THE FEATURES OF ENERGY SPECTRUM OF $Mg_2Si_{1-x}Sn_x$ SOLID SOLUTIONS

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Abstract

Thermoelectrics on the base of magnesium silicide in comparison with traditional thermoelectrics are cheap ones, do not contain rare or toxic elements, have high thermoelectric figure of merit. In the present work the samples of solid solutions $Mg_2Si_{1-x}Sn_x$ ($0 \le x \le 1$) have been produced by direct melting the components. Transport properties (electrical conductivity, Seebeck and Hall coefficients) of produced samples of n- and p-type have been measured in wide temperature range. The parameters of band structure (energy gap, effective mass, mobility ratio) have been calculated for all range of the solid solution existence. It is shown that all the parameters nonlinearly depend on temperature and solid solution composition.

Introduction

In paper [1] was shown that compounds Mg_2B^{IV} have the complex structure of conduction band. It consists of two subbands, which position depends on solid solution composition. That leads to non linear dependence of band parameters on composition of Mg_2Si-Mg_2Sn and Mg_2Ge-Mg_2Sn solid solution. These solid solutions have low thermal conduction in wide region of composition. Up to threefold decrease of heat conduction occurs already at 20 mol% of one component of alloy. It allows to vary the solid solution base for obtaining the optimal band structure parameters for electrons and holes that can result in the increase of power factor. On the base of this approach n-type thermoelectric with $ZT>1$ have been found [2].

Now we study a possibility to produce p-type thermoelectric material based on similar composition of solid solution. Valence band of these alloys appears to have complex structure [3]. Features of conduction and valance band lead to nonlinear dependence of some valence band parameters on composition. It allows to find the best solid solution as a base of p-type thermoelectric. First results of this work were present in [3-5].

Experiment

Polycrystalline ingots were synthesized by direct melting the components using high frequency radiation. Annealing at high temperature was used for homogenization of the samples. The ingot size was about 22mm in diameter and 20 mm in length. Samples of fixed size and shape were cut out from the ingots with diamond disc for further measurements.

Seebeck (S) and Hall (R_h)coefficients and electrical conductivity have been measured in the temperature range 80 – 800 K. Temperature difference about 10 K has been used for Seebeck coefficient measurement. AC Hall coefficient measurements have been made simultaneously with electrical resistivity using the method described in [4].

Temperature dependences of Hall and Seebeck coefficients used for calculating the mobility ratio are shown in figures 1-2.

Discussion

Temperature range for thermoelectric material is restricted by forbidden gap and electron to hole mobility ratio. These parameters specify the temperature of bipolar diffusion beginning. Their

determination can be used for improving the material.

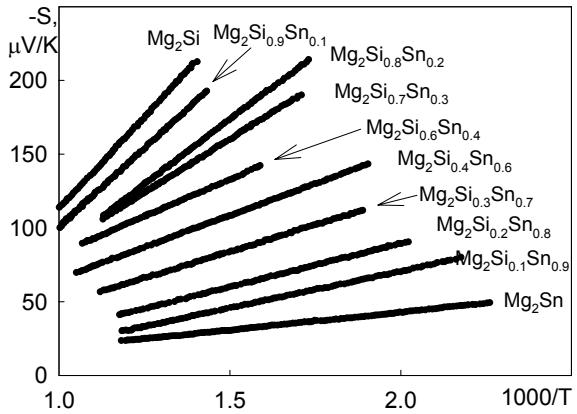

Figure 1. Seebeck coefficient temperature dependences in intrinsic range.

There are two ways to calculate the electron (u_n) to hole (u_p) mobility ratio $\left(b = \frac{u_n}{u_p}\right)$. First, it could be defined by the slope of the Seebeck coefficient temperature dependence in intrinsic range (fig. 1) using formulae (1)[6].

$$b = \frac{\frac{\Delta E_0}{2|e|} - \frac{\partial S}{\partial\left(1/T\right)}}{\frac{\Delta E_0}{2|e|} + \frac{\partial S}{\partial\left(1/T\right)}}, \qquad (1)$$

where ΔE_0 – forbidden gap, T – temperature, e - electron charge.

Second, it could be found from the Hall coefficient temperature dependence of p-type samples (fig. 2) using formulae 2[7].

$$R_{H\max} = -R_{HA}\frac{(b-1)^2}{4b} \qquad (2)$$

where R_{Hmax} – maximum Hall coefficient in intrinsic range, R_{HA} – Hall coefficient in impurity conductivity range.

Disadvantage of the last technique is that p-type doped samples are necessary to obtain required temperature dependence.

Calculation results are presented in fig. 3. There are two data sets. White circles are the data obtained from Hall coefficient, black circles are the data obtained from Seebeck coefficients. Electron mobility higher than hole one for all set of solid solutions.

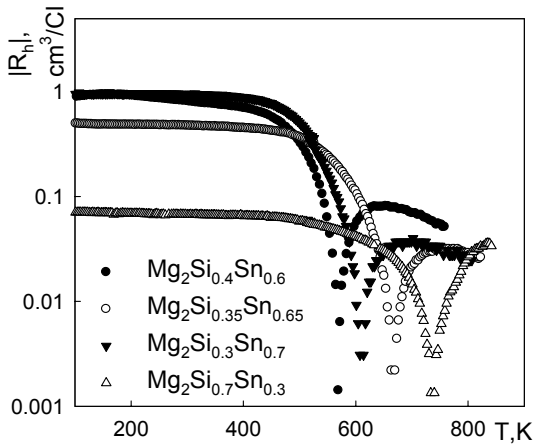

Figure 2. Hall coefficient temperature dependences.

Good agreement in Mg_2Sn-rich alloys with the data obtained by two different techniques on different samples could be seen.

Mg_2Si-rich solid solutions have large mobility ratio. There is no agreement in Mg_2Si-rich solid solutions. It could be caused by using the third group elements to obtain p-type samples. Impurity atom replaces a B^{IV} group atom in crystal lattice and dramatically decreases hole mobility, therefore increases mobility ratio. Because of low hole mobility this side of alloys is not interesting for p-type thermoelectric and was not studied.

There is no such effect in the Mg_2Sn-rich alloys. Probably, it is caused by close hole and electron mobilities values.

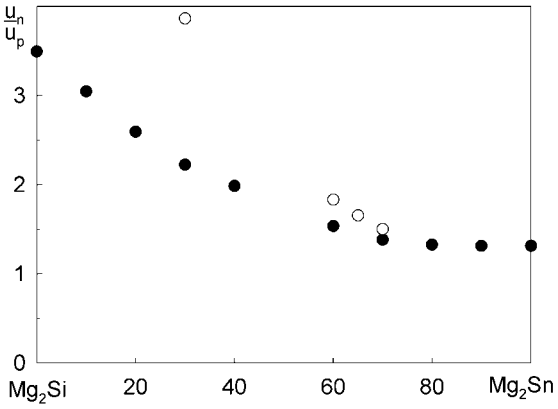

Figure 3. Mobility ratio dependence on solid solution composition.

Hole and electron mobilities dependence on composition are shown in figure 4. White circles are electron mobility at room temperature at electron concentration about $10^{18}cm^{-3}$. White triangles are hole mobility obtained from electron mobility and mobility ratio. Black circles are hole mobility in the samples of p-type with hole concentration about $10^{20}cm^{-3}$.

Hole mobility decreases fast with content of Mg_2Si increasing. At high hole concentration in Mg_2Sn-rich range the mobility of holes is two times less than that of samples of lower hole concentration, whereas hole mobility in Mg_2Si-rich alloys is few times less.

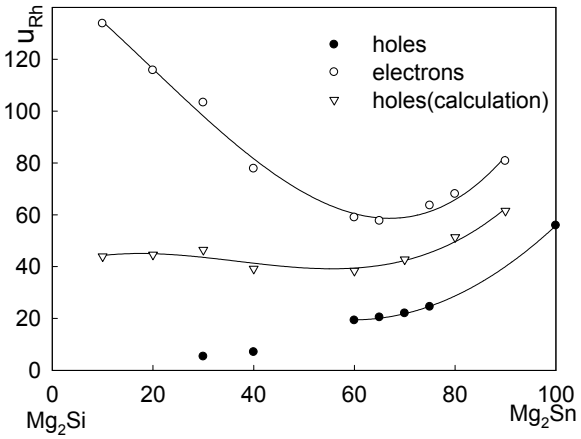

Figure 4. Hole and Electron mobility ratio dependence on solid solution composition.

Conclusion

Transport properties of Mg_2Si-Mg_2Sn solid solutions have been investigated. Hole and electron mobilities, electron to hole mobility ratio have been determined. Nonlinear dependences of these parameters on solid solution composition are found. It is shown that Mg_2Si-rich alloys are a good base for n-type thermoelectric material, whereas Mg_2Sn-rich alloys are the base for p-type thermoelectrics.

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Reference

1. V.K.Zaitsev, M.I.Fedorov, A.T.Burkov, E.A.Gurieva, I.S.Eremin, P.P.Konstantinov, S.V.Ordin, S.Sano, M.V.Vedernikov. "Some features of the conduction band structure, transport and optical properties of n-type Mg_2Si-Mg_2Sn alloys", Proc. of XXI Int. Conf. on Thermoelectrics, 2002, pp. 151-154.
2. V. K. Zaitsev, M. I. Fedorov, E. A. Gurieva, I. S. Eremin, P. P. Konstantinov, A. Yu. Samunin, and M. V. Vedernikov Highly effective $Mg_2Si_{1-x}Sn_x$ thermoelectrics Physical review B 74, 2006
3. G.N.Isachenko, V.K.Zaitsev, M. I. Fedorov, E.A.Gurieva, I.S.Eremin, P.P.Konstantinov, M.V.Vedernikov "The study of P-type material based on Sn-rich Mg2Si-Mg2Sn solid solution". Proc. of XXVI Int. Conf. on Thermoelectrics, 2008, pp.248-250
4. Fedorov M.I., Zaitsev V.K., Eremin I.S., Gurieva E.A., Burkov A.T., Konstantinov P.P., Vedernikov M.V., Samunin A.Yu., Isachenko G.N. Kinetic properties of p-type $Mg_2Si_{0.4}Sn_{0.6}$ solid solutions. Twenty-second International Conference on Thermoelectrics. Proceedings of ICT'03, 2003, IEEE, pp.134-137.
5. Fedorov M.I., Zaitsev V.K., Isachenko G. N., Eremin I.S., Gurieva E.A., Burkov A.T., Konstantinov P.P., Shabaldin A. A.; Kinetic properties of p-type $Mg_2Ge_{0.4}Sn_{0.6}$ solid solutions: Int Conf Thermoelectr ICT Proc, v.2005,
6. Busch G., Winkler U. in "Semiconductors in science and technology" edited by A.F.Ioffe, vol 2, p.605, 1958.(in Russian)
7. Stilbans L.S., Physics of semiconductors, Moscow, 1967, Soviet Radio (in Russian)