Highly effective $Mg_2Si_{1-x}Sn_x$ thermoelectrics

V. K. Zaitsev, M. I. Fedorov,* E. A. Gurieva, I. S. Eremin, P. P. Konstantinov, A. Yu. Samunin, and M. V. Vedernikov
A. F. Ioffe Physico-Technical Institute of the Russian Academy of Sciences, Saint Petersburg, Russia
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Results of detailed investigations of Mg_2B^{IV} (B^{IV}=Si, Ge, Sn) compounds and their quasibinary alloys are presented. Our analysis revealed that Mg_2Si-Mg_2Sn system has the most promising for thermoelectric applications combination of transport properties and band structure features. The *n*-type $Mg_2Si_{1-x}Sn_x$ solid solutions were studied in broad range of compositions and electron concentration (up to 5×10^{20} cm^{-3}). Temperature dependencies of figure of merit were determined in temperature range 300–870 K using results of simultaneous measurements of Seebeck coefficient, electrical, and thermal conductivities. The alloy of optimized composition has reproducible figure of merit $ZT_{max}=1.1$. The results of the present study are compared with the data for best modern thermoelectrics.

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INTRODUCTION

Increasing interest in thermoelectric energy conversion has boosted the search of new efficient thermoelectrics. The main attention is paid to the study of so-called "filled skutterudites," clathrates, oxides, and artificial layered materials. Filled skutterudites of *p* type show the figure of merit $ZT_{max}=1.2$,[1] whereas no high thermoelectric figure of merit has been found in clathrates and oxides. The record dimensionless figure of merit ($ZT_{max}=2.4$ at $T=300$ K)[2] has been achieved in artificial layered materials, but they hardly can be used in thermoelectric generators because of their thermodynamic instability at high temperatures. In spite of reports on very efficient thermoelectrics,[3,4] the maximum dimensionless thermoelectric figure of merit of *n*-type materials used in commercial generator applications at temperatures above 600 K does not exceed unity. The majority of the attempts to increase the figure of merit of bulk materials is based on the use of materials with very low lattice thermal conductivity. However, the optimization of band structure of a solid solution can result in enhanced figure of merit notwithstanding relatively high thermal conductivity of crystal lattice.

EXPERIMENT

Polycrystalline ingots of $Mg_2Si_{1-x}Sn_x$ solid solution were manufactured by direct melting of the components in boron nitride crucibles using high-frequency heating. The diameter of the ingots was about 22 mm and the length, about 20 mm. Long-time annealing was used for homogenization of the samples. X-ray analysis showed that the samples had well-formed structure of a solid solution. Concentration of current carriers was controlled by antimony addition. Samples for the measurements of transport properties were cut out of the ingots by a diamond disk.

The thermal conductivity was measured by stationary absolute method simultaneously with electrical conductivity and Seebeck coefficient.[5,6] The measuring cell is shown schematically in Fig. 1. The temperature (T_4) of the gradient heater (5) is kept equal to the temperature of the shield heater (6), therefore practically whole heat flux, generated in the gradient heater passes through the sample (1). The radiation losses are reduced by the insulating powder (3), having well known thermal conductivity. The heat flux through the insulating powder can be easily calculated with sufficient precision. All measurements are made under steady-state conditions. In measurement of resistance the gradient heater (5) is used as the current lead. Two thermocouple probes are inserted in the sample; they are used to measure the temperature difference and potential difference across the sample. Temperature of the probes (T_2 and T_3), sample dimensions and distance between potential probes are the same in the measurement of Seebeck coefficient, thermal, and electrical conductivity. All measured voltages between probes are interconnected. It allows to avoid some errors in *Z* determination because of mutual cancellation of the errors in separate parameters. The simultaneous measurements of thermal, electrical conductivity, and Seebeck coefficient allow us to decrease the error of determination of the figure of merit due to unavoidable variation of properties, when measurements of various parameters are made using different samples or different setups.

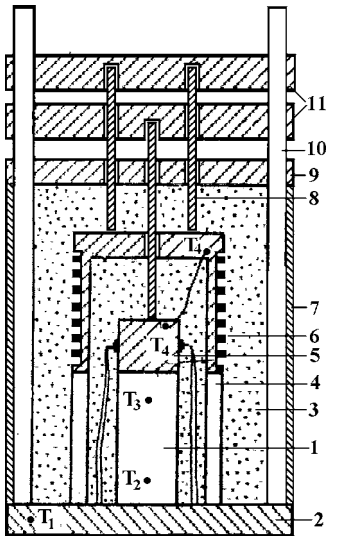

FIG. 1. The high-temperature measuring cell for thermoelectric properties measurement. 1: sample; 2: basement; 3: insulating powder; 4: silica cylinder; 5: gradient heater; 6: shield heater; 7: metallic cylinder; 8: rods; 9: cover; 10: directors; 11: loads.

TABLE I. Properties of Mg_2B^{IV} compounds (Ref. 19).

Compound	Melting point, K	Spacing, Å	Density, g cm^{-3}
Mg_2Si	1375	6.338	1.88
Mg_2Ge	1388	6.3849	3.08
Mg_2Sn	1051	6.765	3.59

Moreover the measurements of the Seebeck coefficient and electrical resistivity of the same material were made additionally in other installations to avoid accidental errors. Temperature difference about 10 K was used in Seebeck coefficient measurement. Hall coefficient and ac electrical resistivity measurements were made simultaneously using the method described in Ref. 7. Seebeck and Hall coefficients, electrical, and thermal conductivities were measured in the temperature range 80–870 K.

BAND STRUCTURE AND THE CHOICE OF BASE MATERIAL

In 1961 Nikitin *et al.*[8] at Ioffe Institute showed that the compounds Mg_2B^{IV} (B^{IV}=Si,Ge,Sn) have favorable complex of physical and chemical properties and could be a good base for the development of new efficient thermoelectrics. All these compounds crystallize in antifluorite structure,[9] are semiconductors, and have no deficit or toxic components. Some of their parameters are shown in Table I.

Band structure of these compounds was studied both experimentally and theoretically.[10–18] It is characterized by splitted conduction band, and the valence band similar to that of silicon or germanium. A part of the band structure of Mg_2B^{IV} near to the Fermi level is shown in the inset to Fig. 2. The parameters of the band structure are listed in Table II. Energy gap (E_g), its temperature coefficient (dE_g/dT), conduction band splitting (ΔE), effective masses for lower conduction band (m_n) and valence band (m_p), electron (u_n), and hole (u_p) mobilities at room temperature and lattice thermal conductivity (κ_L) are shown.

As Tables I and II show, the Mg_2Si and Mg_2Sn compounds along with high enough melting point (Table I) have rather high values of energy gap and mobility (Table II). However, these compounds have too high thermal conductivity to use the pure compounds as thermoelectrics. To increase their figure of merit the solid solutions of these compounds can be used.

To choose the composition of a solid solution the three conditions should be fulfilled: (1) Thermal conductivity should be minimized, (2) energy spectrum of current carriers should be optimized, (3) a method for obtaining necessary current carriers density should be found. Mg_2Si and Mg_2Ge form continuous solid solutions[20] and the other two alloy systems (Mg_2Si-Mg_2Sn and Mg_2Ge-Mg_2Sn) are characterized by peritectic reaction and limited regions of solid solution existence.[21–23] Mg_2Si and Mg_2Sn have the maximum difference in the molecular mass and, as it was shown in Ref. 22, the solid solutions in the system have the lowest lattice thermal conductivity. Therefore, this system is more promising for the creation of good thermoelectrics than the two other systems.

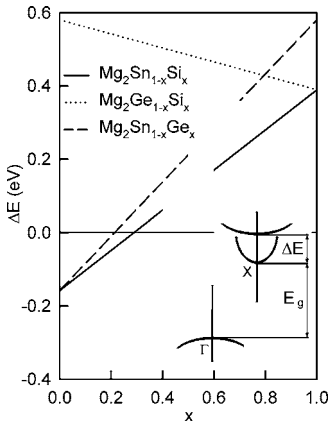

FIG. 2. Dependency of the gap between light and heavy conduction bands on the solid solution composition. The lines are shown only in the regions where solid solutions exist. In the inset a part of the band structure of the Mg_2B^{IV} near the Fermi level is shown.

The system Mg_2Si-Mg_2Sn is very promising not only due to low lattice thermal conductivity but also due to some features of its band structure. It was shown previously that the energy gap dependence on the composition in the solid solutions $Mg_2Si_{1-x}Sn_x$ and $Mg_2Ge_{1-x}Sn_x$ has nonlinear character.[12,23,24] It was suggested in Ref. 11 that there is a change of the nature of extrema of conduction bands in Mg_2Si and Mg_2Sn. Recently, this change was confirmed by band structure calculations of Rauscher.[18] Presently it is proved that in all the compounds under discussion there is another band above the minimum of the conduction band. The second band is separated from the minimum by the gap ranging from 0.2 to 0.6 eV for different compounds (see Table II). The minimum in Mg_2Si and Mg_2Ge is formed by B^{IV} atom states and the minimum in Mg_2Sn is formed by Mg states. The distance between the bands of light and heavy electrons is shown in Fig. 2 together with the scheme of band

TABLE II. Parameters of electron structure for Mg_2B^{IV} compounds (Ref. 19).

Compound	E_g (0 K) eV	dE_g/dT (0 K) 10^{-4} eV/K	ΔE eV	m_n/m_0	m_p/m_0	u_n (300 K) cm^2 V^{-1} s^{-1}	u_p (300 K) cm^2 V^{-1} s^{-1}	κ_L W m^{-1} K^{-1}
Mg_2Si	0.77	−6	0.4	0.50	0.9	405	65	7.9
Mg_2Ge	0.74	−8	0.58	0.18	0.31	530	110	6.6
Mg_2Sn	0.35	−3.2	0.16	1.2	1.3	320	260	5.9

TABLE III. Parameters of electron structure for $Mg_2Si_xSn_{1-x}$ solid solutions.

x	E_g (0 K) eV	ΔE eV	κ_L W m^{-1} K^{-1}	n_1 10^{18} cm^{-3}	u_{n1} (300 K) cm^2 V^{-1} s^{-1}	m_{n1}/m_0	n_2 10^{20} cm^{-3}	u_{n2} (300 K) cm^2 V^{-1} s^{-1}	m_{n2}/m_0
0.8	0.73	0.29	2.1	2.0	96	0.5	1.7	79	1.5
0.7	0.70	0.24	2.0	1.4	48	0.5	1.1	77	1.3
0.6	0.68	0.18	2.0	8.7	35	0.5	2.1	50	1.6
0.4	0.61	0.07	2.0	2.0	27	0.6	2.3	47	2.7

gaps in these materials. The change of the nature of the states forming the lower band is confirmed by our calculation of the density of states effective mass (m_{dn}) made from experimental data on the Hall and Seebeck coefficients.[17] Samples of $Mg_2Si_{1-x}Sn_x$ solid solution with $x \leq 0.6$ and with low electron concentration have $m_{dn} \approx 0.5$, whereas $m_{dn} \approx 1.2$ for the samples with $x \geq 0.7$. These values coincide with those of Mg_2Si and Mg_2Sn correspondingly. Thus, in the solid solutions $Mg_2Si_{1-x}Sn_x$ and $Mg_2Ge_{1-x}Sn_x$ there is a band inversion and, hence at some x the both conduction bands are at the same distance from the maximum of the valence band. Therefore there is a composition in this alloy system at which both bands give practically the same contribution to electrical conductivity. This situation is favorable for thermoelectricity because in this case the density of states can increase without a decrease of electron mobility.

THERMOELECTRIC PROPERTIES OF $Mg_2Si_xSn_{1-x}$ SOLID SOLUTIONS

Table III shows parameters of electron structure and lattice thermal conductivity for a number of $Mg_2Si_xSn_{1-x}$ solid solutions. One can see that these solid solutions have the same lattice thermal conductivity and different values of conduction band splitting (ΔE). The $Mg_2Si_{0.4}Sn_{0.6}$ solid solution has the lowest ΔE value, hence we expect that this alloy has the highest figure of merit at low temperature.

This suggestion is confirmed by Fig. 3 showing the dependencies of Seebeck coefficient on electrical conductivity at room temperature for the solid solutions $Mg_2Si_{0.4}Sn_{0.6}$, $Mg_2Si_{0.6}Sn_{0.4}$. As one can see from Fig. 3 the solid solution $Mg_2Si_{0.4}Sn_{0.6}$ has better properties at room temperature than another one. At higher temperature the second band can give a contribution to the transport properties too and other solid solution can be effective too. Figure 3 also shows the dependencies of Seebeck coefficient on electrical conductivity of the same samples at 700 K. One can see that the difference between the curves for $Mg_2Si_{0.4}Sn_{0.6}$ and $Mg_2Si_{0.6}Sn_{0.4}$ solid solutions is essentially smaller than that at 300 K.

This paper is devoted to the study of the transport properties and the figure of merit mainly in the solid solutions $Mg_2Si_{1-x}Sn_x$ with $x=0.4$ and $x=0.6$, however, some other solid solutions were studied too. The comparison of the temperature dependencies of the thermoelectric properties (Seebeck coefficient, electrical and thermal conductivities) shows that the solid solutions with $x=0.4$ and $x=0.6$ are the most effective thermoelectrics in this system in the high temperature region.

Previously high figure of merit was achieved only in the solid solutions $Mg_2Si_{0.7}Sn_{0.3}$.[25] There have been some reports about very high figure of merit in the solid solutions on the base of Mg_2B^{IV} compounds, but they were not confirmed and hardly could be true. The possible level of the figure of merit in such solid solutions is discussed in Ref. 25.

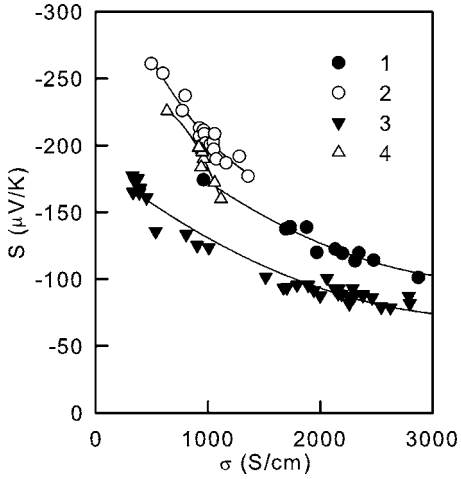

FIG. 3. Dependencies of the Seebeck coefficient on electrical conductivity at room temperature (1, 3) and at 700 K (2, 4) for the solid solutions $Mg_2Si_{0.4}Sn_{0.6}$ (1, 2) and $Mg_2Si_{0.6}Sn_{0.4}$ (3, 4).

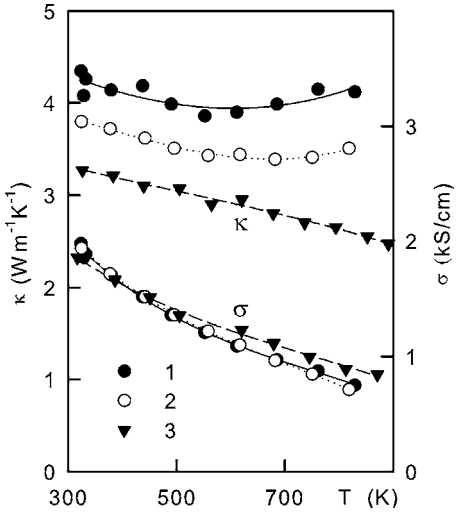

FIG. 4. Temperature dependencies of the thermal (κ) and electrical (σ) conductivities of the solid solution $Mg_2Si_{0.6}Sn_{0.4}$ for the samples of various electron concentration n, 10^{20} cm^{-3}: (1) 1.66; (2) 2.55; (3) 4.54.

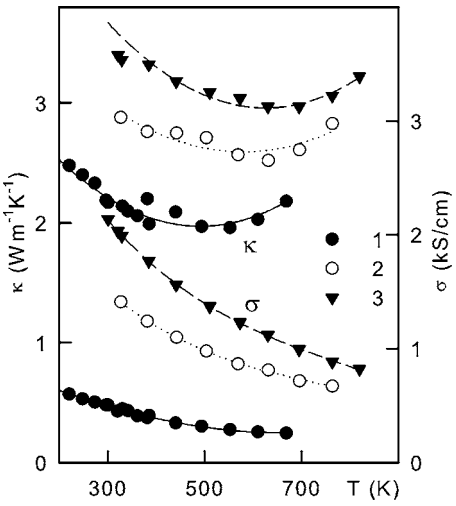

FIG. 5. Temperature dependencies of the thermal (κ) and electrical (σ) conductivities of the solid solution $Mg_2Si_{0.4}Sn_{0.6}$ for the samples of various electron concentration n, 10^{20} cm^{-3}: (1) 0.59; (2) 2.52; (3) 2.99.

Figures 4 and 6 show the temperature dependencies of the thermoelectric properties of the solid solution $Mg_2Si_{0.6}Sn_{0.4}$ for the samples of various electron concentration while Figs. 5 and 7 show the same dependencies for the solid solution $Mg_2Si_{0.4}Sn_{0.6}$. Dimensionless figure of merit was calculated from the experimental data presented in these figures. Figures 6 and 7 show the temperature dependencies of ZT for the solid solutions under discussion.

The both types of the solid solutions have the maximum dimensionless figure of merit above unity. The average value (ZT_{ave}) in the temperature range 400–850 K is about 0.78 for $Mg_2Si_{0.6}Sn_{0.4}$ and 0.83 for $Mg_2Si_{0.4}Sn_{0.6}$. The Fig. 8 shows the ZT temperature dependencies for the best modern, actually used thermoelectrics of n type. Because we cannot estimate the reliability of all published data we used for the comparison the publication of Jet Propulsion Laboratory.[1] One can see that at the temperature 600–870 K the thermoelectrics under discussion have very high thermoelectric figure of merit. The both materials can be applied for thermoelectric generators. The $Mg_2Si_{0.4}Sn_{0.6}$ solid solution has higher average figure of merit but the other solid solution is stronger at high temperature against oxidization and vaporization.

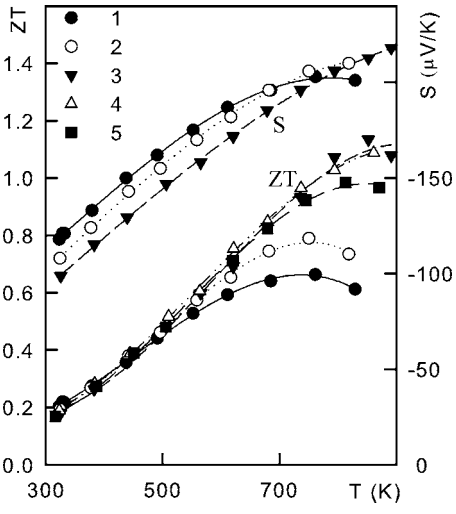

FIG. 6. Temperature dependencies of the Seebeck coefficient (S) and dimensionless figure of merit (ZT) of the solid solution $Mg_2Si_{0.6}Sn_{0.4}$ for the samples of various electron concentration. The curve numbers correspond to the same concentrations as in Fig. 4 and two curves added to ZT plot (n, 10^{20} cm^{-3}: (4) 3.17; (5) 3.83).

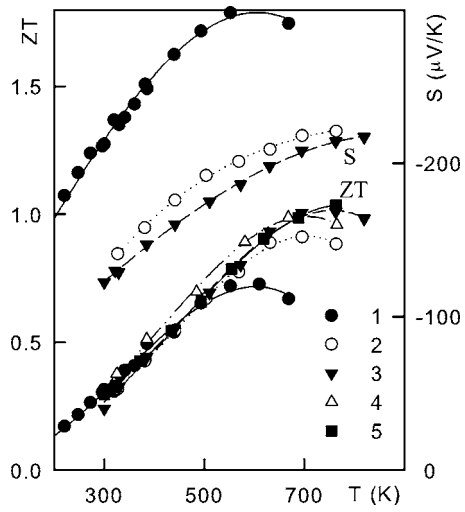

FIG. 7. Temperature dependencies of the Seebeck coefficient (S) and dimensionless figure of merit (ZT) of the solid solution $Mg_2Si_{0.4}Sn_{0.6}$ for the samples of various electron concentration. The curve numbers correspond to the same concentrations as in Fig. 5 and two curves added to ZT plot (n, 10^{20} cm^{-3}: (4) 2.07; (5) 3.10).

CONCLUSION

A detailed study of the solid solutions of Mg_2B^{IV} compounds is carried out. The analysis of the transport properties

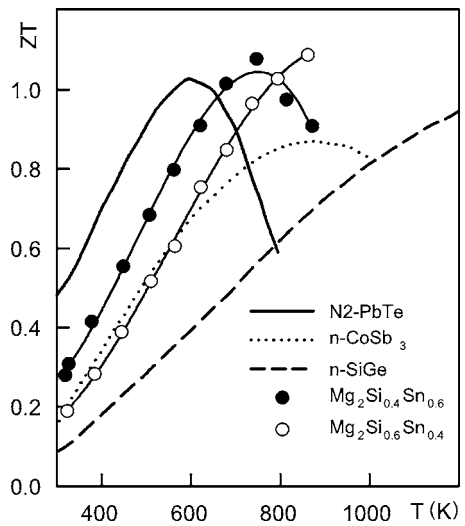

FIG. 8. The comparison of the best modern thermoelectrics with the solid solutions under discussion. Lines show the data published in Ref. 1.

and band structure features has shown that Mg_2Si-Mg_2Sn is the most promising system for the development of efficient thermoelectrics. The solid solutions $Mg_2Si_{1-x}Sn_x$ of various composition and electron concentration were studied. This study revealed the best compositions of the solid solutions and allowed reproducible synthesis of thermoelectrics with $ZT_{max}=1.1$. The results are highly reliable, because they are obtained on a large number of samples, and the same properties are measured on various installations. The comparison of the results obtained with the data for the best modern thermoelectrics showed that these materials are among the best thermoelectrics of *n*-type in the temperature range 600–870 K. It is important that this result is achieved with very cheap, nontoxic, temperature stable, and technologically simple thermoelectrics.

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*Electronic address: m.fedorov@mail.ioffe.ru

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