Thermoelectrical properties of the compounds $ScM^{VIII}Sb$ and $YM^{VIII}Sb$ (M^{VIII} = Ni, Pd, Pt)

2003 J. Phys.: Condens. Matter 15 635

(http://iopscience.iop.org/0953-8984/15/4/304)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **15** (2003) 635–640 PII: S0953-8984(03)52474-2

Thermoelectrical properties of the compounds $ScM^{VIII}Sb$ and $YM^{VIII}Sb$ (M^{VIII} = Ni, Pd, Pt)

J Oestreich, U Probst, F Richardt and E Bucher

University of Konstanz, PO Box X916, D-78457 Konstanz, Germany

Received 16 August 2002, in final form 15 November 2002
Published 20 January 2003
Online at stacks.iop.org/JPhysCM/15/635

Abstract

The research into new materials with good thermoelectric properties has revealed new compounds consisting of metallic elements (Bando Y, Suemitsu T, Takagi K, Tokushima H, Echizen Y, Katoh K, Umeo K, Maeda Y and Takabatake T 2000 *J. Alloys Compounds* **313** 1–6, Ghelani N, Loo S, Chung D, Sportouch S, Nardi S, Kanatzidis M, Hogan T and Nolas G 2000 *Mater. Res. Soc.* **626** Z8.6.1). The half-Heusler compound ZrNiSn, in particular, shows promising thermoelectric properties and has been studied by many scientists during recent years (Uher C, Hu S, Yang J, Meisner G P and Morelli D T 1997 *Proc. ICT'97: 16th Int. Conf. on Thermoelectrics* pp 485–8, Romaka L P, Stadnyk Yu V, Goryn A M, Gorelenko Yu K and Skolozdra R V 1997 *Proc. ICT'97: 16th Int. Conf. on Thermoelectrics* pp 516–19, Hohl H, Ramirez A P, Goldmann C, Ernst G, Wölfing B and Bucher E 1998 *J. Phys.: Condens. Matter* **11** 1697–709, Oestreich J, Käfer W, Richardt F, Probst U and Bucher E 1999 *Proc. 5th European Workshop on Thermoelectrics* pp 192–5). In an effort to find new thermoelectric materials, the half-Heusler compounds of the groups $ScM^{VIII}Sb$ and $YM^{VIII}Sb$ (M^{VIII} = Ni, Pd, Pt) were synthesized by arc melting and the thermoelectric properties were examined by standard characterization methods. Doping experiments showed that it is possible to change the electrical properties of the compounds while retaining the half-Heusler structure. Within the two groups, YPtSb showed the best thermoelectrical properties. At a temperature of 400 K the electrical conductivity of YPtSb is 748 Ω^{-1} cm^{-1} and the Seebeck coefficient is 116.3 μV K^{-1}. The thermal conductivity at 400 K extrapolated using the Wiedemann–Franz law is 2.87 W K^{-1} m^{-1}. This leads to a dimensionless figure of merit of 0.14.

1. Introduction

This paper is based on research done in order to investigate the thermoelectrical properties of new half-Heusler compounds [7]. YNiSb has the MgAgAs-type structure with four

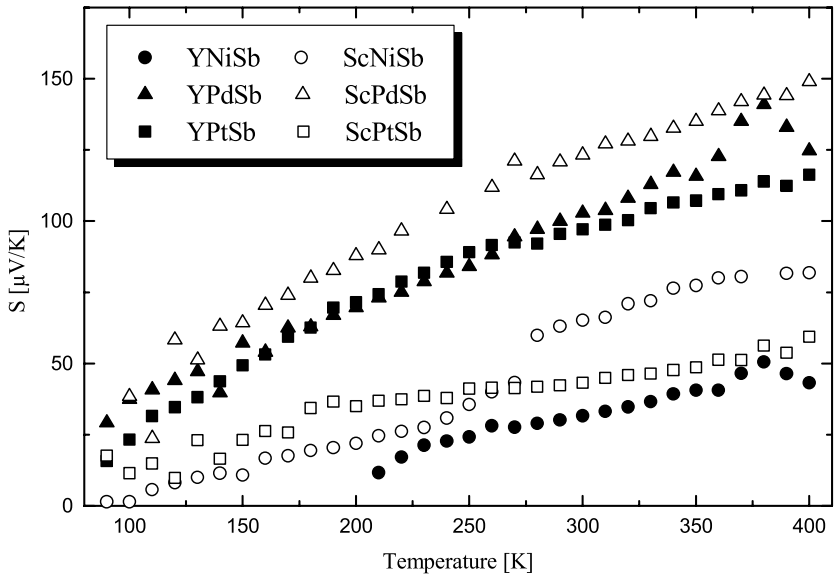

Figure 1. Seebeck coefficient versus temperature.

interpenetrating fcc sublattices [8]. Yttrium, nickel and antimony each occupy one fcc sublattice, while the fourth sublattice is vacant. This is also known as half-Heusler structure. To obtain other half-Heusler compounds, one of the three elements was replaced by an isoelectronic element, i.e. yttrium was replaced by scandium. A very important feature of ZrNiSn is its wide range of dopability, because this provides a way to improve its thermoelectric properties. For doping the compounds investigated, a small amount of the element used was replaced by an element having one valence electron fewer (for p-type doping) or one valence electron more (n-type doping). (All half-Heusler compounds investigated are listed in table 3.)

2. Experimental details

The groups $ScM^{VIII}Sb$ and $YM^{VIII}Sb$ ($M^{VIII} = Ni, Pd, Pt$) were synthesized by melting stoichiometric mixtures of the elements in an arc furnace. As a result, ingots with an average diameter of 10 mm and a thickness of 5 mm were obtained. All samples showed the half-Heusler structure and were annealed for 10–30 days at 1100 K to improve their homogeneity. The lattice parameters shown in table 1 were determined by powder diffraction measurements. The compounds YPdSb and YPtSb show the same lattice parameter as ScPdSb and ScPtSb do within the resolution of our experiments. This can be explained by the similar covalence radii of palladium and platinum.

The annealed samples were cut into rectangular samples with an average size of $1 \times 1 \times 10\,mm^3$ and were polished. Seebeck measurements were performed in a temperature range from 90 to 400 K. The samples were contacted with an InGa eutectic. The results are summarized in figure 1.

The Seebeck coefficient S, for all compounds, is positive in the measurement temperature range and increases with temperature, except for YPdSb, YPtSb and ScNiSb when n-type doped. (The Seebeck coefficients of all compounds investigated are shown in table 3.)

To determine the electrical transport properties, the five-point method and the van der Pauw method were used in the temperature range from 36 to 405 K. Electrical contacts were made

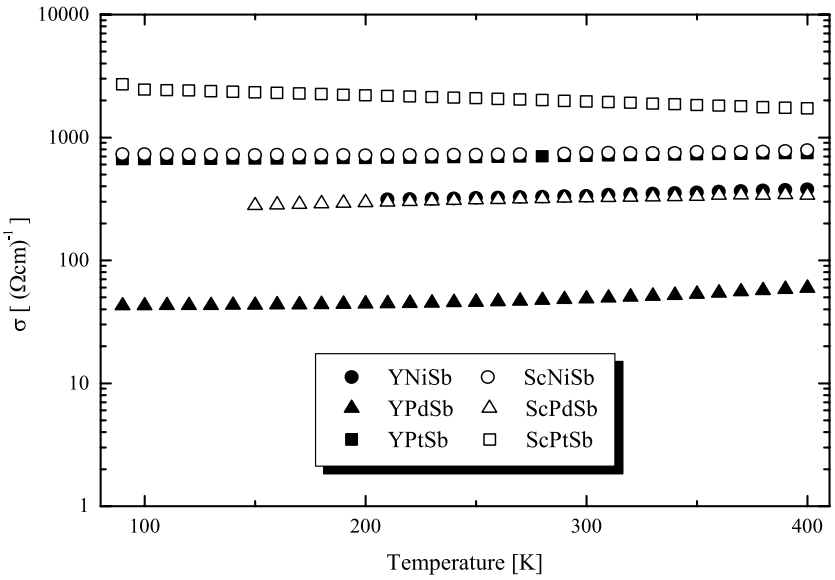

Figure 2. Conductivity versus temperature.

Table 1. Lattice parameters of some of the compounds investigated.

Compound	Lattice parameter (Å)			Literature values (Å) for the undoped compounds
	Undoped	p-type doped	n-type doped	
YNiSb	6.280	—	—	6.246 [8], 6.318 [9]
YPdSb	6.533	6.527	6.531	6.527 [13]
YPtSb	6.532	6.535	6.533	6.538 [10]
ScNiSb	6.062	6.067	6.065	6.062 [14], 6.055(2) [15]
ScPdSb	6.312	—	—	—
ScPtSb	6.312	—	—	6.312 [14]

via gold wires fixed to the sample by a silver–epoxy paste. The results of these measurements are shown in figure 2.

ScPtSb, which exhibits the largest electrical conductivity σ, shows the behaviour of a degenerate semiconductor. All other samples show an activated semiconducting behaviour. In the high-temperature region an activation above the band gap is expected. The activation energy of these samples, except ScPtSb, was determined by means of high-temperature resistivity measurements in a temperature range between 600 and 730 K using the equation

$$\rho \propto \exp\left(\frac{E_{gap}}{2k_B T}\right).$$

The resulting values for the corresponding band gaps are shown in table 2. The result for YNiSb of 0.18 eV obtained from our experiments lies between the theoretical values of Tobola (0.29 eV) [8] and Larson (0.28 eV) [11] and the experimental value of Sportouch (0.09 eV) [12].

The thermal conductivity has been measured using a standard steady-state method for a bar-shaped sample. Figure 3 shows the measured thermal conductivities of some samples. ScPtSb has been omitted due to its high thermal conductivity as compared to the other samples (11.63 W K^{-1} m^{-1} at 300 K). The electronic contribution of the thermal conductivity can be

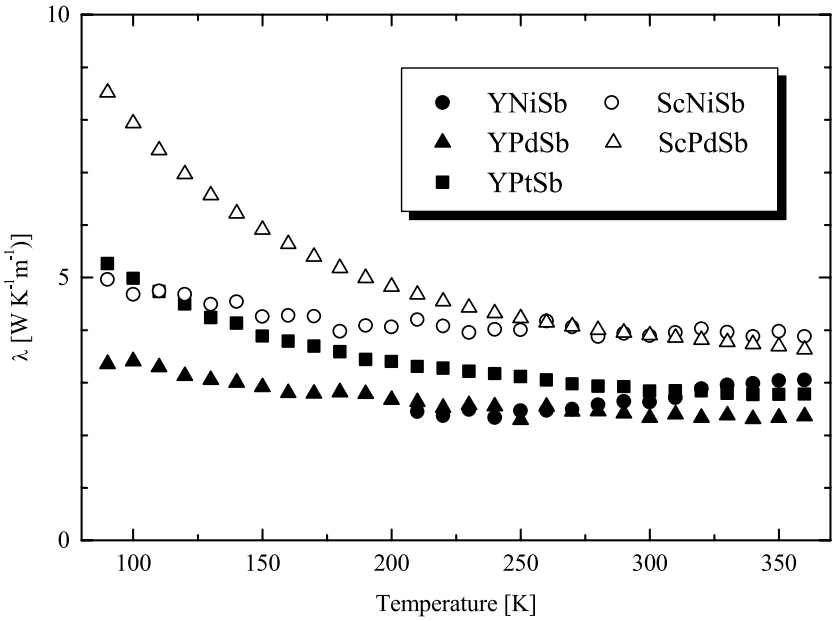

Figure 3. Thermal conductivity versus temperature.

Table 2. Energy gaps of the compounds investigated.

Compound	Energy gap (eV)
YNiSb	0.18
YPdSb	0.27
YPtSb	0.16
ScNiSb	0.11
ScPdSb	0.23

derived from the experimental data using the Wiedemann–Franz law. For this evaluation the Lorenz number for metals and degenerate semiconductors was used. YPtSb, the compound with the best thermoelectric properties among the materials studied, has an overall thermal conductivity of 2.84 W K^{-1} m^{-1} at 300 K with an electronic contribution of 0.52 W K^{-1} m^{-1}.

The lattice thermal conductivity of 2.32 W K^{-1} m^{-1} leaves scope for further reduction, e.g. by isoelectronic alloying. The thermoelectric properties of all samples investigated are shown in table 3.

The power factor (defined as $S^2\sigma$), for all compounds investigated, increases with increasing temperature. YPtSb shows the highest power factor of 1.0×10^{-3} W K^{-2} m^{-1} at 400 K (electrical conductivity: 748 Ω^{-1} cm^{-1}; Seebeck coefficient: 116.3 μV K^{-1}). The thermal conductivity of YPtSb at 400 K can be extrapolated from the experimental values by using the Wiedemann–Franz law to derive the electrical contribution of the thermal conductivity. The contribution of the lattice thermal conductivity can be extrapolated by using the Debye approximation for high temperatures $\lambda_{latt} \sim T^{-1}$. The extrapolated thermal conductivity at 400 K is 2.87 W K^{-1} m^{-1}. This leads to a dimensionless figure of merit (defined as $S^2\sigma\kappa^{-1}$) of 0.14 for YPtSb.

Table 3. Thermoelectric properties of the compounds investigated, at 300 K.

Material	σ (Ω^{-1} cm^{-1})	S (μV K^{-1})	λ (W K^{-1} m^{-1})	ZT
YNiSb	336	+31.7	2.63	0.0039
YPdSb	48.5	+102.8	2.33	0.0066
$YPd_{0,98}Rh_{0,02}Sb_{0,98}Sn_{0,02}$	339	+32.8	7.45	0.0014
$Y_{0,98}Zr_{0,02}PdSb_{0,98}Te_{0,02}$	305	−107.9	1.82	0.0585
YPtSb	709	+97.1	2.84	0.0710
$YPt_{0,98}Ir_{0,02}Sb_{0,98}Sn_{0,02}$	615	+22.0	6.39	0.0140
$Y_{0,98}Zr_{0,02}PtSb_{0,98}Te_{0,02}$	46	−64.2	2.02	0.0028
ScNiSb	745	+65.2	3.89	0.0240
$ScNi_{0,98}Co_{0,02}Sb_{0,98}Sn_{0,02}$	4117	+40.4	7.61	0.0265
$Sc_{0,98}Ti_{0,02}Ni_{0,98}Cu_{0,02}Sb_{0,98}Te_{0,02}$	763	−74.0	3.02	0.0415
ScPdSb	322	+123.2	3.90	0.0376
$ScPdSb_{0,98}Sn_{0,02}$	1965	+40.1	—	—
ScPtSb	1959	+43.2	11.63	0.009
$ScPtSb_{0,98}Sn_{0,02}$	7081	+33.6	—	—

3. Conclusions

The half-Heusler compounds of the groups $ScM^{VIII}Sb$ and $YM^{VIII}Sb$ (M^{VIII} = Ni, Pd, Pt) were synthesized by arc melting and the thermoelectric properties were examined by various characterization methods. Band gaps and lattice constants were also determined. All undoped samples show a positive Seebeck coefficient. YPdSb, YPtSb and ScNiSb were n-type doped by various substitutions. Among the two groups, YPtSb showed the best thermoelectric properties. At 400 K the electrical conductivity of YPtSb is 748 Ω^{-1} cm^{-1}, the Seebeck coefficient is 116.3 μV K^{-1} and the value of the thermal conductivity derived by the Wiedemann–Franz law is 2.87 W K^{-1} m^{-1}. This leads to a dimensionless figure of merit of 0.14. The optimization of YPtSb has not yet been completed. Therefore, the compound is a promising candidate for further investigation.

References

[1] Bando Y, Suemitsu T, Takagi K, Tokushima H, Echizen Y, Katoh K, Umeo K, Maeda Y and Takabatake T 2000 Large thermoelectric power in several metallic compounds of cerium and uranium *J. Alloys Compounds* **313** 1–6

[2] Ghelani N, Loo S, Chung D, Sportouch S, Nardi S, Kanatznidis M, Hogan T and Nolas G 2000 Characterization of new materials in a four-sample thermoelectric measurement system *Mater. Res. Soc.* **626** Z8.6.1

[3] Uher C, Hu S, Yang J, Meisner G P and Morelli D T 1997 Transport properties of ZrNiSn-based intermetallics *Proc. ICT'97: 16th Int. Conf. on Thermoelectrics* (Piscataway, NJ: IEEE) pp 485–8

[4] Romaka L P, Stadnyk Yu V, Goryn A M, Gorelenko Yu K and Skolozdra R V 1997 Structure type solid solutions as new thermoelectric material *Proc. ICT'97: 16th Int. Conf. on Thermoelectrics* (Piscataway, NJ: IEEE) pp 516–19

[5] Hohl H, Ramirez A P, Goldmann C, Ernst G, Wölfing B and Bucher E 1998 Efficient dopants for ZrNiSn-based thermoelectric materials *J. Phys.: Condens. Matter* **11** 1697–709

[6] Oestreich J, Käfer W, Richardt F, Probst U and Bucher E 1999 Thermoelectrical properties of $Zr_{1-X}Y_XNiSn$ *Proc. 5th European Workshop on Thermoelectrics (Pardubice, Czech Republic, 1999)* pp 192–5

[7] Oestreich J 2001 Untersuchungen an neuen thermoelektrischen Materialien *PhD Thesis* Universität Konstanz, http://www.ub.uni-konstanz.de/kops/volltexte/2002/739

[8] Tobola J, Pecheur P, Pierre J and Roche C 1999 Theoretical study of the XYZ (X = Fe, Co, Ni; Y = Ti, V, Zr, Nb; Z = Sn, Sb) semi-Heusler phases for thermoelectrics *Proc. 5th European Workshop on Thermoelectrics (Pardubice, Czech Republic, 1999)* pp 120–5

[9] Teubner J 2001 Optimization of high efficiency thermoelectrics based on Tl_5Te_3 *Diploma Thesis* Universität Konstanz, http://www.ub.uni-konstanz.de/kops/volltexte/2001/672

[10] Wenski G and Mewis A 1986 REPtX compounds with structures related to AlB_2- and MgAgAs-type (RE = Y, rare earth element; X = P, As, Sb) *Z. Kristallogr.* **176** 125–34

[11] Larson P, Mahanti S D, Sportouch S and Kanatzidis M G 1999 Electronic structure of rare-earth nickel pnictides: narrow-gap thermoelectric materials *Phys. Rev.* B **59** 15660–8

[12] Sportouch S, Larson P, Bastea M, Brazis P, Ireland J, Kannewurf C R, Mahanti S D, Uher C and Kanatzidis M G 1999 Potential Thermoelectric Materials *Thermoelectric Materials 1998—the Next Generation Materials for Small-Scale Refrigeration and Power Generation Applications* pp 421–33

[13] Marazza R, Rossi D and Ferro R 1980 $CaIn_2$-type and MgAgAs-type RESbPd compounds (RE = rare earth elements) *J. Less-Common Met.* **75** P25–8

[14] Dwight A E 1974 The crystal structure of DyNiSb, DyPtSb and related compounds *Proc. 11th Rare Earth Research Conf. (MI, 1974)* vol 2, pp 642–50

[15] Pecharskij V K, Pankevich Yu V and Bodak O I 1983 Crystal structures of the compounds RNiSb with various rare earth elements *Sov. Phys.–Crystallogr.* **28** 97–8 (translated from *Kristallografiya*)