Ba_xPd₄Sn_ySb_{12-y}: A New Palladium-Containing Skutterudite

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A new compound with the filled-skutterudite structure, Ba_xPd₄Sn_ySb_{12-y}, was prepared by the flux growth and spark plasma sintering (SPS) techniques. The crystal structure was determined from single crystal and powder x-ray diffraction data. The structure is electronically stabilized by the Sn:Sb ratio, and the lattice parameters depend on this ratio. For magnetic, electrical conductivity, Hall coefficient, Seebeck coefficient and thermal conductivity measurements, single crystal and/or SPS-densified specimens were utilized. Ba_{1.0}Pd₄Sn_{7.1}Sb_{5.2} exhibits diamagnetic behavior. The Hall coefficient is negative and increases with temperature. The lattice thermal conductivity of Ba_{0.97}Pd₄Sn_{6.90}Sb_{4.97} (SPS-densified) is smaller than for CoSb₃, but the thermoelectric figure of merit (*ZT*) is comparatively low due to the low Seebeck coefficient.

Key words: Filled skutterudite, crystal structure, magnetic susceptibility, Hall coefficient, electrical conductivity, Seebeck coefficient, thermal conductivity

INTRODUCTION

There has been considerable interest in the thermoelectric (TE) properties of non-filled and filled skutterudites. The crystal structure of a skutterudite contains two large voids in the unit cell, which may be filled with ions as effective phonon-scattering centers, and, due to the large number of accessible compositions, skutterudites are deemed to be a promising family of TE materials.¹⁻⁵ Ternary skutterudite derivatives with simultaneous substitution of group IV and V atoms on the pnictogen sites, e.g., Yb_xCo₄Sn_ySb_{12-y},^{6,7} Sn_xNi₄Sn_ySb_{12-y}, Eu_{0.8}Ni₄Sn_{6.2}Sb_{5.8}, Yb_{0.6}Ni₄Sn_{5.3}Sb_{6.7},⁸ have previously been reported. Recently, a metallic Sn_xPt₄Sn_ySb_{12-y} filled skutterudite has been studied. In this compound the filler Sn atoms are not located at the center of the cavity but are covalently bonded to the cavity wall.⁹

The effectiveness of Pd substitution on the TE properties has been studied for Pd_xCo_{1-x}Sb₃¹⁰ and

Ba_{0.32}Pd_xCo_{4-x}Sb₁₂.¹¹ To our best knowledge, there are no data on ternary palladium-containing skutterudites, where only palladium atoms occupy the octahedral (8c) position. Here, we report on a new compound, Ba_xPd₄Sn_ySb_{12-y}. Its crystal structure, as determined from single crystal and powder x-ray data, magnetic behavior, Hall effect, and TE properties were investigated.

EXPERIMENTAL

The starting materials for the preparation were metallic barium (99.9%, ChemPur), palladium granules (99.95%, ChemPur), tin granules (99.99%, ChemPur), and antimony granules (99.999%, ChemPur). Tin-rich single crystals were prepared from a Sn flux. The crucible was heated to 700°C for 12 h. Then, the melt was cooled at a rate of 5°C/h to 400°C and kept at this temperature for 24 h. The excess Sn was removed by centrifugation-supported hot filtration^{12,13} at 400°C and by additional treatment with 37% HCl acid to clean the surface of the crystals. The silver-metallic crystals were stable in air and did not react with concentrated HCl acid.

They were not large enough for TE measurement but were suitable for investigation of their magnetization, Hall coefficient, and electrical resistivity. The crystals were reground and powdered by ball-milling, filled into a carbon pressing tool and spark-plasma sintered^{14,15} at 400°C for 2 h. The resulting samples were silver bulk pellets with at least 90% theoretical density.

The samples were characterized by x-ray powder diffraction using the Guinier technique (Huber image plate camera G670, CuK α_1 radiation with $\lambda = 1.54060$ Å, $5^\circ < 2\theta < 100^\circ$, step width 0.005° , and LaB $_6$ with $a = 4.15692$ Å as internal standard). Lattice parameters were refined from powder diffraction data using WinCSD software.¹⁶ For intensity data collection on single crystals, a Rigaku Spider diffraction system was used (AgK α radiation, $\lambda = 0.5608$ Å). The crystal structure of BaPd $_4$ Sn $_{7.34(5)}$ Sb $_{4.92(5)}$ was determined by direct methods using SHELXS-97¹⁷ and refined with the WinCSD program.¹⁶ The phase appearance in the microstructure of the samples was analyzed by optical metallography. The chemical composition of the phases was analyzed by scanning electron microscopy (Philips XL30) and electron microprobe (Cameca SX 100), by energy-dispersive and wavelength-dispersive x-ray analysis (EDXS and WDXS), respectively.

RESULTS AND DISCUSSION

Sn-free filled skutterudites with Pd and Sb could not be synthesized by standard solid-state techniques. Partial substitution of Sb by Sn contributed to stabilization of the structure due to the balancing of charges. The lattice parameter of Ba $_x$ Pd $_4$ Sn $_y$ Sb $_{12-y}$ depended on the Sn:Sb ratio in the framework due to the different ionic radii of the elements, and, to a lesser extent, on the interactions between the filler and the framework. The lattice spacing and compositional changes from Ba $_{1.0(2)}$ Pd $_4$ Sn $_{7.1(2)}$ Sb $_{5.2(2)}$ (EDXS composition; $a = 9.4139(2)$ Å) to Ba $_{0.97(1)}$ Pd $_4$ Sn $_{6.90(2)}$ Sb $_{4.97(1)}$ (WDXS composition; $a = 9.4165(2)$ Å) after spark plasma sintering indicated a complex homogeneity range of Ba $_x$ Pd $_4$ Sn $_y$ Sb $_{12-y}$. According to the EDXS or WDXS measurements, the samples were homogeneous. This was confirmed by the x-ray powder diffraction patterns (Fig. 1).

The composition BaPd $_4$ Sn $_{7.34(5)}$ Sb $_{4.92(5)}$, as concluded from the crystal structure refinement, agreed well with that obtained by EDXS (Ba $_{1.0(2)}$ Pd $_4$ Sn $_{7.1(2)}$ Sb $_{5.2(2)}$). The details of the structure determination are shown in Table I. The final values of the atomic coordinates and the displacement parameters are summarized in Table II. Table III presents the interatomic distances. BaPd $_4$ Sn $_{7.34(5)}$ Sb $_{4.92(5)}$ crystallized in the body-centered cubic LaFe $_4$ Sb $_{12}$ -type structure¹⁸ (Fig. 2). The Sn/Sb atoms were randomly located on the 24g (1/2 y z) position, with slightly different coordinates y and z, forming

Fig. 1. Experimental x-ray powder diffraction patterns for Ba $_{0.97}$ Pd $_4$ Sn $_{6.90}$ Sb $_{4.97}$ and Ba $_{1.0}$ Pd $_4$ Sn $_{7.1}$ Sb $_{5.2}$ in comparison with a simulated diffraction picture.

Table I. Crystallographic data and details of the crystal structure determination of BaPd $_4$ Sn $_{7.34}$ Sb $_{4.92}$

Space group	$Im\bar{3}$ (no. 204)
Formula units per unit cell	$Z = 2$
Composition	BaPd $_4$ Sn $_{7.34(5)}$ Sb $_{4.92(5)}$
Unit cell parameter a	9.4139(2) Å (from powder diffraction data)
Unit cell volume	834.27(5) Å 3
Calculated density	8.10 g/cm 3
Data collection	Rigaku Spider; AgK α ($\lambda = 0.5608$ Å, multilayer optics)
Measured range ($\sin \theta/\lambda$) $_{\max}$	$8.4^\circ \leq 2\theta \leq 123.0^\circ$; 1.57
Absorption correction	Empirical
Absorption coefficient	32.92 mm $^{-1}$
Extinction coefficient	0.00125 (7)
$R_{\text{gt}}(F)/wR_{\text{ref}}(F^2)$	0.042/0.025

two kinds of large voids. Pd atoms were located in the octahedral voids at 8c (1/4 1/4 1/4) position. The voids at the 2a position were filled by Ba atoms, which were coordinated by 12 tin/antimony atoms to form a distorted icosahedron.

Magnetic susceptibility $\chi = M/H_{\text{ext}}$ of Ba $_{1.0}$ Pd $_4$ Sn $_{7.1}$ Sb $_{5.2}$ versus temperature is shown in Fig. 3. Ba $_{1.0}$ Pd $_4$ Sn $_{7.1}$ Sb $_{5.2}$ exhibited diamagnetic behavior in the temperature range from 1.8–400 K. Considering paramagnetic impurities as the origin of the Curie-like contribution at low temperatures, we could extrapolate a $\chi_0 \approx -160(10) \times 10^{-6}$ emu/mol. In a low-field measurement a superconducting signal was observed (T_c ($H = 0$) = 3.9 K; H_c (1.8 K) $\approx$ 500 Oe; volume fraction 7% after zero-field cooling and 1% during field cooling), which was due to residual Sn-Sb alloy. The onset of a superconducting

Table II. Atomic coordinates and displacement parameters ($\text{\AA}^2$) in the crystal structure of BaPd₄Sn_{7.34}Sb_{4.92}

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	Occ.	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃	<i>U</i> _{eq}
Ba	2 <i>a</i>	0	0	0	1	0.01116(1)	<i>U</i> ₁₁	<i>U</i> ₁₁	0	0	0	0.01116(7)
Pd	8 <i>c</i>	1/4	1/4	1/4	1	0.00650(5)	<i>U</i> ₁₁	<i>U</i> ₁₁	0.00081(6)	<i>U</i> ₁₂	<i>U</i> ₁₂	0.00650(3)
Sb	24 <i>g</i>	1/2	0.1547(2)	0.34681(1)	0.410(4)	0.0068(4)	0.0088(4)	0.0083(2)	0	0	-0.0004(2)	0.0080(2)
Sn	24 <i>g</i>	1/2	0.15129(1)	0.33840(1)	0.612(4)	0.0066(2)	0.0085(2)	0.00885(1)	0	0	0.0002(2)	0.00798(1)

Table III. Interatomic distances ($\text{\AA}$) in BaPd₄Sn_{7.34}Sb_{4.92}

Atoms	Distance	Atoms	Distance
Ba 8 Pd	4.0763(1)	Pd 2 Ba	4.0763(1)
12 { Sn	3.618(1)	6 { Sn	2.6636(5)
12 { Sb	3.556(2)	6 { Sb	2.6784(8)
Sn 2 Pd	2.6636(5)	Sb 2 Pd	2.6784(8)
12 { Ba	3.618(1)	12 { Ba	3.556(2)
1 { Sn	2.849(2)	1 { Sn	2.882(2)
1 { Sb	2.882(2)	1 { Sb	2.884(2)
1 { Sn	3.043(1)	1 { Sn	2.964(2)
1 { Sb	2.964(2)	1 { Sb	2.913(3)
4 { Sn	3.491(1)	4 { Sn	3.503(1)
4 { Sb	3.503(1)	4 { Sb	3.563(1)
4 { Sb	3.563(1)	4 { Sb	3.575(2)

Fig. 2. Crystal structure of BaPd₄Sn_{7.34}Sb_{4.92}. The palladium atoms (dark gray balls) are octahedrally coordinated by Sn/Sb atoms (small light gray balls). In the framework only Sb atoms are shown in the 24*g* position. The barium atoms (large light gray balls) are icosahedrally coordinated by eight Pd atoms and 12 Sn/Sb atoms.

transition temperature of 4.1 K was reported for the composition 'Sn₃Sb₂'¹⁹ and was confirmed by our own measurements on a sample of Sn₆₀Sb₄₀ ($T_{c,onset} = 3.95$ K).

The Hall coefficient of Ba_{1.0}Pd₄Sn_{7.1}Sb_{5.2} obtained from a linear fit of $\rho_{Hall}(H)$ is presented in Fig. 4. Fits in different field ranges served as rough estimates of errors in the Hall coefficient obtained

Fig. 3. Molar magnetic susceptibility of Ba_{1.0}Pd₄Sn_{7.1}Sb_{5.2} versus temperature in a magnetic field of 70 kOe.

Fig. 4. Hall coefficient as a function of temperature for Ba_{1.0}Pd₄Sn_{7.1}Sb_{5.2} in fields of $|H| < 20$ kOe (filled symbols) and $|H| < 90$ kOe (empty symbols).

from transverse magnetoresistance. R_H was negative and increased with temperature, indicating that the charge carriers were mainly electrons.

Figure 5 presents the temperature dependence of electrical resistivity $\rho(T)$ for Ba_xPd₄Sn_ySb_{12-y}. While Ba_{1.0}Pd₄Sn_{7.1}Sb_{5.2} showed metallic behavior, Ba_{0.97}Pd₄Sn_{6.90}Sb_{4.97} revealed a changeover from metal-like to semiconductor-like temperature characteristics. The resistivity drop for Ba_{0.97}Pd₄Sn_{6.90}Sb_{4.97} below 4.0 K was due to the superconducting impurity as discussed above.

Fig. 5. Electrical resistivity as a function of temperature for $\text{Ba}_{1.0}\text{Pd}_4\text{Sn}_{7.1}\text{Sb}_{5.2}$ and $\text{Ba}_{0.97}\text{Pd}_4\text{Sn}_{6.90}\text{Sb}_{4.97}$.

Fig. 6. Seebeck coefficient as a function of temperature for $\text{Ba}_{0.97}\text{Pd}_4\text{Sn}_{6.90}\text{Sb}_{4.97}$.

The Seebeck coefficient of $\text{Ba}_{0.97}\text{Pd}_4\text{Sn}_{6.90}\text{Sb}_{4.97}$ (Fig. 6) exhibited a negative value throughout the temperature range. The absolute value of the Seebeck coefficient was very low ($\sim -4.2 \mu\text{V/K}$ at room temperature) compared with that of pnictogen skutterudites.

The temperature-dependent thermal conductivity $\kappa(T)$ of $\text{Ba}_{0.97}\text{Pd}_4\text{Sn}_{6.90}\text{Sb}_{4.97}$ is displayed in Fig. 7. The electronic thermal conductivity $\kappa_e(T)$ can be estimated using the Wiedemann–Franz relationship from the measured ρ . In this approximation, for $\text{Ba}_{0.97}\text{Pd}_4\text{Sn}_{6.90}\text{Sb}_{4.97}$, the major contribution to the thermal conductivity stems from lattice phonons (in the whole temperature range). At room temperature, approximately 60% of the total thermal conductivity was due to the contribution of the lattice phonons. The value of the lattice thermal conductivity ($< 3.0 \text{ W/Km}$ at room temperature) was smaller than that of CoSb_3 ($\sim 8 \text{ W/Km}$ at room temperature).^{20,21}

Fig. 7. Thermal conductivity as a function of temperature for $\text{Ba}_{0.97}\text{Pd}_4\text{Sn}_{6.90}\text{Sb}_{4.97}$. Data above 150 K are influenced by radiation heat losses, leading to an additional contribution $\kappa_{\text{loss}} \sim T^3$.

From the values of the electrical resistivity, Seebeck coefficient and thermal conductivity, we found a TE figure of merit (ZT) of the compound $\text{Ba}_{0.97}\text{Pd}_4\text{Sn}_{6.90}\text{Sb}_{4.97}$. The ZT value was far too low ($\sim 3.3 \times 10^{-4}$ at room temperature) for any TE applications.

CONCLUSIONS

We expanded the family of filled skutterudites by synthesizing the new phase $\text{Ba}_x\text{Pd}_4\text{Sn}_y\text{Sb}_{12-y}$. The crystal structure and physical properties were studied. $\text{Ba}_{1.0}\text{Pd}_4\text{Sn}_{7.1}\text{Sb}_{5.2}$ exhibited diamagnetic behavior. The charge carriers were mainly electrons, and the system showed metallic behavior in the overall temperature range, while $\text{Ba}_{0.97}\text{Pd}_4\text{Sn}_{6.90}\text{Sb}_{4.97}$ exhibited a changeover from metal-like to semiconductor-like temperature characteristics of $\rho(T)$ below 350 K. The ZT value was very low due to the small Seebeck coefficient. In spite of this metallic behavior, the lattice thermal conductivity was low, which is a typical characteristic of filled skutterudites.

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REFERENCES

1. D.T. Morelli and G.P. Meisner, *J. Appl. Phys.* 77, 3777 (1994).
2. B.C. Sales, D. Mandrus, and R.K. Williams, *Science* 272, 1325 (1996).
3. B. Chen, J.H. Xu, C. Uher, D.T. Morelli, G.P. Meisner, J.P. Fleurial, T. Caillat, and A. Borshchevsky, *Phys. Rev. B: Condens. Matter Mater. Phys.* 55, 1476 (1997).
4. E. Bauer, A. Galatanu, H. Michor, G. Hilscher, P. Rogl, P. Boulet, and H. Noël, *Eur. Phys. J. B.* 14, 483 (2000).
5. N.R. Dilley, E.D. Bauer, M.B. Maple, S. Dordevic, D.N. Basov, F. Freibert, T.W. Darling, A. Migliori, B.C. Chakoumakos, and B.C. Sales, *Phys. Rev. B: Condens. Matter Mater. Phys.* 61, 4608 (2000).
6. N.R. Dilley, E.D. Bauer, M.B. Maple, and B.C. Sales, *J. Appl. Phys.* 88, 1948 (2000).
7. J. Yang, D.T. Morelli, G.P. Meisner, W. Chen, J.S. Dyck, and C. Uher, *Phys. Rev. B: Condens. Matter Mater. Phys.* 67, 165207 (2000).
8. A. Grytsiv, P. Rogl, St. Berger, Ch. Paul, H. Michor, E. Bauer, G. Hilscher, C. Godart, P. Knoll, M. Musso, W. Lottermoser, A. Saccone, R. Ferro, T. Roisnel, and H. Noël, *J. Phys.: Condens. Matter* 14, 7071 (2002).
9. Y. Liang, H. Borrmann, M. Baenitz, W. Schnelle, S. Budnyk, J.T. Zhao, and Y. Grin, *Inorg. Chem.* 47, 9489 (2008).
10. K. Matsubara, T. Iyanaga, T. Tsubouchi, K. Kishimoto, and T. Koyanagi, *Proceedings of the 13th International Conference on Thermoelectrics*, AIP Conf. Proc. no. 316 (New York: AIP, 1995), pp. 226–229.
11. Y.Z. Pei, L.D. Chen, S.Q. Bai, X.Y. Zhao, and X.Y. Li, *Scr. Mater.* 56, 621 (2007).
12. Z. Fisk and J.P. Remeika, *Handbook on the Physics and Chemistry of the Rare Earths*, Vol. 12, ed. K.A. Gschneider and L.R. Eyring (Amsterdam: North-Holland, 1989), pp. 53–70.
13. M. Boström and S. Hövöller, *J. Alloys Compd.* 314, 154 (2001).
14. Yu. Grin, N. Reinfried, C.P. Sebastian, P. Höhn, S. Budnyk, A. Leithe-Jasper, C. Recknagel, Y. Liang, G. Friedemann, and M. Tokita, *7th Pacific Rim Conference on Ceramics and Glass Technology, Book of Abstracts* (Shanghai: Shanghai Institute of Ceramics, Chinese Academy of Sciences, 2007), p. 170.
15. N. Reinfried, P. Höhn, and Yu. Grin, *Scientific Report MPI CPfS* (Dresden: Max-Planck-Institut für Chemische Physik fester Stoffe, 2005), pp. 28–31.
16. L.G. Akselrud, P.Y. Zavalii, Y.N. Grin, V.K. Pecharski, B. Baumgartner, and E. Woelfel, *Mater. Sci. Forum* 133–136, 335 (1993).
17. G.M. Sheldrick, *SHELXS-97. Program for the Automatic Solution of Crystal Structures* (University of Göttingen, Germany 1997).
18. D.J. Braun and W. Jeitschko, *J. Less-Common Met.* 72, 147 (1980).
19. E. Van Aubel, W.J. De Haas, and J. Voogd, *Commun. Kamerlingh Onnes Lab, Univ. Leiden* 18, 193c (1930).
20. J. Yang, D.T. Morelli, G.P. Meisner, W. Chen, J.S. Dyck, and C. Uher, *Phys. Rev. B: Condens. Matter Mater. Phys.* 65, 094115 (2002).
21. J. Yang, G.P. Meisner, D.T. Morelli, and C. Uher, *Phys. Rev. B: Condens. Matter Mater. Phys.* 63, 014410 (2000).