Enhancement of high temperature thermoelectric properties of intermetallic compounds based on a Skutterudite IrSb$_3$ and a half-Heusler TiNiSb

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Abstract

Phonon glass and electron crystal (PGEC) thermoelectric materials have been expected to be a new class of thermoelectric materials for high temperature applications. Among the efforts to optimize the high temperature thermoelectric properties of various PGEC thermoelectric materials, recent experimental works on the Skutterudite IrSb$_3$ and half-Heusler TiNiSb intermetallic compounds are presented herein by which the material design concept for high energy conversion efficiency, i.e. a high figure of merit, is suggested. It is revealed that the thermoelectric efficiency of IrSb$_3$ can be increased by the decrease of lattice thermal conductivity due to the rattling effect of La atoms filled in the structural vacancies of the Skutterudite crystal structure. In the half-Heusler TiNiSb, high temperature thermoelectric properties are improved by Hf substitution to the Ti sites by reducing lattice thermal conductivity and also by Sb doping to increase power factor. It is concluded that the proper alloy designing for controlling crystal structure and carrier concentration could enable these intermetallic compounds to exhibit a high potential for elevated temperature thermoelectric applications.

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1. Introduction

Ability of a material to perform as a thermoelectric cooler or generator is characterized by the dimensionless figure of merit, ZT

$$ZT = \frac{\alpha^2 T}{\rho \kappa}$$

(1)

where $\alpha$ is the Seebeck coefficient, $\rho$, electrical resistivity, $\kappa$, thermal conductivity and $T$, temperature in K [1]. In the equation, the parameter, $\alpha^2/\rho$, is called as power factor, which represents the electrical properties of thermoelectric materials. The total thermal conductivity, $\kappa$, is a combination of the lattice or phonon thermal conductivity $\kappa_{\text{lat}}$, and the electronic thermal conductivity $\kappa_{\text{el}}$

$$\kappa = \kappa_{\text{lat}} + \kappa_{\text{el}}$$

(2)

Therefore, a high figure of merit is basically expected in a material with a high power factor and a low thermal conductivity.

Recently, a group of complex compounds called as phonon glass and electron crystal (PGEC) has been investigated extensively as a potential high performance thermoelectric materials. The PGEC is a material in which the phonon mean free paths can be controlled as short as possible and at the same time the electron mean free paths as long as possible [2]. Among them the focus of the researches on thermoelectric materials is placed on such semiconducting compounds as Skutterudite, Clathrate, Chevrel and half-Heusler [3–10]. In these compounds if such a small thermal conductivity of 0.1–0.5 W/mK is achieved and if they exhibit moderate electrical properties, the dimensionless figure of merit will be over that of state-of-the-art Bi–Te thermoelectric material.
Although many Skutterudite and half-Heusler materials have been investigated as promising thermoelectric materials due to the good electrical properties, a relatively high thermal conductivity (about 10 W/mK) of binary Skutterudite and ternary half-Heusler inhibits these materials to be used for thermoelectric applications [11,12]. In the present work, IrSb$_3$ based Skutterudite and TiNiSn based half-Heusler compounds are chosen as candidate materials and the optimization on electrical properties and the reduction of thermal conductivity are pursued by additions of ternary and quaternary elements.

2. Experimental procedure

Compounds based on IrSb$_3$ Skutterudite were prepared by a powder metallurgy technique. Additions of La and Ge are made systematically according to the formula La$_x$Ir$_4$Ge$_3$Sb$_{12-3x}$. In the process of fabrication the quaternary compounds, La powder was first reacted with Ge powder at a molar ratio of 1:3 at 1233 K for 4 days in order to obtain an intimate mixture of La with Ge (LaGe$_2$ + Ge). The resulting powder was then mixed and reacted with the proper amounts of Ir, and Sb powders at 1233 K for 2 days. This reaction was also conducted in the carbon-coated quartz under a vacuum. And then the reacted powders were hot pressed at 1023 K for 3 h under a pressure of 35 MPa.

TiNiSn based Half-Heusler compounds were prepared also by using a similar powder metallurgy technique. Additions of Hf, Zr to substitute for the Ti sites, and Pt, Si to substitute for the Ni sites are made. Also dopings by Sb on the Sn site are attempted. The compounds were first made by arc melting the raw materials and then the ingots were ground by mortal and separated into under 45 μm in diameter. Then, the separated powders were hot pressed at 1073 K for 5 h under a pressure of 35 MPa followed by annealing at 1073 for 2 weeks in evacuated quartz tubes.

Crystal structure analysis of the compounds was carried out by X-ray diffractometry using a Rigaku RAD-IIA diffractometer with a Cu $K_a$ radiation. Thermoelectric properties, Seebeck coefficient, $\alpha$, and the electrical resistivity, $\rho$, were simultaneously measured in a temperature range from room temperature to 1000 K in a He atmosphere using ZEM-1 (ULVAC, Shinkuriko). Pellets obtained were cut into pillars with a dimension of $3 \times 3 \times 15$ mm$^3$ for the measurement of electrical properties and into discs with dimensions of 10 mm $\phi$ and of thickness $\sim 3$ mm for the measurement of thermal conductivity. Thermal conductivity, $\kappa$, was measured by a laser flash technique with ULVAC-RIKO TC-7000 in the similar temperature range from room temperature to 1000 K.

3. Results and discussions

3.1. IrSb$_3$ based Skutterudite compounds

Skutterudite compounds among PGEC materials have drawn attentions owing to their unique electrical properties caused by the complex structure [4]. The most remarkable electrical transport property for Skutterudite compounds is the extremely high Hall mobility, giving a low electrical resistivity and a moderate Seebeck coefficient over an entire temperature range as shown in Fig. 1 for the binary stoichiometric IrSb$_3$.

An interesting characteristic of the Skutterudite crystal structure is the existence of two structural vacancies in the unit cell as shown in Fig. 2. It is known that two structural vacancies can be filled with lanthanide and other elements. The most distinct property of so-called filled-Skutterudite is characterized by the weakly bonded lanthanide and other atoms in an oversized structural vacancy in its crystal structure [13]. Atoms that filled the structural vacancies in such a manner will undergo large local anharmonic vibrations and hence will be referred to as a rattler. Rattlings in structural vacancy of Skutterudite can in some cases dramatically scatter the phonon of neighbour atoms, resulting in effectively reducing the lattice thermal conductivity [13]. However, in order for a Skutterdite compounds to maintain its good semiconducting properties, additional alloying to the Sb sites must generally be made to compensate the effect in the Valence Electron Count of the compound to maintain its semiconducting properties. For that purpose, additions of Ge is made according to the formula La$_x$Ir$_4$Ge$_{3x}$Sb$_{12-3x}$.

Fig. 3 shows the temperature dependence of total thermal conductivity and lattice thermal conductivity for La$_x$Ir$_4$Ge$_{3x}$Sb$_{12-3x}$ Skutterudite compounds. Estimation of lattice thermal conductivity is made by using the Wiedemann–Franz law from the measured total thermal conductivity. It is shown that thermal conductivity of all La-filled and Ge

![Fig. 1. Temperature dependence of Seebeck coefficient and electrical resistivity of the binary IrSb$_3$ Skutterudite compound.](image-url)
compensated compounds is effectively reduced as compared to that of binary IrSb₃ owing to the reduction in lattice thermal conductivity.

It is, however, confirmed by the precise structure analysis using Rietveld method that not all La atoms added to the compound occupy the structural vacancies. It indicates that the amount of Ge doped for the charge compensation is in excess of that theoretically required, resulting in providing metallic electrical properties. Therefore, in the concept of the material design, semiconducting electrical properties of binary Skutterudite compound should be maintained by a proper balance of La and Ge amount. If semiconducting electrical properties are maintained with the drastically decreased lattice thermal conductivity by a rattling effect of La atoms, the dimensionless figure of merit, ZT of Skutterudite materials could be over that of state-of-the-art Bi–Te thermoelectric materials which are commercially available for ambient temperature applications.

3.2. Half-Heusler thermoelectric materials

For the enhancement of dimensionless figure of merit, ZT, for TiNiSn based half-Heusler compounds, the initial effort has been concentrated on the reduction of thermal conductivity of the compounds [14]. Fig. 4 shows the effect of alloying elements on thermal conductivity for TiNiSn based half-Heusler compound. It is found that thermal conductivity decreases by all additions excluding Si. Among the alloying elements, Hf and Zr, which substitute for the Ti sites, and Pt for the Ni sites effectively, reduce the thermal conductivity of TiNiSn. Similar analysis on the measured thermal conductivity applied for Skutterudite compounds was carried out and it is shown that the additions of these elements are also to reduce the lattice thermal conductivity. It would come from the fact that these elements enhance the point-defect phonon scattering by structural disordering. By further investigations, it is revealed that the most effective alloying element is Hf to improve thermal property. When the effects of Hf (M_Hf = 179) and Zr (M_Zr = 91) substitutions for the Ti (M_Ti = 48) sites are compared, where M_x is atomic mass of an element x, Hf addition is more effectively reduces the lattice thermal conductivity. It is presumably because of a larger atomic mass of Hf enhances the mass fluctuation phonon scattering [15].

For an optimization of electrical properties of the TiNiSn based half-Heusler compounds, Sb doping on the Sn sites which should affect the carrier concentration...
of the compound was investigated. Temperature dependence of power factor is shown in Fig. 5 for the ternary and Sb-doped TiNiSn compounds. It is shown that Sb doping on Sn site reduces the electrical resistivity presumably by the increase of the carrier concentration maintaining a moderate Seebeck coefficient. The maximum power factor is obtained at 600 K being 3.2 mW/mK², which gives a value for ZT being 0.5, and it is being much higher value than the ternary TiNiSn compound. However, Sb doping should lead to the increase in thermal conductivity because of the increase in contribution of electronic thermal conductivity due to the increase in carrier concentration. Then the effect of concurrent additions of Sb and Hf should be considered for the optimization between electrical and thermal properties for a higher dimensionless figure of merit ZT.

Figs. 6 and 7 show the electrical resistivity and thermal conductivity of Ti_{1-x}Hf_{x}NiSn_{0.99}Sb_{0.01} compounds fabricated by hot pressing and subsequent annealing.

It is found that the electrical resistivity decreases with Sb doping by 0.01 at.% and its temperature dependence becomes slightly positive, indicating the appearance of metallic nature by the doping. Together with the results on the measurement of Seebeck coefficient, the highest value for the power factor is obtained in Ti_{0.95}Hf_{0.05}NiSn_{0.99}Sb_{0.01} compound being 4.5 mW/mK² at 670 K. In Fig. 7, it is found that thermal conductivity of the Ti_{0.95}Hf_{0.05}NiSn_{0.99}Sb_{0.01} compound is higher than that of the ternary TiNiSn, but is lower than that with 0.01 at.% Sb, and TiNiSn_{0.99}Sb_{0.01}. To be noted is that even a stronger effect of Hf alloying in reducing thermal conductivity is found in Ti_{0.8}Hf_{0.2}NiSn_{0.99}Sb_{0.01} compound.

The dimensionless figure of merit of the TiNiSn based compounds obtained by the present work is summarized in Fig. 8. The effective reduction in thermal conductivity by substitution of the Ti sites by Hf and the enhanced power
factor by Sb doping on Sn site result in high values of ZT over 0.7 at 670–770 K. The value obtained being 0.78 at 770 K for Ti$_{0.95}$Hf$_{0.05}$NiSb$_{0.99}$Sb$_{0.01}$ compound is the highest among half-Heusler compounds reported so far.

4. Conclusions

A systematic investigation has been conducted aiming at the improvement of high temperature thermoelectric properties of IrSb$_3$ based Skutterudite and TiNiSn based half-Heusler compounds. Efforts to enhance thermoelectric efficiency were concentrated on the reduction of thermal conductivity while maintaining electrical properties. The followings are the conclusions drawn.

1. Lattice thermal conductivity of Skutterudite IrSb$_3$ is effectively reduced by filling La into the structural vacancies within the crystal structure. Charge compensation is necessary by Ge additions to La-added IrSb$_3$ compounds. A high figure of merit could be achieved in the compound by optimization on the amount of La and Ge additions.

2. A dramatic improvement on the thermoelectric properties of half-Heusler TiNiSn compounds is achieved by Hf alloying on the Ti sites and Sb doping on the Sn sites. The former effectively reduces thermal conductivity, while the latter improves the electrical properties. The highest value for ZT obtained is 0.78 at 770 K for Ti$_{0.95}$Hf$_{0.05}$NiSb$_{0.99}$Sb$_{0.01}$ compound, which is the highest among values reported so far for this compound.

References

[1] A.F. Ioffe, Semiconductor Thermoelements and Thermoelectric Cooling, Inforsearch Ltd, London, 1957.
[2] G.A. Slack, New materials and performance limit for thermoelectric cooling, in: D.M. Rowe (Ed.), CRC Handbook of Thermoelectrics, 1995, pp. 407–440.
[3] G.A. Slack, V.G. Tsoukala, Some properties of semiconductor IrSb$_3$, J. Appl. Phys. 76 (3) (1994) 1665–1671.
[4] A. Borschchevsky, J.P. Fleurlis, E. Allevato, T. Calliat, CoSb$_3$–IrSb$_3$ solid solution: preparation and characterization, in: B. Mathurprakash, P. Heenan (Eds.), Proceedings of the 13th International Conference on Thermoelectrics, Kansas City, MO, 1995, pp. 3–6.
[5] F.G. Aliev, N.B. Brandt, V.V. Moshchalkov, V.V. Kozyrykov, R.V. Scolozdra, A.I. Belogorokhov, Gap at the Fermi level in the intermetallic vacancy system RNiSn (R = Ti, Zr, Hf), Z. Phys. B: Condens. Matter 75 (1989) 167–171.
[6] J.L. Cohn, G.S. Nolas, V. Fessatidis, T.H. Metcalf, G.A. Slack, Glasslike heat conduction in high-mobility crystalline semiconductors, Phys. Rev. Lett. 82 (1999) 779–782.
[7] B.C. Sales, B.C. Chakoumakos, R. Jin, J.R. Thompson, D. Mandrus, Structural, magnetic, thermal, and transport properties of X$_8$Ga$_{16}$Ge$_{30}$ (X = Eu, Sr, Ba) single crystals, Phys. Rev. B 63 (2001) 245113.1–245113.8.
[8] B.C. Chakoumakos, B.C. Sales, D.G. Mandrus, G.S. Nolas, Structural disorder and thermal conductivity of the semiconducting clathrate Sr$_8$Ga$_{16}$Ge$_{30}$, J. Alloys Compd 296 (2000) 80–86.
[9] B.C. Chakoumakos, B.C. Sales, D.G. Mandrus, Structural disorder and magnetism of the semiconducting clathrate Eu$_8$Ga$_{16}$Ge$_{30}$, J. Alloys Compd 322 (2001) 127–134.
[10] I. Fisher, Chevrel phases: superconducting and normal state properties, Appl. Phys. 16 (1978) 1–28.
[11] J.W. Sharp, E.C. Jones, R.K. Williams, P.M. Martin, B.C. Sales, Thermoelectric properties of CoSb$_3$ and related alloys, J. Appl. Phys. 78 (1995) 1013–1018.
[12] H. Hohl, A.P. Ramirez, C. Goldmann, G. Ernst, B. Woelfing, E. Bucher, Efficient dopants for ZnNiSn-based thermoelectric materials, J. Phys.: Condens. Matter 11 (1999) 1697–1709.
[13] B.C. Sales, D. Mandrus, R.K. Williams, Filled Skutterudite antimonides: a new class of thermoelectric materials, Science 272 (1996) 1325–1328.
[14] Q. Shen, L. Chen, T. Goto, T. Hirai, J. Yang, G.P. Meissner, C. Uher, Effects of partial substitution of Ni by Pd on the thermoelectric properties of ZnNiSn-based half-Heusler compounds, Appl. Phys. Lett. 79 (2002) 4165–4167.
[15] C.B. Vining, A model for the high-temperature transport properties of heavily doped n-type silicon–germanium alloys, J. Appl. Phys. 69 (1990) 331–341.