Thermoelectric Properties of Some Cobalt Phosphide-Arsenide Compounds

Anucha Watcharapasorn[*], Robert C. DeMattei[†], and Robert S. Feigelson[*†]
[*]Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305, U.S.A.
[†]Laboratory for Advanced Materials, McCullough Bldg., Rm. 119, Stanford University, Stanford, CA 94305-4045, U.S.A.

Thierry Caillat, Alexander Borshchevsky, G. Jeffrey Snyder, and Jean-Pierre Fleurial
Jet Propulsion Laboratory, California Institute of Technology, MS 277/207, 4800 Oak Grove Drive, Pasadena, CA 91109, U.S.A.

ABSTRACT

Samples of CoP_3, $CoAs_3$ and $CoP_{1.5}As_{1.5}$ have been synthesized and their thermoelectric properties measured. All three samples show semiconducting behavior. The Seebeck coefficients of CoP_3 and $CoAs_3$ are weakly dependent on temperature and are relatively small with maximum values of about 40 and 50 $\mu V/K$, respectively. The Seebeck coefficient of the solid solution gradually decreases with increasing temperature and the values are larger than those of CoP_3 and $CoAs_3$ in the temperature range investigated, with a maximum value of about 89 $\mu V/K$ near room temperature. The thermal conductivity of CoP_3 and $CoAs_3$ are higher than that of $CoSb_3$, as can be expected from the effect of anionic size on lattice vibration. A substantial reduction in thermal conductivity was observed for the solid solution compared to the constituent binary compounds due to additional phonon scattering from lattice disorder and other possible point defects such as vacancies. Other compositions in the $CoP_{3-x}As_x$ system have also been synthesized and their thermoelectric properties are currently being investigated to provide essential information about lattice thermal conductivity reduction by point defect scattering and to further develop strategies for optimizing the thermoelectric properties of skutterudite materials.

INTRODUCTION

Over the last decade, a large number of skutterudite materials have been synthesized and their thermoelectric properties studied. Large ZT values have been obtained for $CeFe_{4-x}Co_xSb_{12}$ (0<x<1) samples near 600 °C [1,2]. Other antimonide skutterudites have also been prepared by substituting Fe with other types of cations such as Ru and, in some cases, with Ge or As for anion substitution [3]. However, these materials show semimetallic behavior and their electrical properties are difficult to optimize. The preparation of semiconducting skutterudite compositions are of interest because they can potentially be doped n- and p-type as are most state-of-the-art thermoelectric materials [4]. Some semiconducting phosphide compounds such as CoP_3, $CeFe_4P_{12}$, and $CeRu_4P_{12}$ have been synthesized and their thermoelectric properties measured [5, 6]. A systematic study of phosphide and arsenide skutterudite compounds would help establish trends leading to the optimization of the transport properties of this class of materials. In particular, information about lowering the lattice thermal conductivity by incorporating filling ions and through anion substitutions would provide the critical information necessary to improve further the ZT values in these materials.

Lutz and Kliche [7] have found that CoP_3 and $CoAs_3$ can form complete solid solutions which renders this system very attractive. They also reported that an extra vibrational mode was observed when some amount of P was substituted into As sites and this would indicate the possibility of a reduction in thermal conductivity. In this paper, the synthesis of CoP_3, $CoAs_3$ and $CoP_{1.5}As_{1.5}$ samples is discussed along with their thermoelectric properties.

EXPERIMENTAL PROCEDURES

Phase pure samples of CoP_3, $CoAs_3$, and $CoP_{1.5}As_{1.5}$ have been made by direct synthesis of the pure elements. Cobalt powder (99.999%), crushed red phosphorus (99.995%), arsenic powder (99.999+%) and arsenic pieces (99.9998%) were used. These materials were mixed together in stoichiometric amounts, placed in evacuated and sealed fused silica tubes, and then slowly heated to a temperature between 700 - 950 ºC for about one week. In all experiments, small amount of excess phosphorus and arsenic were used to compensate for decomposition of the samples. The lattice constants were calculated using least square fit program from powder x-ray diffraction experiments.

The synthesized powders were hot-pressed in graphite dies at temperatures between 800 - 1000 ºC under an Ar atmosphere. Dense samples having dimensions of approximately 2.0 mm long and 12.0 mm in diameter were prepared. Chemical composition was determined by microprobe analysis. The density of the samples was calculated from the measured weight and dimensions. One mm thick disks were then cut from these samples for Seebeck coefficient, Hall effect, electrical resistivity and thermal conductivity measurements in the 300 - 900 K temperature range. Detailed measurement techniques have been described elsewhere [5].

RESULTS AND DISCUSSION

Some of the room temperature physical properties of the samples synthesized are listed in table I. The properties are compared to those of an undoped $CoSb_3$ sample [8]. Except for the solid solution, all other samples had a measured density close to theoretical. Electron probe microanalysis showed that the CoP_3 sample contained about 99.5% skutterudite phase having composition of $Co_{1.00}P_{2.91}$. $CoAs_3$ was also single phase, having the composition, $Co_{1.00}As_{2.98}$. X-ray diffraction analysis of the hot-pressed $CoP_{1.5}As_{1.5}$ sample showed that it contained about 90-95% skutterudite phase and had a lattice constant of 7.9624 Å, which was slightly smaller than that of the as-synthesized sample.

All samples exhibited p-type conduction. The relatively high electrical resistivity of $CoAs_3$ is due mainly to its relatively low carrier concentration, which was about one order of magnitude less than that of the other samples. The room temperature Seebeck coefficients of CoP_3 and $CoAs_3$ are relatively low when compared to the solid solution and $CoSb_3$. Carrier

Table I. Some room temperature properties of CoP_3, $CoAs_3$, $CoP_{1.5}As_{1.5}$ and $CoSb_3$ [8].

	Units	CoP$_3$	CoAs$_3$	CoP$_{1.5}$As$_{1.5}$	CoSb$_3$
Lattice constant	(Å)	7.7073	8.2045	7.9645	9.0345
Percentage of theoretical density	%	97.5	99.6	86.5	99.9
Type of conductivity		p	p	p	p
Electrical resistivity	mΩ-cm	0.47	8.40	1.57	0.44
Seebeck coefficient	μV/K	30	26	89	108
Hall carrier concentration	10^{19} cm^{-3}	2.69	0.057	0.51	1.00
Hall mobility	cm^2/Vs	493	1316	783	1432
Thermal conductivity	mW/cmK	258	125	44	100

effective masses were estimated to be $0.135m_0$, $0.009m_0$ and $0.132m_0$ (where m_0 is the free electron mass) for CoP_3, $CoAs_3$ and $CoP_{1.5}As_{1.5}$ samples, respectively, using a single band model with the acoustic phonon scattering approximation [8]. The calculated effective mass of CoP_3 and $CoP_{1.5}As_{1.5}$ was about two times less than that of $CoSb_3$. The room temperature thermal conductivity decreased from CoP_3 to $CoAs_3$ to $CoSb_3$. The thermal conductivity of the solid solution sample showed an even lower value than $CoSb_3$ and is in agreement with the far-infrared spectra study of this solid solution [7], where an extra lattice vibration mode was identified.

The variation of the electrical resistivity as a function of temperature is shown in figure 1. The values for undoped $CoSb_3$ are also shown for comparison. CoP_3, $CoAs_3$ and $CoP_{1.5}As_{1.5}$ show semiconducting behavior. Above 580K, the electrical resistivity of $CoP_{1.5}As_{1.5}$ becomes higher than that of CoP_3 and $CoAs_3$. The weak temperature dependence of the electrical
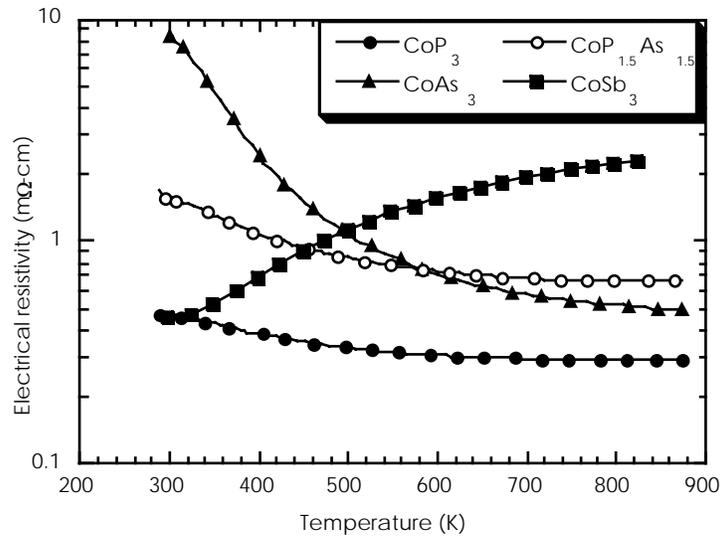
Figure 1. Electrical resistivity of CoP_3, $CoAs_3$, $CoP_{1.5}As_{1.5}$ and $CoSb_3$ [8] as a function of temperature.

resistivity for the CoP_3 and $CoP_{1.5}As_{1.5}$ sample suggest that these materials may be narrow indirect band gap semiconductors in agreement with theoretical predictions by Llunell et al. who calculated a band gap of 0.07 eV for CoP_3 [9].

The Seebeck coefficient as a function of temperature for these three compounds are plotted in figure 2. $CoP_{1.5}As_1.5$ had larger Seebeck coefficient in the entire temperature range of measurement compared to CoP_3 and $CoAs_3$.

Figure 3 shows the temperature dependence of thermal conductivity. For binary compounds, the thermal conductivity decreases from CoP_3 to $CoAs_3$ to $CoSb_3$, which is in
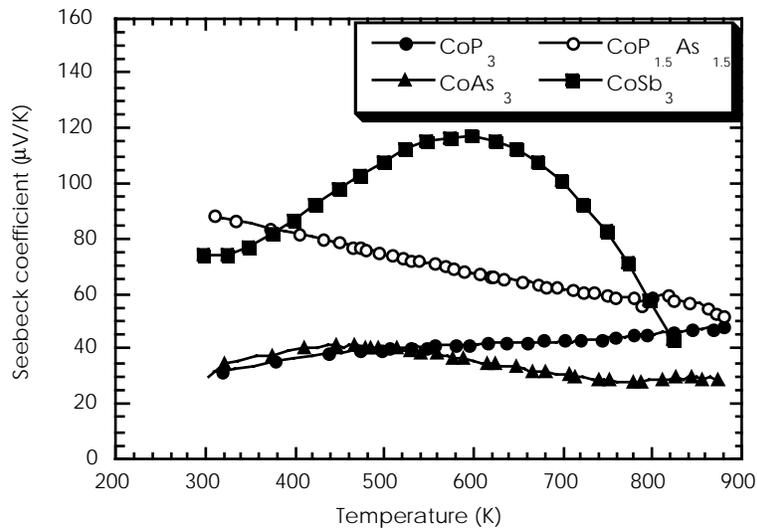
Figure 2. Seebeck coefficient of CoP_3, $CoAs_3$, $CoP_{1.5}As_{1.5}$ and $CoSb_3$ [8] as a function of temperature.
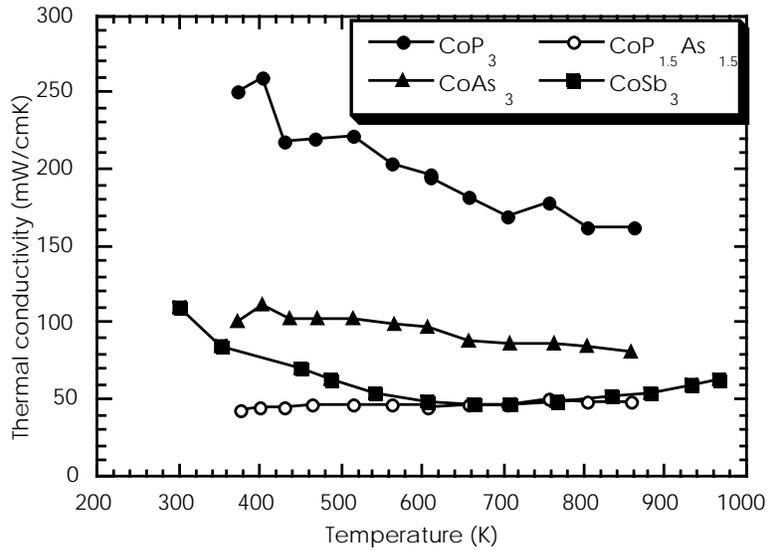
Figure 3. Thermal conductivity of CoP_3, $CoAs_3$, $CoP_{1.5}As_{1.5}$ and $CoSb_3$ [8] as a function of temperature.

agreement with the observed trends in other binary compounds having the same crystal structure for the dependence of lattice vibration on the mass of atoms in the unit cell, i.e. a decrease in lattice thermal conductivity with increasing anionic atomic mass. A 1/T temperature dependence of the thermal conductivity was also observed for the binary compounds.

For the $CoP_{1.5}As_{1.5}$ sample, the thermal conductivity was substantially lower than that for CoP_3 and $CoAs_3$ in the whole temperature range of measurement and it is comparable to the undoped $CoSb_3$ at high temperatures. The substantial reduction in lattice thermal conductivity for the solid solution is primarily due to phonon scattering by point defects. It is to be noted that the experimental density of this sample was only about 86.5% of the theoretical density.

CONCLUSIONS

CoP_3, $CoAs_3$ and $CoP_{1.5}As_{1.5}$ have been synthesized and their thermoelectric properties measured. All three compounds show semiconducting behavior. Larger values of the Seebeck coefficient were observed for the solid solution compared to the two end compounds. The substantial reduction in thermal conductivity for the solid solution was in agreement with earlier lattice vibration studies in the $CoP_{3-x}As_x$ system. More $CoP_{3-x}As_x$ samples are being synthesized and their thermoelectric properties measured in order to fully investigate the variations of the thermoelectric properties as a function of composition. This will provide critical information for the optimization of the thermoelectric efficiency of this class of materials.

ACKNOWLEDGMENTS

REFERENCES

1. C. Sales, D. Mandrus, and R. K. Williams, *Science* **272**, 1325 (1996).
2 . J-P. Fleurial, T. Caillat, A. Borshchevsky, D. T. Morelli, and G. P. Meisner, in *Proceedings of the 15th International Conference on Thermoelectrics*, edited by T. Caillat (Institute of Electrical Engineers, Piscataway, NJ, 1996), p.91
3. J-P. Fleurial, T. Caillat, G.J. Snyder and A. Borshchevsky, Thermoelectric Workshop, Herndorn, VA, 1997
4. A.F. Ioffe, *Semiconductor Thermoelements and Thermoelectric Cooling*, Infosearch, London, 1957
5. A. Watcharapasorn, R.C. DeMattei, R.S. Feigelson, J-P. Fleurial, T. Caillat, G.J. Snyder and A. Borshchevsky, *J. Appl. Phys.*, **86**, 11, 1 (1999)
6. A. Watcharapasorn, R.C. DeMattei, R.S. Feigelson, J-P. Fleurial, T. Caillat, G.J. Snyder and A. Borshchevsky, to be published in the International Conference on Thermoelectrics proceedings, 1999
7. H.D. Lutz and G. Kliche, *J. Solid State Chem.*, **40**, 64-68 (1981)
8. T. Caillat, A. Borshchevsky, and J. -P. Fleurial, *J. Appl. Phys.*, **80**, 4442 (1996)
9. M. Llunell, P. Alemany, S. Alvarez, and V. Zhukov, *Phys Rev. B* **53**, 10605 (1996)