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PROGRESS IN THE SEARCH FOR ADVANCED THERMOELECTRIC MATERIALS FOR TERRESTRIAL APPLICATIONS AT THE JET PROPULSION LABORATORY

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ABSTRACT

The thermoelectric properties of several materials with the skutterudite structure have been investigated at the Jet Propulsion Laboratory (JPL). Based on literature data and experimental findings at JPL, semiconductors with the skutterudite structure have interesting transport properties and show a good potential for high ZT values. A large number of binary and ternary compounds, solid solutions with the skutterudite crystal structure are known. The composition, band gap and doping level can bc tailored to optimize the thermoelectric properties for a specific range of temperature. The investigation of the potential of skutterudite materials as advanced thermoelectric materials was initially focused on antimonide compounds. This paper describes the progress made in the preparation and characterization of the arsenide compounds $CoAs_3$, $RhAs_3$ and $IrAs_3$. Preliminary results obtained on hot-pressed samples are presented and discussed.

INTRODUCTION

The search for new thermoelectric materials has recently focused at JPL on compounds with the skutterudite structure (Caillat et al., 1994a). Experimental data obtained on the binary skutterudite compounds $CoSb_3$ (Caillat et al., 1994b), $IrSb_3$ (Caillat et al., 1994c) and their solid solutions (Borshchevsky et al., 1994) have indicated these materials combine interesting electrical and thermal properties: high carrier mobility, low electrical resistivity, moderate Seebeck coefficient and thermal conductivity.

Binary skutterudite compounds are formed with all "nine possible combinations of Co, Rh, Ir with P, As and Sb. We prepared and characterized of the antimonide compounds first. Little information is available in the literature on the properties of binary phosphides and arsenides compounds. The investigation of the properties of these binary compounds has been recently started at JPL. We report in this paper on the preliminary results obtained on the preparation and characterization of the binary arsenides compounds $CoAs_3$, $RhAs_3$ and $IrAs_3$.

SAMPLE PREPARATION

Samples of $CoAs_3$ and $RhAs_3$ were successfully prepared b y annealing stoichiometric mixtures of the elements in sealed quartz ampoules. The arsenic (99.9995%), cobalt (99.998%) and rhodium (99.9 5%) powders were loaded in an argon atmosphere inside a glove-box to prevent any oxidation. The quartz ampoules containing the mixtures were transferred to a vacuum station, evacuated and scaled under 105 Torr vacuum. The ampoules were introduced in an isothermal furnace and annealed for 8 days at 600°C. After annealing the products were analyzed by X-ray diffractometry (XRD) which was conducted on a Siemens D-500 diffractometer with the Cu-Kα radiation. Silicon powder was used as a standard and mixed to the samples. The products were found to be single phase materials with the skutterudite structure. The materials were then hot-pressed at 800°C for 2 hours in graphite dies of 6.35 mm ID at a pressure of 15,000 psi. An "Astro" hot-pressing furnace with a constant flow of argon was used. Compact cylindrical pellets from 5 to 8 mm long were obtained. The density of the samples was measured by the immersion technique using toluene as the liquid. The measured densities were found to be between 98 and 99% of the theoretical density. Selected samples were polished and their microstructure was investigated under an optical microscope. Microprobe analysis (MPA) was also performed on the same

samples on a JEOL JXA-733 superprobe to check their microstructure and composition. The samples were characterized at room temperature by Seebeck coefficient, Hall effect and resistivity measurements High temperature resistivity, Hall effect, Seebeck coefficient and thermal conductivity measurements were conducted on selected samples between room temperature and about 600"C.

For the compound $IrAs_3$, attempts to prepare samples by direct reaction of stoichiometric mixtures of arsenic and iridium powders always failed and XRD showed that the mixtures were composed of two phases: $IrAs_3$ and $IrAs_2$. Attempts to prepare samples with excess arsenic in several different amounts added to the stoichiometric mixtures also failed. The preparation of single phase $IrAs_3$ samples might be possible using a diffusion technique in a two-zone furnace by establishing a pressure of arsenic inside a sealed ampoule. The arsenic would diffuse into the iridium which would be maintained at a temperature substantially higher than the arsenic. This technique will be tried in the near future.

RESULTS AND DISCUSSION

The room temperature properties of hot-pressed samples $RhAs_3$ and $CoAs_3$ are presented in Table 1. The lattice constant determined form XRD analyses is in good agreement with the literature data. MPA showed that the samples were single phase materials with a stoichiometry close to 1:3.

TABLE 1: SOME PROPERTIES OF HOT-PRESSED RhAs AND $CoAs_3$ SAMPLES AT ROOM TEMPERATURE

	$CoAs_3$	$RhAs_3$
Decomposition temperature (°C)	960	
Lattice constant (A)	8.204 * 8.206	8.443 ● 8.451
X-ray density (g/cm^3)	6.813	7.203
Experimental density (g/cm^3)	6.7	7.16
Type of conductivity	P	P
Electrical resistivity (mΩ.cm)	3.02	0.262
Hall mobility ($cm^2/V.s$)	3378	2368
Hall carrier concentration (cm^{-3})	6.11e+17	1.01e+19
Seebeck coefficient (μV/K)	74	23
Thermal conductivity (mW/cm.K)	-	130

● Literature tindings

Room temperature van der Pauw, Hall effect and Seebeck coefficient are also summarized in Table 1 and the results clearly show that $RhAs_3$ and $CoAs_3$ are semiconductors. Both samples showed p-type conductivity. The hole nobilities for the arsenides were found to be very high. These results arc similar to our earlier results on antimonides. A value of 3378 $cm^2.V^{-1}.s^{-1}$ was measured for the $CoAs_3$ sample with a Hall carrier concentration of about 6.11 x 10^{17} cm^{-3}. This value is close to the value obtained for p-type $CoSb_3$ single crystals at the same carrier concentration (Caillat et al., 1994 b). The mobilities for $CoAs_3$ single crystals should be higher than for the hot-pressed samples that wc prepared. However, the hole mobil ity for the $RhAs_3$ sample is substantially higher than for $CoSb_3$ at the same doping level. The hole nobilities for $RhSb_3$ were also found to be substantially higher than those for $CoSb_3$ and $IrSb_3$ (Caillat et al., 1994d).

Figure 1 shows the electrical resistivity values for the p-type $RhAs_3$ and $CoAs_3$ samples. The electrical value for the $RhAs_3$ sample is about 0.25 mΩ.cm and almost constant with temperature. The electrical resistivity of the lightly doped $CoAs_3$ sample decreases with increasing temperature corresponding to an intrinsic behavior. From the variations of the Hall coefficient with temperature, wc estimated a band gap of 0.7 CV for $CoAs_3$ and that the band gap of $RhAs_3$ is greater than 0.8 eV.

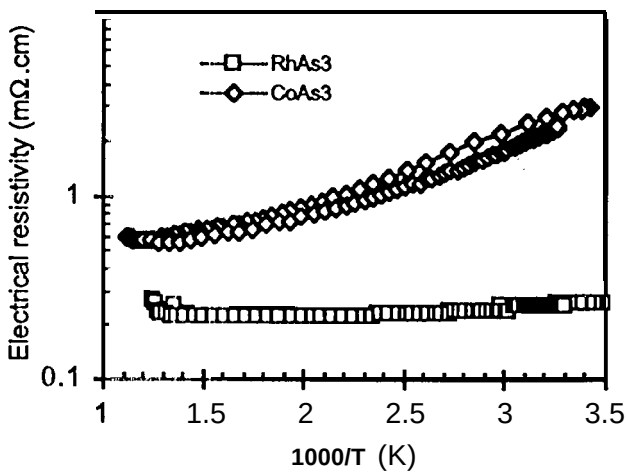

FIGURE 1: ELECTRICAL RESISTIVITY AS A FUNCTION OF TEMPERATURE FOR P-TYPE $RhAs_3$ AND $CoAs_3$.

Figure 2 shows the variations of the Hall mobility as a function of temperature for p-type $RhAs_3$ and $CoAs_3$. The Hall mobility decreases sharply with temperature, reaching a value of about 500 $cm^2.V^{-1}.s^{-1}$ for both samples at about 500°C. The Hall mobility varies with temperature as $T^{-1.3}$ for both COAS3 and $RhAs_3$ which suggests that the predominant scattering mechanism is acoustic phonons. The Seebeck coefficient variations for the p-type $RhAs_3$ and $CoAs_3$ samples arc shown in Figure 3. Similarly to the antimonide compounds, the Seebeck coefficients values are relatively low. For the $RhAs_3$ sample, the Seebeck coefficient increases slowly with temperature, reaching a value of about 50 $\mu V.K^{-1}$ at 500°C. The Seebeck coefficient of the $CoAs_3$ sample decreases with

increasing temperature similarly to the variations of the electrical resistivity. Both the variations of the electrical resistivity and Seebeck coefficient show that both electrons and holes contribute significantly to the transport properties.

Finally, preliminary results of the thermal conductivity measurements are shown in Figure 4. The room temperature thermal conductivity of the p-type $RhAs_3$ sample is about 130

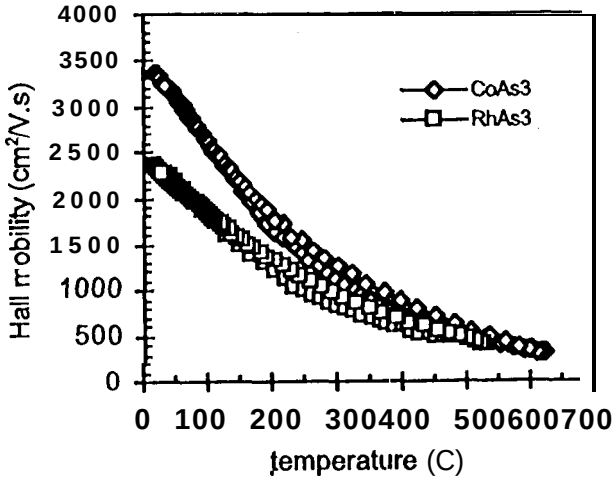

FIGURE 2: HALL MOBILITY AS A FUNCTION OF TEMPERATURE FOR P-TYPE $RhAs_3$ AND $CoAs_3$.

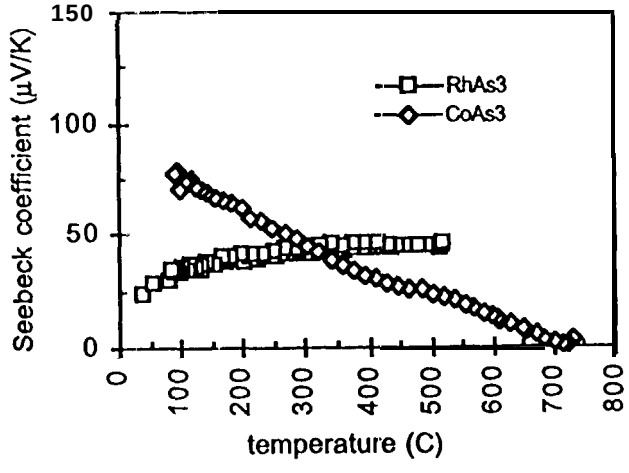

FIGURE 3: SEEBECK COEFFICIENT AS A FUNCTION OF TEMPERATURE FOR P-TYPE $RhAs_3$ AND $CoAs_3$.

$mW.cm^{-1}.K^{-1}$. The thermal conductivity decreases with increasing temperature up to 600°C, reaching a minimum value of about 70 $mW.cm^{-1}.K^{-1}$ and then increases slightly up to 800°C. At low temperatures, the thermal conductivity decreases as 1/T and then increases slightly when the electronic contribution is predominant. The room temperature value for the $RhAs_3$ sample is of the same order of magnitude of those for $CoSb_3$ and $IrSb_3$. This value is too high to achieve high ZT values for the binary compounds. Alloys between binary compounds and other ternaries should have substantially lower thermal conductivity which, combined with high nobilities values, might result in large ZT values. Such possibilities are currently being investigated at JPL.

CONCLUSION

preliminary results obtained on the prepsration and characterization of the binary skutterudite compounds $CoAs_3$, $RhAs_3$ and $IrAs_3$. Single phase hot-pressed samples of $CoAs_3$ and $RhAs_3$ have been prepared and some of their properties measured. The samples are characterized by large Hall hole nobilities, relatively low Seebeck coefficient and thermal conductivity. Future experiments will focus on preparing $IrAs_3$ samples and n-type $CoAs_3$ and $RhAs_3$ samples in order to fully investigate the thermoelectric properties of these compounds and estimate their potential as new thermoelectric materials.

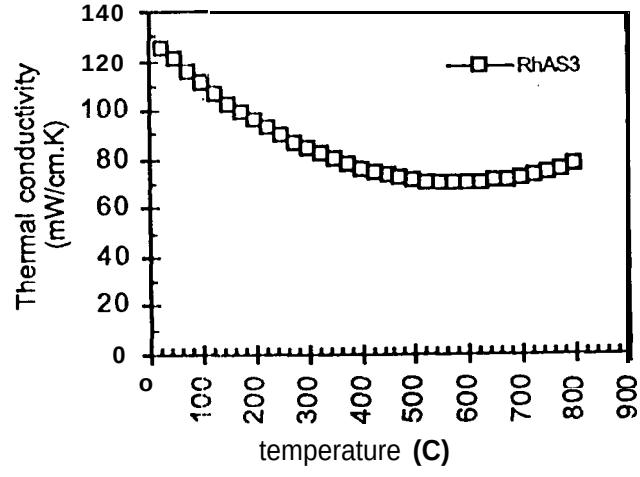

FIGURE 4: THERMAL CONDUCTIVITY AS A FUNCTION OF TEMPERATURE FOR P-TYPE $RhAs_3$.

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