

Band structure parameters influence on the thermoelectric figure of merit

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Abstract

Many compounds which can be used as thermoelectrics have complex structure of conduction or valence band. Sometimes the parameters of the band structure can be changed. How should be they changed – it is the main question which is discussed in the present work. Some approaches discussed in the paper have been applied to the development of thermoelectrics on the base of silicon compounds. In the paper some recent achievement in the increase of dimensionless thermoelectric figure of merit (ZT) are discussed from the point of view of the electronic structure of these compounds.

Introduction

As it is well known in the simplest case the maximum of thermoelectric figure of merit (Z) can be written as:

$$Z_{\max} \sim m_d^{3/2} u / \kappa_{\text{ph}}, \quad (1)$$

where m_d is density of states effective mass, u – current carrier mobility, κ_{ph} – thermal conductivity of crystal lattice. So, the first conclusion of the formula (1) is, that to increase thermoelectric figure of merit it is necessary to decrease thermal conductivity of crystal lattice without significant decrease of mobility.

Let us write the formula (1) in the following view:

$$Z_{\max} \sim m_d^{3/2} m^{-1} \tau / \kappa_{\text{ph}}, \quad (2)$$

where m – is inertial effective mass and τ – current carrier relaxation time. In this case the first factor is determined by band structure of a material, whereas the second one – by scattering mechanisms of current carriers and phonons. The second factor can be increased significantly only if the scattering of phonons and current carriers are mutually independent mechanisms. The first factor the most easy can be high when conduction or valence band extremum is located outside of the center of Brillouin zone. In these case we have multi-valley band which is extremely good for the increase of thermoelectric figure of merit. The majority of the best thermoelectrics has multi-valley band structure.

Recently we tried to attract the attention of thermoelectric community to the fact that band structure parameters can play more essential role in the increase of figure of merit than the decrease of lattice thermal conductivity [1, 2]. This time we want to discuss this item in more details.

We shall discuss only bulk materials and the possibility to change band structure only either by the creation of solid solutions or by other method of crystal structure change. We shall not discuss the change of energy gap but only the change of the parameters of conduction/valence band.

The solid solution method suggested by A.F.Ioffe [3] was the first principal approach to thermoelectric development. In this case, due to stronger phonon scattering by isovalent impurity atoms and weaker electron scattering, the thermoelectric figure of merit increases due to the growth of the mobility to lattice thermal conductivity ratio. This approach have allowed to produce many good thermoelectrics and is one of the main approaches up to now.

Another approach was suggested in the nineties of the XX century. It was proposed to fill in the voids in crystal structure by additional atoms. This approach gave excellent results for the first time when it was applied to skutterudites [4].

If the solid solution method allows to decrease lattice thermal conductivity and only sometimes it allows to change the band structure parameters, the method of voids filling has to change the energy spectrum of current carriers. Really, any additional atom has few extra electrons, which have to create additional levels in the energy spectrum. Very often, the filling the voids results in metallic conductivity of the material, in comparison with unfilled material being a semiconductor. The occupation of the additional levels can be changed by varying the composition of the basic compound, for example.

The solid solution method has not exhausted the possibilities to increase thermoelectric figure of merit. One of such possibilities was used in the development of thermoelectrics on the base of $\text{Mg}_2\text{X-Mg}_2\text{Y}$ ($\text{X, Y} = \text{Si, Ge, Sn, Pb}$) solid solutions [5]. Let us discuss the mentioned methods in more details.

The method of voids filling.

As it was indicated above, the voids filling was applied for the first time to the materials with skutterudite structure. The unit cell of skutterudites consists of 8 cubes. The cube corners are occupied by transition metal atoms. Six of the eight cubes contain 4 pnictogen atoms each, and the other two contains no atoms except transition metal. They are so called “voids” of crystal structure. These materials, especially CoSb_3 , has been studied as thermoelectric since the end of the fifties of the last century [6]. The CoSb_3 energy gap is $E_g = 0.63$ eV [7]. Mobility of current carriers at room temperature and $n, p = 1 \cdot 10^{19} \text{ cm}^{-3}$ are $u_p \approx 1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $u_n \approx 100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and effective masses are $m_p = 0.13 m_e$, $m_n = 1.4 m_e$ at $n, p = 1 \cdot 10^{18} \text{ cm}^{-3}$ [8]. Because of high lattice thermal conductivity only solid solutions could be used as thermoelectrics. For the best of our knowledge the maximum figure of merit ($ZT=0.6$ at 700 K) was achieved in the n-type multicomponent solid solution $\text{Co}_{0.97}\text{Ir}_{0.03}\text{Sb}_{2.81}\text{Te}_{0.04}\text{As}_{0.15}$ [9], which had the same crystal lattice as CoSb_3 . When filling the voids of crystal structure by

Ce atoms and compensating extra electrons of Ce by substituting a part of Co atoms by Fe ones the figure of merit was changed to $ZT_{\max} \sim 1.4$ at 900 K [4].

Let us estimate the contributions of lattice conductivity and band structure parameters in thermoelectric figure of merit. First of all it is necessary to mention that experimental data for thermal conductivity in the paper [9] were presented only for three lowest temperatures and the high temperature data were approximated by linear dependence of thermal resistance on temperature. For the small temperature range 300-700 K it is a good dependence, which is reasonable one for heavily doped crystal. Fig.1 shows the dependencies of the thermoelectric figure of merit and thermal conductivity for usual and filled skutterudites.

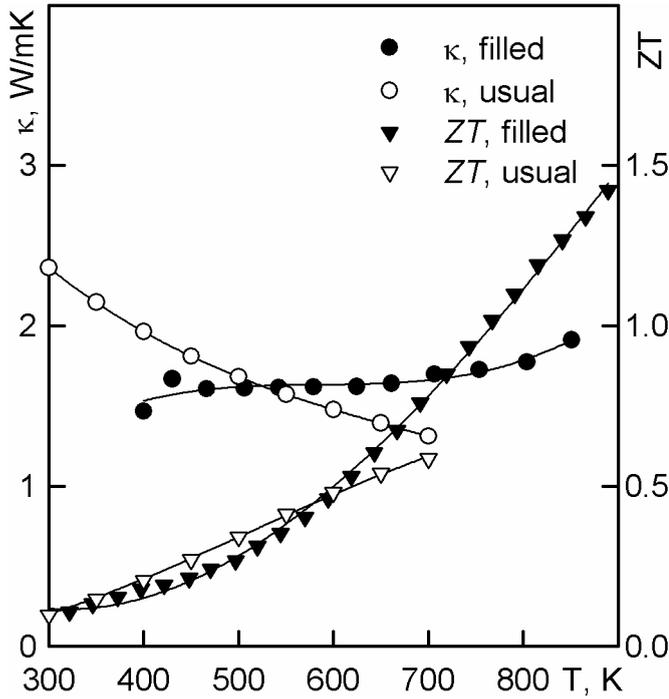


Figure 1: Temperature dependencies of the thermoelectric figure of merit (ZT) and thermal conductivity (κ) for $\text{Co}_{0.97}\text{Ir}_{0.03}\text{Sb}_{2.81}\text{Te}_{0.04}\text{As}_{0.15}$ [9] (hollow symbols) and $\text{CeFe}_4\text{Sb}_{12}$ [4] (filled symbols).

As one can see from the fig.1 total thermal conductivity of these materials has practically the same value but different character. According to the estimation made in [9] electron component of thermal conductivity does not exceed 5-15% of total thermal conductivity, so, the dependence shown in the fig.1 can be considered as that of lattice thermal conductivity. Thermal conductivity of $\text{CeFe}_4\text{Sb}_{12}$ has more essential contribution of electronic component because current carrier concentration is two orders higher ($5.5 \cdot 10^{21} \text{cm}^{-3}$) than that of $\text{Co}_{0.97}\text{Ir}_{0.03}\text{Sb}_{2.81}\text{Te}_{0.04}\text{As}_{0.15}$ ($4 \cdot 10^{19} \text{cm}^{-3}$). According to the data of [4] we calculated electronic and lattice thermal conductivities of this materials. We supposed that the principal scattering mechanism is the scattering by acoustic phonons and from the value of Seebeck coefficient ($S = 59 \mu\text{V/K}$) and hole concentration ($p = 5.5 \cdot 10^{21} \text{cm}^{-3}$) at room temperature calculated hole effective mass of density of states ($m_p = 8.9m_e$). Considering the hole concentration

independent of temperature, we calculated temperature dependencies of chemical potential, Seebeck coefficient and both components of thermal conductivity. The calculated dependencies of both components of thermal conductivity and Seebeck coefficient together with the experimental data of [4] are shown in the Fig.2.

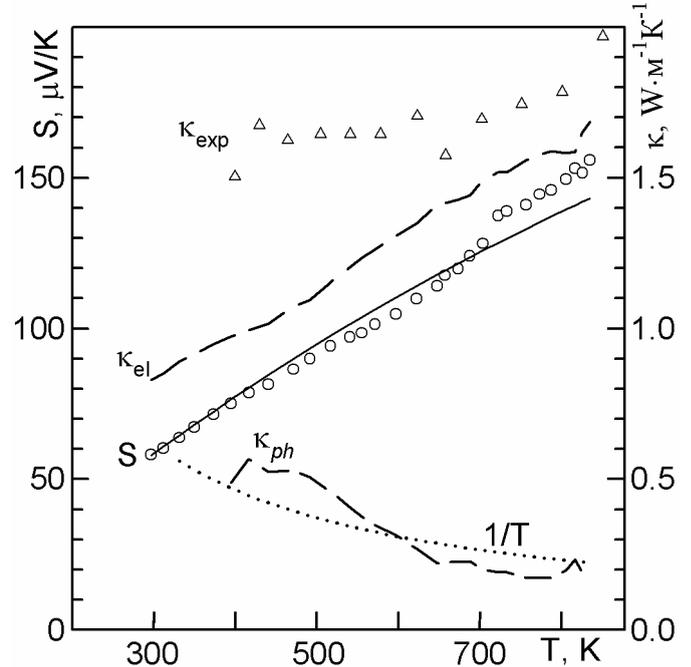


Figure 2: Temperature dependencies of total (κ_{exp}), electronic (κ_{el}) and lattice thermal conductivity (κ_{ph}) of $\text{CeFe}_4\text{Sb}_{12}$ and experimental and calculated Seebeck coefficient. (according to the data of [4]). Experimental data from [4] are shown by symbols and the results of our calculations by lines. Pointed line shows $1/T$ dependence.

Really, the voids filling resulted in significant decrease of lattice thermal conductivity (more than 3 times at room temperature in comparison with $\text{Co}_{0.97}\text{Ir}_{0.03}\text{Sb}_{2.81}\text{Te}_{0.04}\text{As}_{0.15}$), but the mobility of holes decreased much more $40 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ in $\text{Co}_{0.97}\text{Ir}_{0.03}\text{Sb}_{2.81}\text{Te}_{0.04}\text{As}_{0.15}$ and $1.5 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ in $\text{CeFe}_4\text{Sb}_{12}$. So the main idea of standard approach: to decrease u/κ_{ph} value failed. While both materials have practically the same figure of merit at low temperature and material with filled voids has very high figure of merit at high temperature? It can be connected with the change of energy spectrum of current carriers. This suggestion is confirmed by the fact that the hole effective mass in filled skutterudites is about $9 m_e$ whereas in CoSb_3 the highest effective mass is $1.4 m_e$ [8]. This conclusion is confirmed by band structure calculations of CoSb_3 [10] and $\text{CeFe}_4\text{Sb}_{12}$ [11].

As one can see from the fig.3 in $\text{CeFe}_4\text{Sb}_{12}$ the bands have lower curvature than that in CoSb_3 , and there are many sub-bands which are close to the Fermi level. So, filling the voids allows to produce higher current carrier concentration at lower Fermi level position. It results in higher Seebeck coefficient at the same current carrier concentration.

As it is well known, the electron and phonon systems are tightly connected. Any attempts to decrease the lattice thermal conductivity results in the decrease of electron

mobility. When the decrease of lattice thermal conductivity is accompanied by appropriate change of band spectrum there is additional increase of thermoelectric figure of merit in comparison with the usual growth of mobility to lattice thermal conductivity ratio.

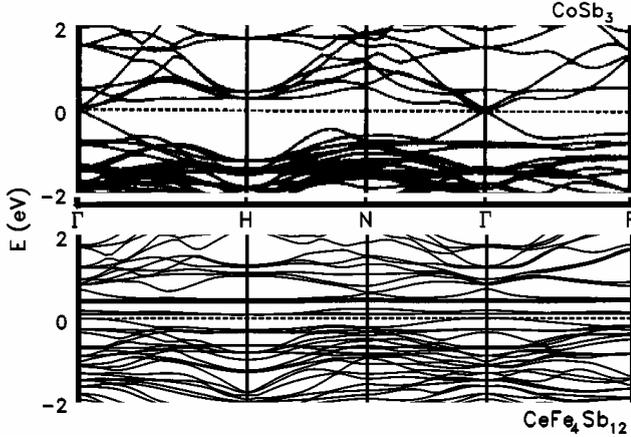


Figure 3: Results of band structure calculations of CoSb₃ [10] and CeFe₄Sb₁₂ [11].

The case of two sub-bands

Often a conduction or valence band consists of two sub-bands. They could be degenerated in the extremum point or separated by some gap. If there is another compound of the same crystal structure, where the sub-bands are separated by other gap, it could be possible to find a solid solution where the gap is optimum for the obtaining the highest figure of merit. In the paper [12] it was studied how the gap and effective masses of these sub-band influence on thermoelectric figure of merit.

For simplicity sake let us consider to sub-bands of conduction band which will be denoted as SB1 and SB2. We shall assume that the scattering on acoustic phonos is the main mechanism of electron scattering. We shall consider the temperature where the holes contribution in transport properties is negligible small.

In this case electrical conductivity can be written as:

$$\sigma_i = \sigma_{0i} F_1(\mu_i), \quad (3)$$

where index $i = 1, 2$ denotes the sub-band number, σ_{0i} – a factor that determines the value of electrical conductivity of the i^{th} sub-band, $F_n(\mu)$ – Fermi integral

$$F_n(\mathbf{m}) = \int_0^{\infty} \left(-\frac{\partial f_0(x - \mathbf{m})}{\partial x} \right) x^n dx,$$

$f_0(x - \mu)$ – Fermi-Dirac distribution function, μ – normalized chemical potential (in k_0T units, where k_0 is the Boltzman constant and T – temperature). The factor σ_{0i} depends only on temperature, effective mass (m_i^*) and deformation potential constant (Ξ_i).

The Seebeck coefficient \mathbf{a}_i and Lorenz number L_i can be written as follows

$$\mathbf{a}_i = \frac{k_0}{e} \left(\frac{F_2(\mathbf{m})}{F_1(\mathbf{m})} - \mathbf{m} \right), \quad (4)$$

$$L_i = \left(\frac{k_0}{e} \right)^2 \left(\frac{F_3(\mathbf{m})}{F_1(\mathbf{m})} - \left(\frac{F_2(\mathbf{m})}{F_1(\mathbf{m})} \right)^2 \right), \quad (5)$$

where e is the electron charge.

Using (3)-(5) one can write the following expression for dimensionless figure of merit

$$ZT = \frac{\left[\sum_i b_i (F_2(\mathbf{m}) - \mathbf{m} F_1(\mathbf{m})) \right]^2}{\sum_i b_i F_1(\mathbf{m}) \left[\sum_i b_i \left(F_3(\mathbf{m}) - \frac{F_2^2(\mathbf{m})}{F_1(\mathbf{m})} \right) + \mathbf{b}^{-1} \right]}, \quad (6)$$

where $b_i = \sigma_{0i} / \sigma_{01}$, ($b_1 \equiv 1$) being the parameter characterizing mobility of the carriers in the i^{th} band compared with the carrier mobility in the first band and $\mathbf{b} = k_0^2 T \sigma_{01} / (\mathbf{k}_{ph} e^2)$ is related to the material quality parameter (see e.g. [13]). κ_{ph} is thermal conductivity of crystal lattice. According to [14] $\kappa_{ph} \sim T^{1/2}$.

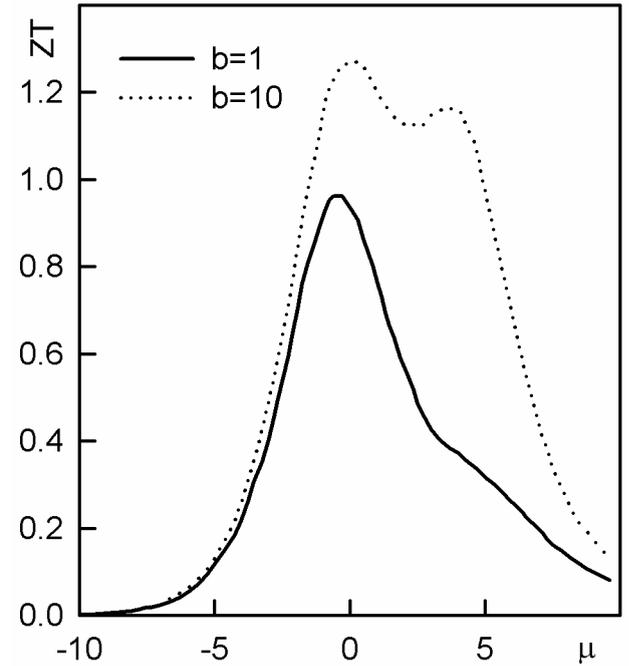


Figure 4: The dimensionless figure of merit dependence on chemical potential for $\Delta = 5k_0T$, $\mathbf{b} = 0.33$, $b = 1$ and 10.

In the presence of two sub-bands let us measure the chemical potential from the energy position of the minimum of the first sub-band and denote the energy position of second sub-band as Δ in k_0T units. Then $\mu_1 = \mu$ and $\mu_2 = \mu - \Delta$. In this case we can denote $b_2 \equiv b$ and for acoustical scattering $b = m_1^* \Xi_1^2 / (m_2^* \Xi_2^2)$. The value of the ZT for two-bands model depends only on chemical

potential, relative position of energy minima of the sub-bands and the parameters b and \mathbf{b} .

Omitting calculations, which are presented in [12], let us discuss the dependence of ZT on chemical potential.

Fig. 4. shows the dependencies of ZT on chemical potential at two values of b and certain values of Δ and β . From this figure one can see that the contribution of electrons from SB2 is small due to low carrier concentration at $b=1$ but it can be increased if the mobility of the carriers in the second band is relatively high ($b=10$). One can see that depending on b value the ZT dependence on μ can have one or two maximums.

Let us now consider the dependencies of the maximum figure of merit at the optimal chemical potential on the parameters b , \mathbf{b} and Δ . The decrease of \mathbf{b} corresponds to the increase of the contribution of lattice thermal conductivity to the total one. This leads to decrease of the figure of merit. The increase of b leads to growth of the figure of merit due to the increase of second sub-band contribution at constant energy distance between the band energy minima. We can consider only the case when $b \geq 1$ because the thermoelectric efficiency ZT remains unchanged if b , Δ and \mathbf{b} is replaced with $1/b$, $-\Delta$ and $\mathbf{b}b$ respectively.

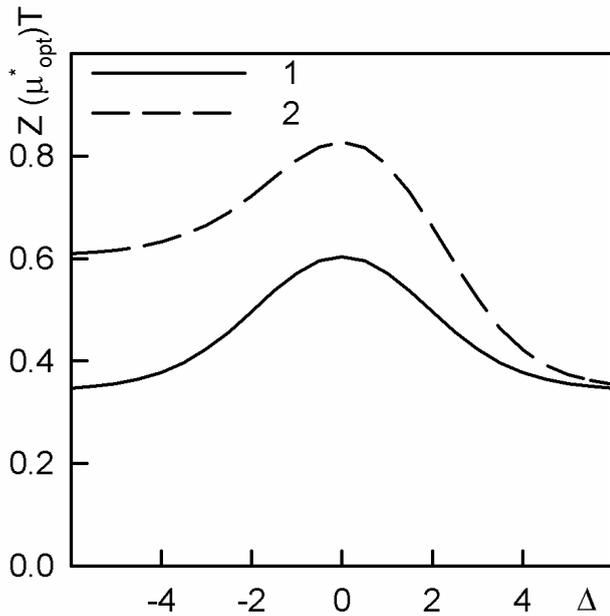


Figure 5: The dependence of the optimized the thermoelectric figure of merit $ZT(\mu_{opt})$ on the relative energy position of the second conduction band Δ for $\mathbf{b} = 0.1$. 1 – $b = 1.0$, 2 – $b = 2.0$.

The maximum value of ZT at any values of b and \mathbf{b} the can be obtained for $\Delta = 0$ (fig.5). Usually the ratio of effective masses in solid solutions is fixed and only the relative position of energy band minimum changes with the composition. If the composition with the $\Delta = 0$ cannot be reached or it is obtained for some composition of solid

solution only at certain temperature, then the most preferable situation for ZT optimization is when the energy minimum of the conduction band with lower mobility is higher (i.e. $\Delta < 0$ for $b > 1$, see fig. 5).

This situation is valid when the interband scattering is negligible low. The increase of interband scattering results in the decrease of figure of merit. Sometimes the high interband scattering can result in different signs of Hall and Seebeck coefficients (see e.g. [15]), but in the case of solid solutions Mg_2Si-Mg_2Sn it is negligibly low [16].

Solid solutions Mg_2X-Mg_2Y ($X, Y = Si, Ge, Sn, Pb$)

There are four compounds Mg_2X ($X=Si, Ge, Sn, Pb$). They all are crystallized in cubic antiferroite structure. The conduction band of all these compounds is multi-valley one. They have mutual solid solutions with various solubility regions [17]. The systems Mg_2Si-Mg_2Ge and, probably, Mg_2Si-Mg_2Sn has continuous solid solutions and the other systems have restricted regions of solubility. The most promising from the point of view of the decrease of lattice thermal conductivity is the system Mg_2Si-Mg_2Pb due to the highest molecular masses difference, but because of low Mg_2Pb stability in air, this system is the least studied. The most studied is the system Mg_2Si-Mg_2Sn . The solid solutions of this system can have low enough thermal conductivity and conduction band in these materials consists of two subbands. These subbands are created by Mg and Si states [18]. The energy gap between these subbands can be changed from 0.25 to -0.2 eV as it is shown in the fig. 6.

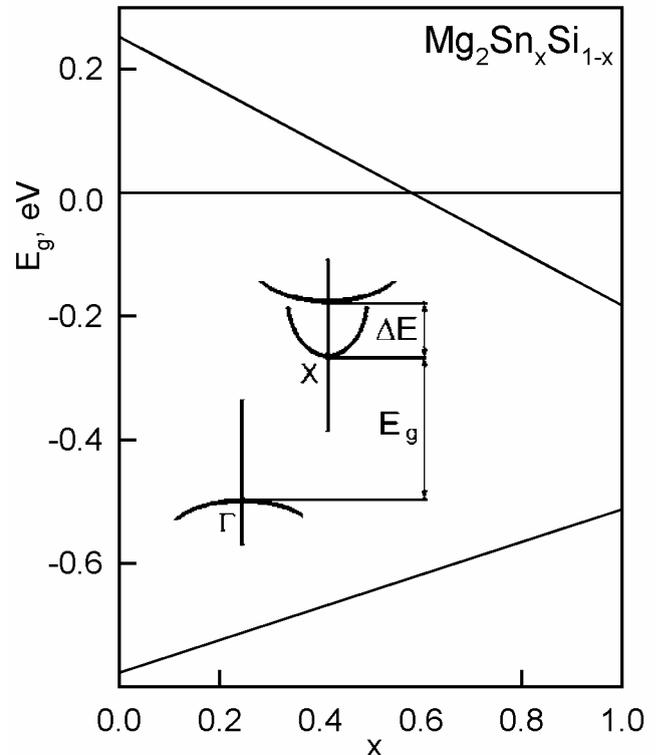


Figure 6: Scheme of positions of energy bands extrema in the $Mg_2Si_{1-x}Sn_x$ solid solutions relatively the minimum of

Mg₂Si conduction band. In the insertion the Mg₂Si band scheme in *k*-space is shown.

As it is shown above the most profitable positions of these minima are when they located at the same energy level. If the bands are not located at the same energy level, it is better to have in upper position the sub-band of heavier electrons. So the most efficient solid solutions should have composition Mg₂Si_{0.4-δ}Sn_{0.6+δ} where δ value depends on the temperature shift of these sub-band minima. We used δ=0. There is practically no difference in lattice thermal conductivity of the solid solutions of 0.3 x 0.7. As it was shown in [5], the change of conduction band minima positions results in higher Seebeck coefficient for Mg₂Si_{0.4}Sn_{0.6} solid solution than that of Mg₂Si_{0.7}Sn_{0.3} and Mg₂Si_{0.6}Sn_{0.4} solid solutions. Temperature dependencies of energy gap of Mg₂Si and Mg₂Sn [19] show that the sub-band created by silicon states (Mg₂Si conduction band minimum) shifts faster to the valence band than the sub-band created by magnesium states (Mg₂Si conduction band minimum). It results in practically the same relative contributions of the both sub-bands in all temperature range.

In a good crystal lattice thermal resistivity increases proportional to *T* when temperature growing and in a glass it practically does not depend on temperature. In solid solutions having essential shares of every component, the temperature dependence of lattice thermal resistivity has an intermediate character. It is the price which we have to pay for the total increase of thermal resistivity. In the Mg₂Si_{0.4}Sn_{0.6} solid solution it depends on temperature as *T*^{0.5} (Fig. 7). The index of power coincides with that predicted by Klemens' theory [14].

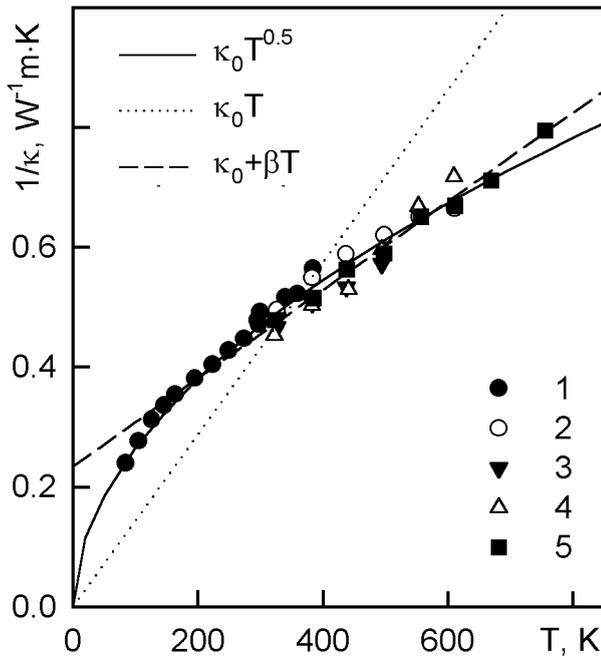


Figure 7: Thermal resistivity of crystal lattice of Mg₂Si_{0.4}Sn_{0.6} solid solution at various electron concentration *n*, 10²⁰cm⁻³: 1 – 0.14; 2 - 1.4; 3 - 1.9; 4 - 2.4; 5 - 4.0. Lines show

various possible temperature dependencies of thermal resistivity.

Energy band parameters optimization allows to produce very efficient thermoelectrics. Fig. 8 shows the temperature dependencies of dimensionless thermoelectric figure of merit of Mg₂Si_{0.4}Sn_{0.6} solid solution at various electron concentration. If electron concentration is not too low, the maximum dimensionless figure of merit is ≈1.1. The variation of electron concentrations allows to change slightly the temperature position of *ZT*_{max}.

In comparison with this solid solution the Mg₂Si_{0.6}Sn_{0.4}, having non-optimum sub-bands positions has significantly lower figure of merit (curve 5 in the fig.8).

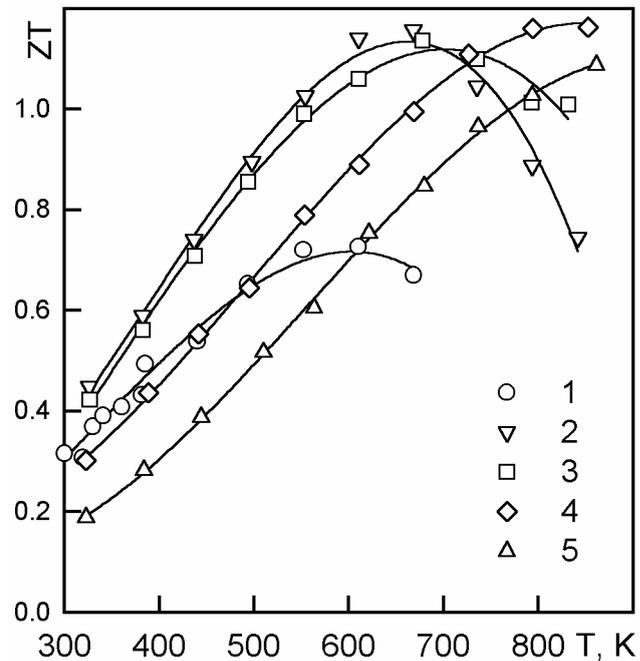


Figure 8: Temperature dependencies of dimensionless thermoelectric figure of merit of Mg₂Si_{0.4}Sn_{0.6} solid solution at various electron concentration *n*, 10²⁰cm⁻³: 1 – 0.6; 2 - 1.4; 3 - 1.9; 4 – 4.2, and 5 - that of Mg₂Si_{0.6}Sn_{0.4} solid solution at optimum electron concentration (3.3·10²⁰cm³).

So, the solid solution method when it is aimed to the optimization of the band structure parameters allows to receive significantly higher figure of merit than when it aimed only on the lattice thermal conductivity decrease.

Conclusions

Optimization of of band structure parameters plays very important role in the development of efficient bulk thermoelectrics.

In both main methods – solid solutions and voids filling the change of band structure parameters allows to receive additional increase of thermoelectric figure of merit.

Sometimes the change of band structure parameters gives much more essential contribution into *ZT* increase than the decrease of lattice thermal conductivity.

The mentioned above ideas, were the base of development of very efficient thermoelectrics in the Mg_2Si-Mg_2Sn system.

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