

## Synthesis and thermoelectric properties of some materials with the $\text{PbBi}_4\text{Te}_7$ crystal structure

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### Abstract

Polycrystalline samples of some compounds with the  $\text{PbBi}_4\text{Te}_7$  crystal structure have been synthesized and characterized by x-ray and microprobe analysis. Seebeck coefficient, electrical resistivity, and thermal conductivity measurements were also performed in the 300-650K temperature range. Their thermoelectric properties vary widely from semiconducting to semimetallic with both n- and p-type conduction and are anisotropic. All samples possess thermal conductivity values comparable or lower to those obtained for  $\text{Bi}_2\text{Te}_3$ -based alloys. The estimated lattice thermal conductivity values range from 4 to 6 mW/cmK at 350K. The best ZT value obtained was 0.55 at 400K for the  $\text{SnBi}_{2.5}\text{Sb}_{1.5}\text{Te}_7$  composition.

### Introduction

$\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$  alloys are the best alloys for thermoelectric applications around room temperature. They are currently used in thermoelectric modules for cooling and power generation applications. Extensive research has been performed on these materials over the last 40 years to improve their thermoelectric efficiency but the best ZT achieved for these materials at 300 K is about 1. A broad search to identify and develop advanced bulk and low dimensional thermoelectric materials was started about 10 years ago. Several promising classes of new materials have been identified including skutterudites [1-4], half-Heusler alloys [5], and clathrates [6]. Some success has been achieved in breaking the ZT barrier of 1 common to all thermoelectric materials over the last 40 years.  $ZT \sim 1.4$  have been recently obtained in the 600-900K temperature range [1,4,7].  $\text{CsBi}_4\text{Te}_6$  was also recently reported as a high-performance thermoelectric material with a maximum  $ZT \sim 0.8$  at 225K [8].  $\text{CsBi}_4\text{Te}_6$  is a layered, anisotropic compound like  $\text{Bi}_2\text{Te}_3$  but possesses a different crystal structure. The Cs ions are located between the  $[\text{Bi}_4\text{Te}_6]$  layers and show some large vibrational amplitude and contribute to the low thermal conductivity observed for this compound. It therefore seems that M- $\text{Bi}_2\text{Te}_3$  compounds are of interest as new thermoelectric materials.

Many M- $\text{Bi}_2\text{Te}_3$  compounds have been reported in the literature and their crystal structure have been studied. Among them the tetradymite compounds such as  $\text{PbBi}_4\text{Te}_7$  seem to present attractive features for possible new thermoelectric materials. The crystal structure has been described by several authors [9-12]. The unit cell (space group  $P3m1$ ) contains 12 layers of atoms made out of one five-layer  $\text{TeBiTeBiTe}$  and one seven-layer  $\text{TeBiTePbTeBiTe}$  stacks. The octahedral coordination of the structure is generally linked to low lattice thermal conductivity [13]. In addition, the bonding is predominantly covalent which can give high carrier mobility

[14]. Although some information and thermoelectric properties can be found in the literature for the compound  $\text{GeBi}_4\text{Te}_7$  [15], limited information can be found about the thermoelectric properties of these materials [11]. A recent paper was devoted to the thermoelectric properties of  $\text{PbBi}_4\text{Te}_7$  [16]. In order to further investigate these compounds as potential thermoelectric materials, we have synthesized and measured the properties of several materials with the  $\text{PbBi}_4\text{Te}_7$  structure. The results are reported and discussed in this paper.

### Experimental

Single phase, polycrystalline samples of  $(\text{Sn,Pb})(\text{Bi,Sb})_4\text{Te}_7$  were synthesized as follows. Pb, Sn, Bi, Sb, and Te pieces in the 1:4:7 stoichiometric ratio were loaded into quartz ampoules which were evacuated and sealed. The ampoules were then heated at 1000K for 1 day and subsequently water quenched. The ingots were then crushed into a powder with grains size  $< 125 \mu\text{m}$ . The samples were analyzed by x-ray diffractometry (XRD) to check that they were single phase. The powders were then hot-pressed in graphite dies into dense samples, 10 mm long and 12 mm in diameter. The hot-pressing was conducted at a pressure of about 20,000 psi and at a temperature of 773 K for about 2 hours under argon atmosphere. The density of the samples was calculated from the measured weight and dimensions and was found to be about 97% of the theoretical density. The samples were also characterized by microprobe analysis which was performed using a JEOL JXA-733 electron superprobe operating at  $20 \times 10^3$  Volts (V) of accelerating potential and  $25 \times 10^{-9}$  Amperes (A) of probe current. All samples were found to be single phase by microprobe analysis.

Samples in the form of disks (typically a 1.0 mm thick, 12 mm diameter slice) were cut from the cylinders using a diamond saw (perpendicular and parallel to the pressing direction) for electrical and thermal transport property measurements. All samples were characterized at room temperature by Seebeck coefficient, Hall effect and electrical resistivity measurements. Temperature dependence of electrical resistivity, Hall effect, Seebeck coefficient, thermal diffusivity, and heat capacity measurements were also conducted on selected samples between 300 and 675K [17]. The carrier density was calculated from the Hall coefficient, assuming a scattering factor of 1.0 in a single carrier scheme, by  $n$  or  $p = 1/R_H e$ , where  $p$  and  $n$  are the densities of holes and electrons, respectively, and  $e$  is the electron charge. The Hall mobility ( $\mu_H$ ) was calculated from the Hall coefficient and the resistivity values by  $\mu_H = R_H/\rho$ . Errors were estimated to be  $\pm 0.5\%$  and  $\pm 2\%$  for the resistivity and Hall coefficient data, respectively. The Seebeck coefficient ( $\alpha$ ) of the samples was measured on the same samples used for electrical resistivity and Hall coefficient measurements using a high

temperature light pulse technique [18]. The error of the Seebeck coefficient measurement was estimated to be less than  $\pm 3\%$ . The heat capacity and thermal diffusivity were measured using a flash diffusivity technique [19]. The thermal conductivity ( $\lambda$ ) was calculated from the experimental density, heat capacity, and thermal diffusivity values. The overall error in the thermal conductivity measurements was estimated to be about  $\pm 10\%$ .

## Results and discussion

A list of the compositions investigated is shown in Table I. In addition to the previously reported compounds  $\text{SnBi}_4\text{Te}_7$  and  $\text{PbBi}_4\text{Te}_7$  [9,11,12], a new compound with the same crystal structure was identified by x-ray and microprobe analysis:  $\text{SnSb}_4\text{Te}_7$ . The x-ray diffraction pattern for several  $\text{SnBi}_{4-x}\text{Sb}_x\text{Te}_7$  compositions with  $0 \leq x \leq 2$  is shown in Figure 1.  $\text{SnBi}_4\text{Te}_7$  and  $\text{SnSb}_4\text{Te}_7$  seem to form some solid solutions in the composition range investigated as evidenced by x-ray and microprobe results.

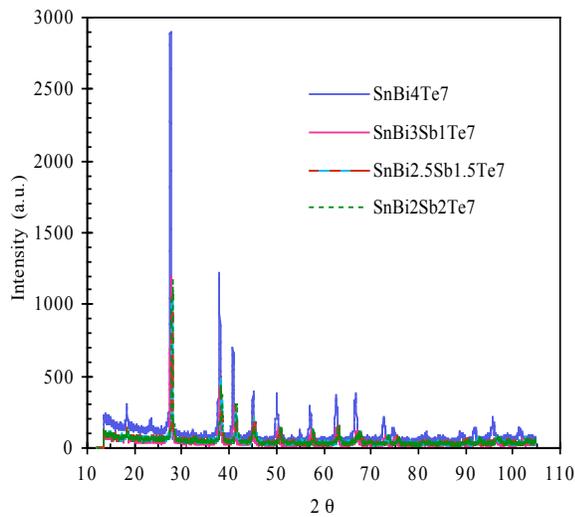


Figure 1: X-ray diffraction pattern for the  $\text{SnBi}_{4-x}\text{Sb}_x\text{Te}_7$  series

Table I. Room temperature Seebeck coefficient ( $\alpha$ ) in  $\mu\text{V}/\text{K}$ , electrical resistivity ( $\rho$ ) in  $\text{m}\Omega\text{cm}$ , Hall mobility ( $\mu$ ) in  $\text{cm}^2/\text{Vs}$ , Hall carrier concentration ( $n$ ) in  $\times 10^{20}\text{cm}^{-3}$ , and thermal conductivity ( $\lambda$ ) in  $\text{mW}/\text{cmK}$  for  $\text{SnSb}_4\text{Te}_7$  (DM63),  $\text{SnBi}_4\text{Te}_7$  (DM64),  $\text{SnBi}_3\text{Sb}_1\text{Te}_7$  (DM76),  $\text{SnBi}_{2.5}\text{Sb}_{1.5}\text{Te}_7$  (DM77),  $\text{SnBi}_2\text{Sb}_2\text{Te}_7$  (DM78), and  $\text{PbBi}_4\text{Te}_7$  (DM65) in the directions // and  $\perp$  to the pressing.

		DM63	DM64	DM76	DM77	DM78	DM65
$\alpha$	//	+25.6	+120	+152	+110	+90	-53
	$\perp$	+23.5	+102	+141	+98	+80	-51
$\rho$	//	0.45	3.71	3.52	1.36	1.12	0.61
	$\perp$	0.39	2.84	2.16	1.08	0.81	0.51
$\mu$	//	17	13	29	30	29	45
	$\perp$	16	14	18	28	26	36
$n$	//	9.63	1.65	0.99	1.89	2.62	2.72
	$\perp$	8.65	1.13	0.939	1.62	2.16	2.8
$\lambda_{@350\text{K}}$	//	14	11	9	6	8	10

Some room temperature properties are listed in Table I for the compositions investigated. Some anisotropy in the transport properties can be expected considering the non-cubic crystal structure of these materials. Most of the transport properties have been measured // and  $\perp$  to the pressing direction. At 300K, the properties range from semiconducting to semimetallic with n- and p-type conduction. The Pb compound is n-type while the Sn compounds and their solid solutions are p-type. Some anisotropy is observed in both the Seebeck coefficient and the electrical resistivity. For the Pb compound, the n-type behavior is in agreement with recent results on polycrystalline samples [16] but p-type behavior was observed for single crystals [11]. Measured carrier concentration range from  $0.9$  to  $9 \times 10^{20}\text{cm}^{-3}$ , in agreement with electronic structure calculations showing these materials as being degenerate semiconductors [12]. The total thermal conductivity values at 350K range from 6 to 14  $\text{mW}/\text{cmK}$ .

In order to compare the room temperature properties of  $\text{PbBi}_4\text{Te}_7$  type compounds to those of  $\text{Bi}_{0.4}\text{Sb}_{1.4}\text{Te}_3$  alloys, we have plotted in Figure 2 the Seebeck coefficient and Hall mobility for these materials as a function of carrier concentration. The data for  $\text{Bi}_{0.4}\text{Sb}_{1.4}\text{Te}_3$  alloys are from reference [20]. Although the Seebeck coefficient values are similar when extrapolated at the same carrier concentration, the Hall mobility for  $\text{PbBi}_4\text{Te}_7$  type compounds are significantly lower, resulting in much higher electrical resistivity at a given carrier concentration. Since the data for both type materials are not available in the same carrier concentration range, one need to be cautious about such analysis since band effects can dramatically change the carrier mobility at different Fermi levels. The reduction in carrier mobility for  $\text{PbBi}_4\text{Te}_7$  type compounds can be attributed to the introduction of the metal atoms inside the Van-der-Waals gap of the  $\text{Bi}_2\text{Te}_3$  structure which results in stronger scattering of the charge carriers.

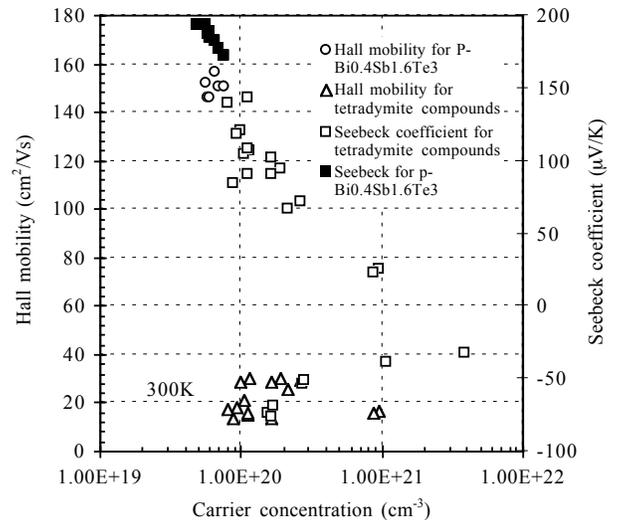


Figure 2: Comparison at 300K of Seebeck coefficient and Hall mobility values for  $\text{PbBi}_4\text{Te}_7$  type compounds and  $\text{Bi}_{0.4}\text{Sb}_{1.4}\text{Te}_3$  alloys.

The variations of the electrical resistivity and Seebeck coefficient values are reported as a function of temperature in Figures 3 and 4, respectively. With the exception of  $\text{SnBi}_4\text{Te}_7$

and  $\text{SnBi}_3\text{Sb}_1\text{Te}_7$ , the samples show an extrinsic behavior with increasing electrical resistivity with increasing temperature. There is no indication of intrinsic conduction even at high temperatures except for the Bi-rich  $\text{SnBi}_{4-x}\text{Sb}_x\text{Te}_7$  compositions that show a small leveling of the electrical resistivity at the highest temperatures of measurements. The variations of the electrical resistivity for the  $\text{SnBi}_4\text{Te}_7$  and  $\text{SnBi}_3\text{Sb}_1\text{Te}_7$  samples is typical of intrinsic semiconductors. An activation energy of 0.21 eV was calculated for the  $\text{SnBi}_4\text{Te}_7$  compound from the linear variation of the electrical resistivity at high temperatures. The results obtained for the  $\text{SnBi}_{4-x}\text{Sb}_x\text{Te}_7$  series show that it is possible to some extent to control the carrier concentration by varying the Bi/Sb ratio.

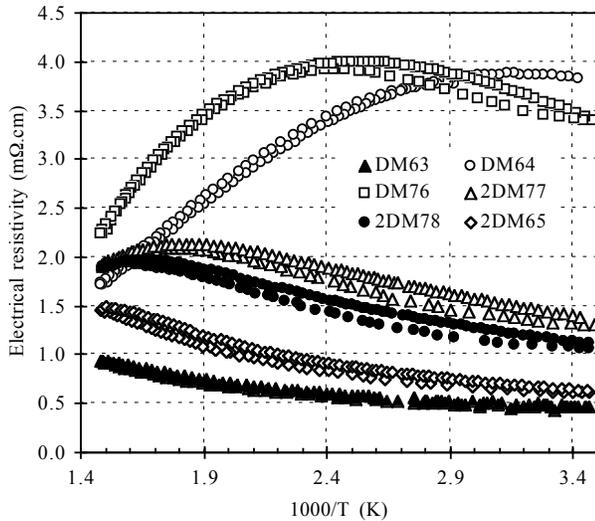


Figure 3: Electrical resistivity versus inverse temperature for some  $\text{PbBi}_4\text{Te}_7$ -based materials – See Table I for samples composition. The samples were measured in the direction // to the pressing direction.

The variations of the Seebeck coefficient are consistent with the electrical resistivity variations. The variations observed for  $\text{PbBi}_4\text{Te}_7$  are somewhat different to those previously reported for polycrystalline samples but the doping level investigated in the previous studies was not reported and a direct comparison is difficult [16].

The results of the thermal conductivity measurements are shown in Figure 5. The thermal conductivity values are compared to p-type  $\text{Bi}_2\text{Te}_3$ -based alloys, state-of-the-art thermoelectric materials around room temperature. At room temperature, the thermal conductivity values for  $\text{PbBi}_4\text{Te}_7$ -based materials are ranging from 6 to 14  $\text{mW/cmK}$  and are lower than for p-type  $\text{Bi}_2\text{Te}_3$ -based alloys. Using the Wiedemann-Franz law, the lattice thermal conductivity values were estimated to range from 4 to 7  $\text{mW/cmK}$  at 350K. Although the carrier mobility is substantially lower for tetradymite compounds compared to  $\text{Bi}_2\text{Te}_3$  alloys, the lattice thermal conductivity is also much lower suggesting that these materials might have some potential as thermoelectric materials. The thermal conductivity of the tetradymite compounds increases with increasing temperature which suggests that these materials are small band gap semiconductors in which minority carriers increasingly

contribute to the electronic conduction at high temperatures, increasing the electronic portion of the total thermal conductivity. In the  $\text{SnBi}_{4-x}\text{Sb}_x\text{Te}_7$  series, the 350K thermal conductivity decreases with increasing Sb amount showing that point defect scattering is an efficient phonon scattering mechanisms in these materials.

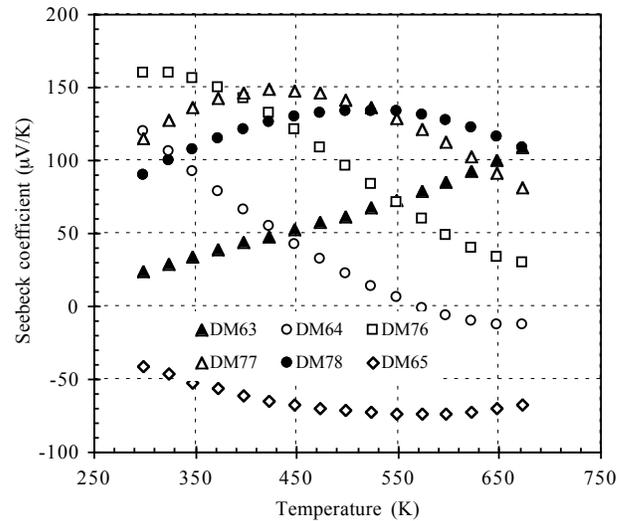


Figure 4: Seebeck coefficient versus temperature for some  $\text{PbBi}_4\text{Te}_7$ -based materials – See Table I for samples composition. The samples were measured in the direction // to the pressing direction.

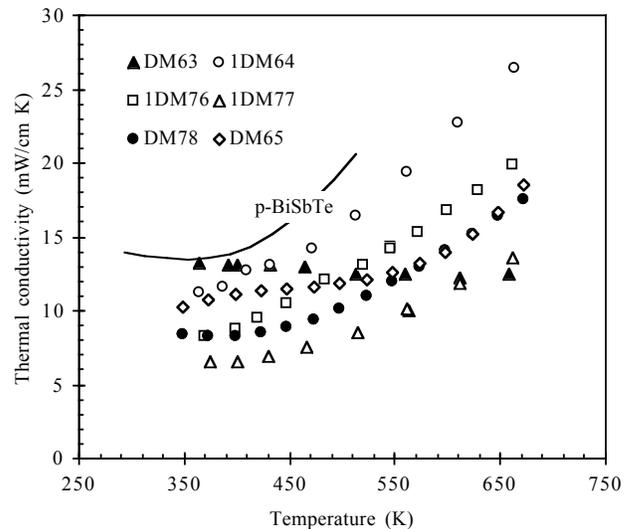
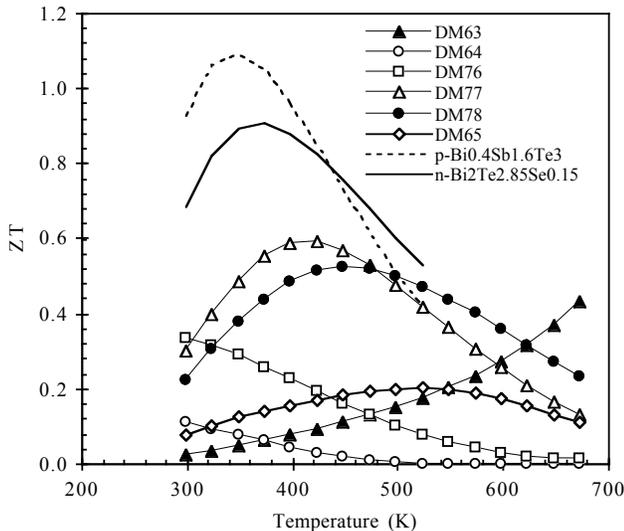


Figure 5: Thermal conductivity versus temperature for some  $\text{PbBi}_4\text{Te}_7$ -based materials – See Table I for samples composition. The samples were measured in the direction // to the pressing direction. The values for p-type state-of-the-art  $\text{Bi}_2\text{Te}_3$  thermoelectric materials are also reported for comparison.

ZT values are shown in Figure 6 as a function of temperature. The best ZT value obtained is 0.55 at 400K for the  $\text{SnBi}_{2.5}\text{Sb}_{1.5}\text{Te}_7$  composition. This is somewhat promising considering that the samples investigated were not optimized and considering the numerous possibilities for potentially further improving the properties of these materials through

doping and/or alloying. Substituting As for Bi or Sb or Se for Te will create further disorder and might result in even lower lattice thermal conductivity values and possibly favorable band structure modifications. It seems however that single crystals are desirable to further assess the potential of these materials for thermoelectric applications taking into account their anisotropic nature. Crystal growth experiments are underway in an attempt to obtain crystals for several of these materials.



**Figure 6:** ZT (// to the pressing direction) versus temperature for some  $\text{PbBi}_4\text{Te}_7$ -based materials – See Table I for samples composition. The values for state-of-the-art p-type  $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$  and n-type  $\text{Bi}_2\text{Te}_{2.85}\text{Se}_{0.15}$  thermoelectric materials are also reported for comparison.

### Conclusion

Several samples of some compounds with the  $\text{PbBi}_4\text{Te}_7$  crystal structure have been synthesized, including a new compound  $\text{SnSb}_4\text{Te}_7$ . Seebeck coefficient, electrical resistivity, and thermal conductivity measurements show that their properties vary widely from semiconducting to semimetallic with both n- and p-type conduction. All samples possess thermal conductivity values comparable or lower to those obtained for  $\text{Bi}_2\text{Te}_3$ -based alloys. The estimated lattice thermal conductivity values range from 4 to 6 mW/cmK at 350K. The best ZT value obtained was 0.55 at 400K for the  $\text{SnBi}_{2.5}\text{Sb}_{1.5}\text{Te}_7$  composition. Preliminary data obtained indicate that these compounds show some potential as thermoelectric materials and further optimization is currently being investigated through various alloying and doping schemes. Crystal growth experiments are also in progress to measure the properties of some of these materials on crystals and determine the anisotropy of the transport properties.

### Acknowledgments

The work described in this paper was carried out at the Jet Propulsion Laboratory/California Institute of Technology, under contract with the National Aeronautics and Space Administration. This work is supported by the U. S. Defense Advanced Research Projects Agency, Grant No. E754.

### References

1. J. -P. Fleurial, A. Borshchevsky, T. Caillat, D. T. Morelli and G. P. Meisner, *Proceedings of the XV International Conference on Thermoelectrics*, Pasadena, CA, USA, IEEE Catalog Number 96TH8169, p. 91 (1996).
2. D. T. Morelli and G. P. Meisner, *J. Appl. Phys.* 77, 3777 (1995).
3. G. S. Nolas, G. A. Slack, D. T. Morelli, T. M. Tritt, and A. C. Ehrlich, *J. Appl. Phys.* 79, 4002 (1995).
4. B. C. Sales, D. Mandrus, R. K. Williams, *Science* 272, 1352 (1996).
5. C. Uher *et al.*, *Phys. Rev. B*, 59, 8615 (1999)
6. G. Nolas, J. L. Cohn, G. Slack, and S. B. Schujman, *Appl. Phys. Lett.* 73, 178 (1998).
7. T. Caillat, J. -P. Fleurial, A. Borshchevsky, *J. Phys. Chem. Solids*, Vol. 58, 7, pp. 1119-1125 (1997).
8. D. Y. Chung, T. Hogan, P. Brazis, M. Rocci-Lane, C. Kannewurf, M. Bastea, C. Uher, M. Kanatzidis, *Science* 287, 5455 (2000).
9. T. B. Zhulova, A. I. Zaslaskii, *Soviet Physics Crystallography*, Vol 16, 5, 796 (1972).
10. O. G. Karpinsky, L. E. Shelimova, M. A. Kretova, J.-P. Fleurial, *Journal of Alloys and Compounds*, 265, 170 (1998)
11. M. Frumar and J. Horak, *Phys. Stat. Sol.*, (a) 6 K133 (1971).
12. F. Casula, L. Deiana, A. Podda, *J. Phys. Condens. Matter* 3, 1461 (1991)
13. D. Spitzer, *J. Phys. Chem. Solids* 31, 19 (1970).
14. G. A. Slack, *Thermoelectric Handbook*, edited by M. Rowe (CRC, Boca Raton, FL, 1995), p. 407.
15. L. E. Shelimova, P. P. Konstantinov, O. G. Karpinsky, E. S. Avilov, M. A. Kretova, J. -P. Fleurial, *Proceedings of the XVIII International Conference on Thermoelectrics*, Baltimore, MD, USA, IEEE Catalog Number 99TH8407, p. 536 (1999).
16. Y. Oosawa, Y. Tateno, M. Mukaida, T. Tsunoda, Y. Imai, Y. Isoda, I. A. Nishida, *Proceedings of the XVIII International Conference on Thermoelectrics*, Baltimore, MD, USA, IEEE Catalog Number 99TH8407, p. 550 (1999).
17. J. A. McCormack and J. -P. Fleurial, *Modern Perspectives on Thermoelectrics and Related Materials*, MRS Symp. Proc. 234 (Materials Research Society, Pittsburgh, Pennsylvania), p. 135 (1991)
18. C. Wood, D. Zoltan and G. Stapfer, *Rev. Sci. Instrum.* 56, 5, 719 (1985).
19. J. W. Vandersande, C. Wood, A. Zoltan and D. Whittenberger, *Thermal Conductivity*, Plenum Press, New York, 445 (1988).
20. T. Caillat, M. Carlé, P. Pierrat, H. Scherrer, S. Scherrer, *J. Phys. Chem. Solids*, Vol. 53, 8, pp. 1121-1129 (1992)