and Mg_2Si derivatives. Journal of Solid State Chemistry. 2012;193:109–113. DOI: 10.1016/j.jssc.2012.03.070

[47] Samunin AYu, Zaitsev VK, Konstantinov PP, Fedorov MI, Isachenko GN, Burkov AT, Novikov SV, Gurieva EA.: Thermoelectric properties of hot-pressed materials based on $Mg_2Si_nSn_{1-n}$. Journal of Electronic Materials. 2013;42(7):1676–1679. DOI: 10.1007/s11664-012-2372-3

[48] Tani J-I, Kido H.: First-principles and experimental studies of impurity doping into Mg_2Si. Intermetallics. 2008;16(3):418–423. DOI: 10.1016/j.intermet.2007.12.001

[49] Tani J-I, Kido H.: Thermoelectric properties of Al-doped $Mg_2Si_{1-x}Sn_x$ (x ≦ 0.1). Journal of Alloys and Compounds. 2008;466(1–2):335–340. DOI: 10.1016/j.jallcom.2007.11.029

[50] Tani J-I, Kido H.: Impurity doping into Mg_2Sn: A first-principles study. Physica B. 2012;407(17):3493–3498. DOI: 10.1016/j.physb.2012.05.008

[51] Isoda Y, Tada S, Nagai T, Fujiu H, Shinohara Y.: Thermoelectric properties of p-type Mg$_{2.00}$Si$_{0.25}$Sn$_{0.75}$ with Li and Ag double doping. Journal of Electronic Materials. 2010;39(9):1531–1535. DOI: 10.1007/s11664-010-1280-7

[52] Tada S, Isoda Y, Udono H, Fujiu H, Kumagai S, Shinohara Y.: Thermoelectric properties of p-type Mg$_2$Si$_{0.25}$Sn$_{0.75}$ doped with sodium acetate and metallic sodium. Journal of Electronic Materials. 2014;43(6):1580–1584. DOI: 10.1007/s11664-013-2797-3

[53] Fedorov M I, Zaitsev VK, Eremin IS, Gurieva EA, Burkov AT, Konstantinov PP, Vedernikov MV, Samunin AYu, Isachenko GN, Shabaldin AA.: Transport properties of Mg$_2$X$_{0.4}$Sn$_{0.6}$ solid solutions (X = Si, Ge) with p-type conductivity. Physics of the Solid State. 2006;48(8): 1486–1490. DOI: 10.1134/S1063783406080117

[54] Tani J-I, Kido H.: Thermoelectric properties of Bi-doped Mg$_2$Si semiconductors. Physica B: Condensed Matter. 2005;364(1-4):218–224. DOI: http://dx.doi.org/10.1016/j.physb.2005.04.017

[55] Choi SM, Kim KH, Kim IH, Kim SU, Seo WS.: Thermoelectric properties of the Bi-doped Mg$_2$Si system. Current Applied Physics. 2011;11(3):S388–S391. DOI: 10.1016/j.cap.2011.01.031

[56] Tani J-I, Kido H.: Thermoelectric properties of Sb-doped Mg$_2$Si semiconductors. Intermetallics. 2007;15(9):1202–1207. DOI: 10.1016/j.intermet.2007.02.009

[57] Tani J-I, Kido H.: Thermoelectric properties of P-doped Mg$_2$Si semiconductors. Japanese Journal of Applied Physics. 2007;46(6A):3309–3314. DOI: 10.1143/JJAP.46.3309

[58] Akasaka M, Iida T, Nemoto T, Soga J, Sato J, Makino K, Fukano M, Takanashi Y.: Non-wetting crystal growth of Mg$_2$Si by vertical Bridgman method and thermoelectric characteristics. Journal of Crystal Growth. 2007;304(1):196–201. DOI: 10.1016/j.jcrysgro.2006.10.270

[59] Akasaka M, Iida T, Matsumoto A, Yamanaka K, Takanashi Y, Imai T, Hamada N.: The thermoelectric properties of bulk crystalline n- and p-type Mg$_2$Si prepared by the vertical Bridgman method. Journal of Applied Physics. 2008;104(1):013703. DOI: 10.1063/1.2946722

[60] Farahi N, VanZant M, Zhao J, Tse JS, Prabhudev S, Botton GA, Salvador JR, Borondics F, Liu Z, Kleinke H.: Sb- and Bi-doped Mg$_2$Si: location of the dopants, micro- and nanostructures, electronic structures and thermoelectric properties. Dalton Transactions. 2014;43(40):14983–14991. DOI: 10.1039/C4DT01177E

[61] Bux SK, Yeung MT, Toberer ES, Snyder GJ, Kaner RB, Fleurial JP.: Mechanochemical synthesis and thermoelectric properties of high quality magnesium silicide. Journal of Materials Chemistry. 2011;21(33):12259–12266. DOI: 10.1039/C1JM10827A

[62] Satyala N, Vashaee D.: Detrimental influence of nanostructuring on the thermoelectric properties of magnesium silicide. Journal of Applied Physics. 2012;112(9):093716. DOI: 10.1063/1.4764872

[63] Pshenai-Severin DA, Fedorov MI, Samunin AYu. The influence of grain boundary scattering on thermoelectric properties of Mg_2Si and $Mg_2Si_{0.8}Sn_{0.2}$. Journal of Electronic Materials. 2013;42(7):1707–1710. DOI: 10.1007/s11664-012-2403-0

[64] Wang S, Mingo N.: Improved thermoelectric properties of $Mg_2Si_xGe_ySn_{1-x-y}$ nanoparticle-in-alloy materials. Applied Physics Letters. 2009;94(20):203109. DOI: 10.1063/1.3139785

[65] Bochkov LV, Fedorov MI, Isachenko GN, Zaitsev VK, Eremin IS.: Influence of germanium on lattice thermalconductivity of the magnesium silicide solid solutions. Vestnik MAH. 2014;3(52):26.

[66] Khan A, Vlachos N, Hatzikraniotis E, Polymeris G, Lioutas C, Stefanaki E, Paraskevopoulos K, Giapintzakis I, Kyratsi T.: Thermoelectric properties of highly efficient Bi-doped $Mg_2Si_{1-x-y}Sn_xGe_y$ materials. Acta Materialia. 2014;77:43–53. DOI: 10.1016/j.actamat.2014.04.060

[67] Samunin AYu, Zaytsev VK, Pshenay-Severin DA, Konstantinov PP, Isachenko GN, Fedorov MI, Novikov SV.: Thermoelectric properties of n-type Mg_2Si-Mg_2Sn solid solutions with different grain sizes. Physics of the Solid State. 2016;58(8):1528–1531. DOI: 10.1134/S1063783416080242

[68] Isachenko GN, Samunin AYu, Gurieva EA, Fedorov MI, Pshenay-Severin DA, Konstantinov PP, Kamolova MD.: Thermoelectric properties of nanostructured p-$Mg_2Si_xSn_{1-x}$ (x=0.2 to 0.4) solid solutions. Journal of Electronic Materials. 2016;45(3):1982–1986. DOI: 10.1007/s11664-016-4345-4

[69] Ihou-Mouko H, Mercier C, Tobola J, Pont G, Scherrer H.: Thermoelectric properties and electronic structure of p-type Mg_2Si and $Mg_2Si_{0.6}Ge_{0.4}$ compounds doped with Ga. Journal of Alloys and Compounds. 2011;509(23):6503–6508. DOI: 10.1016/j.jallcom.2011.03.081

[70] Jiang G, Chen L, He J, Gao H, Du Z, Zhao X, Tritt TM, Zhu T.: Improving p-type thermoelectric performance of $Mg_2(Ge,Sn)$ compounds via solid solution and Ag doping. Intermetallics. 2013;32:312–317. DOI: 10.1016/j.intermet.2012.08.002

[71] Zhang Q, Cheng L, Liu W, Zheng Y, Su X, Chi H, Liu H, Yan Y, Tang X, Uher C.: Low effective mass and carrier concentration optimization for high performance p-type $Mg_{2(1-x)}Li_{2x}Si_{0.3}Sn_{0.7}$ solid solutions. Physical Chemistry Chemical Physics. 2014;16(43):23576–23583. DOI: 10.1039/C4CP03468F