Kinetic properties of solid solutions $Mg_2Si_{1-x-y}Sn_xGe_y$

Fedorov M.I.[1], Gurieva E.A.[1], Eremin I.S.[1], Konstantinov P.P.[1], Samunin A.Yu.[1], Zaitsev V.K.[1], Sano S.[2], Rauscher L.[2]

[1]Ioffe Physico-technical Institute, Russian Academy of Sciences, 194021 St. Petersburg, Russia

[2]Komastsu Ltd. Hiratsuka-shi, Japan

Abstract

Theoretical calculations of band structure of Mg_2B^{IV} (B^{IV}=Si, Ge, Sn) compounds and their solid solutions were fulfilled. Electrical conductivity, Hall and Seebeck coefficients were investigated for polycrystalline samples of the solid solutions ($Mg_2Ge_{0.40}$ $Sn_{0.60}$; $Mg_2Si_{0.35}Ge_{0.05}Sn_{0.60}$; $Mg_2Si_{0.36}Ge_{0.04}$ $Sn_{0.60}$) in the temperature range 80-800 K. X-ray analysis showed that the solid solutions were formed well. Electron concentration was varied from $2\cdot10^{18}$ up to $1\cdot10^{19}$ cm^{-3}. Energy gap,and temperature dependencies of electron mobility were determined. The analysis of obtained results shows a complicated structure of conduction band.

Introduction

N-type $Mg_2Si_{1-x}Sn_x$ solid solutions are known as efficient thermoelectrics for middle temperature range [1]. High figure of merit of this material could be explained by the features of its band structure [2]. However direct study of band structure of the solid solutions was not fulfilled yet. In some papers very high figure of merit was obtained due to Ge addition [3]. In this paper the results of theoretical study of band structure and experimental study Ge influence on energy gap and mobility are presented.

Band structure calculations

First-principle investigations were performed following the density functional theory (DFT). We used the program package WIEN2k, which is based on the full-potential (linearized) augmented plane-wave ((L)APW) + local orbitals (LO) method, one among the most accurate schemes for band structure calculations.

To investigate the solid solutions a super cell containing 8 primitive unit cells was derived from the original crystals with varying composition. It was possible to reveal the band structure and band characteristics, the density of states, and spatial electron-density distribution for the pure crystals as well as for the intermediate compounds.

The calculation showed that all three compounds are indirect semiconductors with a small gap. The conduction band is dominated by Si electrons for Mg_2Si and Mg_2Ge and by Mg (2s) electrons for Mg_2Sn. Accordingly there must be a transition in conduction dominated by Si- or Mg-electrons for intermediate n-type solid solutions. There is a conduction band splitting in the solid solutions. An example of such splitting for $Mg_2Si_{1-x}Sn_x$ solid solutions is shown in Fig.1. A similar splitting takes place in other solid solutions based on Mg_2B^{IV} compounds.

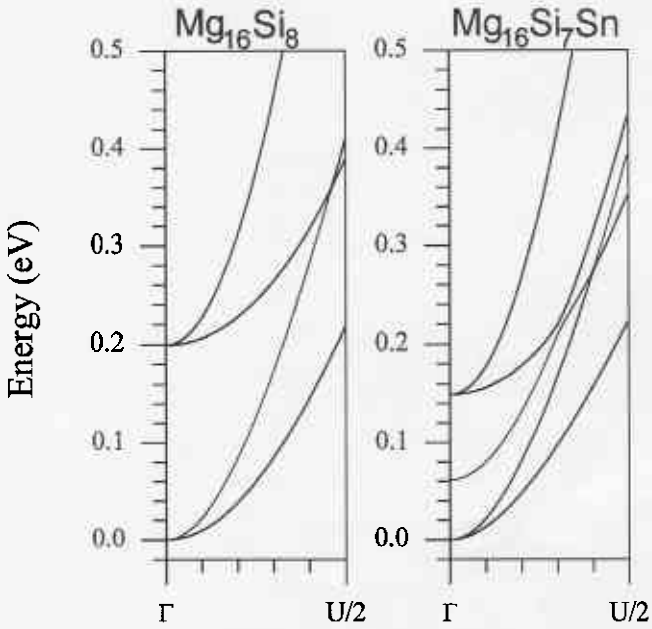

Figure 1. Conduction band splitting in the solid solutions $Mg_2Si_{1-x}Sn_x$.

Experient

The polycristalline samples were prepared by direct melting from the source components as it was described earlier [4]. The melted ingots were annealed for long time. X-ray analysis showed that the solid solutions were formed well. Electron concentration was varied from $2\cdot10^{18}$ up to $1\cdot10^{19}$ cm^{-3}.

Figures 2 – 7 show temperature dependencies of electrical conductivity and Hall coefficient for the samples of solid solutions of various composition and electron concentration. On the base of these results the energy gap (Table 1) and Hall mobility (Figure 8) were calculated.

As the table 1 shows there is essential difference between E_g (R_H) and E_g (σ). This difference is connected probably with the temperature dependence of current carrier mobility. If we suggest that the mobility (u) at high temperature can be described by the power dependence $u\sim T^s$, it allows to receive the same values of E_g.

Figure 8 shows the temperature dependencies of Hall mobility for the samples of the solid solutions of various composition and electron concentration. Figure 8 shows also the power dependencies of mobility with the parameter g, showed in the table 1. So strong dependence of the mobility on temperature could be connected with the complex band structure of the solid solutions. It is in agreement with the conduction band splitting obtained in theoretical calculations.

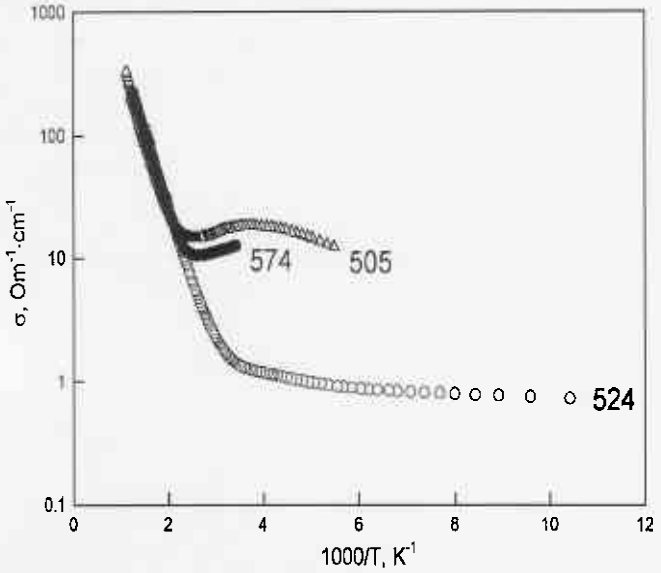

Fig.2. Temperature dependencies of electrical conductivity for $Mg_2Ge_{0.40}$ $Sn_{0.60}$ solid solutions.

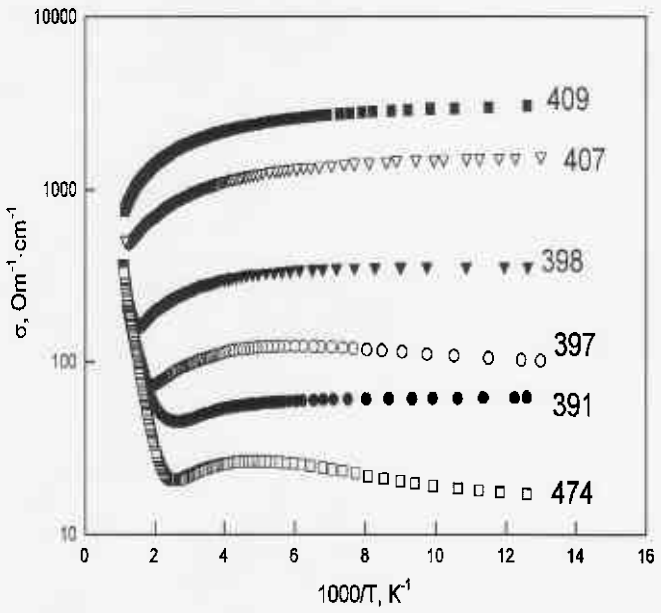

Fig.3. Temperature dependencies of electrical conductivity for $Mg_2Si_{0.35}Ge_{0.05}Sn_{0.60}$ $Mg_2Si_{0.36}Ge_{0.04}$ $Sn_{0.60}$ solid solutions.

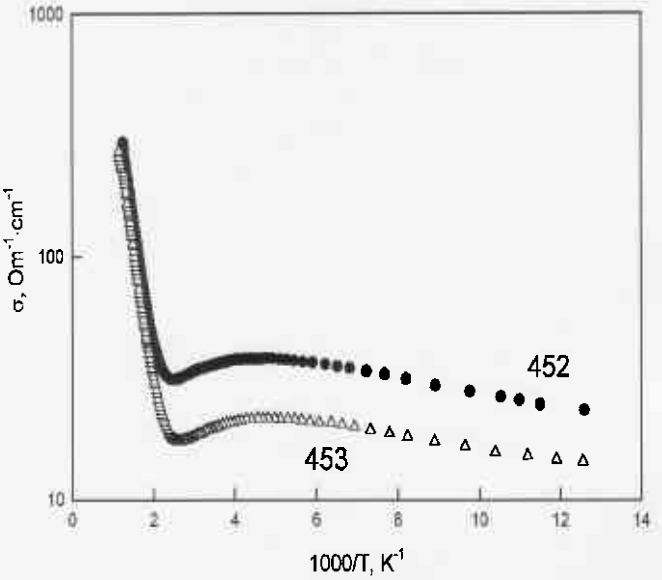

Fig.4. Temperature dependencies of electrical conductivity for $Mg_2Si_{0.36}Ge_{0.04}$ $Sn_{0.60}$ solid solutions.

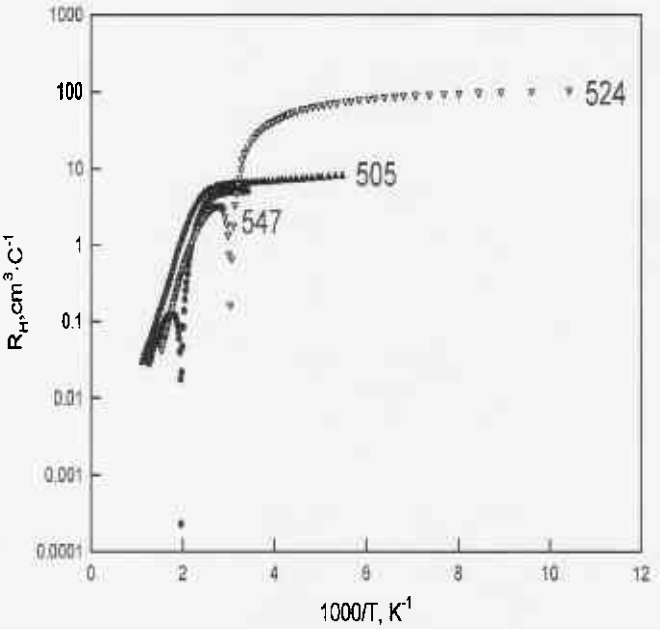

Fig.5. Temperature dependencies of Hall coefficient for $Mg_2Ge_{0.40}$ $Sn_{0.60}$ solid solutions.

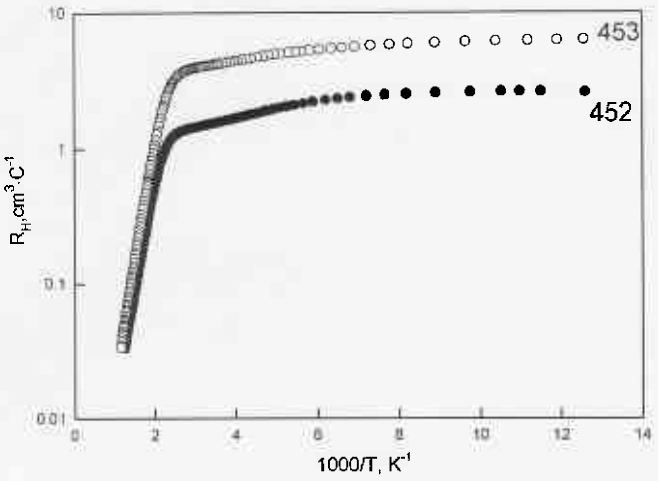

Fig.6. Temperature dependencies of Hall coefficient for $Mg_2Si_{0.35}Ge_{0.05}$ $Sn_{0.60}$ solid solutions.

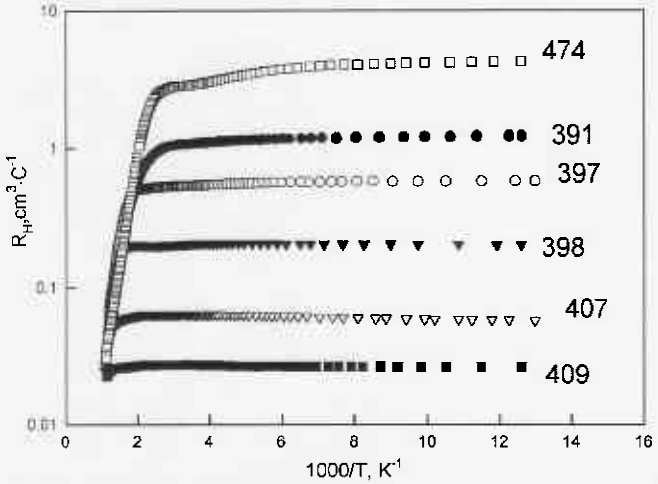

Fig.7. Temperature dependencies of Hall coefficient for $Mg_2Si_{0.36}Ge_{0.04}$ $Sn_{0.60}$ solid solutions.

Table 1. Energy gap, calculated from Hall coefficient (E_g (R_H)) and electrical conductivity (E_g (σ)) and temperature coefficient of mobility (g).

Composition	E_g (R_H), eV	E_g (σ), eV	g
$Mg_2Ge_{0.4}Sn_{0.6}$	0.62	0.51	-2.35
$Mg_2Si_{0.36}Ge_{0.04}Sn_{0.6}$	0.48	0.44	-1.85
$Mg_2Si_{0.35}Ge_{0.05}Sn_{0.6}$	0.52	0.44	-2.19

Conclusion

It is shown that there is a strong dependence of the mobility on temperature. It could be connected with the complex band structure of the solid solutions. It is in agreement with the conduction band splitting obtained in theoretical calculations. There are solid solutions with weaker temperature dependence of mobility. They could be a base for elaboration of effective thermoelectric for middle temperature range.

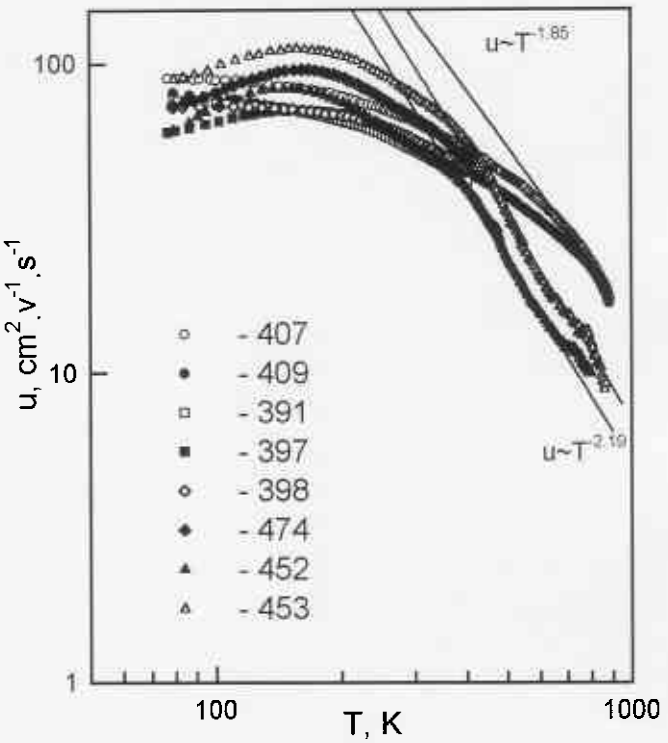

Figure 8. Temperature dependencies of Hall mobility for $Mg_2Si_{0.4-x}Ge_xSn_{0.6}$ solid solutions. Solid lines show the power dependencies of mobility with the parameter g, showed in the table 1.

Acknowledgements

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References

[1] Zaitsev V.K., Fedorov M.I. "Optimizing the parameters and energy capabilities of thermoelectric materials based on silicon compounds", *Semiconductors,* Vol.29, No. 5 (1995), pp. 490-497.

[2] Zaitsev V.K., Nikitin E.N., Tkalenko E.N. "Width of forbidden band in solid solutions Mg_2Si-Mg_2Sn". *Soviet Physics of Solid State*, Vol.11, No.12 (1969), pp.3000-3002.

[3] Nicolau M.C. "Material for direct thermoelectric energy conversion with a high figure of merit" *Proc. of the Intern. Conf. on thermoelectric energy conversion,* Arlington, Texas, 1976, pp.59-63,.

[4] Burkov A.T., Zaitsev V.K., Fedorov M.I., Gurieva E.A., Eremin I.S., Konstantinov P.P., Ordin S.V., Sano S., Vedernikov M.V. Some Features of the Conduction Band Structure, Transport and Optical Properties of n-type Mg_2Si-Mg_2Sn Alloys. *Proceedings ICT'02, XXI International Conference on Thermoelectrics*, Long Beach, CA USA, 2002. pp. 151-154.