

FABRICATION OF IMPROVED SIGE ALLOYS FOR AN 18-COUPLE MODULE TEST

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Abstract

N- and p-type $\text{Si}_{0.78}\text{Ge}_{0.22}$ alloys were fabricated to determine if recently reported improvements in the figure-of-merit, Z , could be realized in devices. These will be tested in an 18-couple module to directly compare the performance of these materials with that of standard coarse-grain SiGe used in flight programs. We describe the synthesis by vacuum casting and hot pressing p-type SiGe and mechanical alloying and hot-isostatic pressing n-type SiGe. Improved materials and standard materials are characterized and compared. The integrated average figures-of-merit (573-1273 K) of the improved materials were $\overline{Z}_p^{\text{impr}} = 0.59 \times 10^{-3} \text{ K}^{-1}$ and $\overline{Z}_n^{\text{impr}} = 0.85 \times 10^{-3} \text{ K}^{-1}$ compared with $\overline{Z}_p^{\text{std}} = 0.52 \times 10^{-3} \text{ K}^{-1}$ and $\overline{Z}_n^{\text{std}} = 0.76 \times 10^{-3} \text{ K}^{-1}$ for the standard materials. We also report the power factors for improved and standard materials removed from fabricated devices to gain insight as to how subsequent processing impacts performance.

INTRODUCTION

The composition of the $\text{Si}_{0.78}\text{Ge}_{0.22}$ thermoelectric alloys which are currently operating in the Radioisotope Thermoelectric Generators (RTGs) on board the Voyager, Galileo, and Ulysses spacecraft, are doped with less boron, for p-type, and phosphorus, for n-type, than is currently considered optimal. Recent improvements in the thermoelectric figure-of-merit of SiGe alloys have been reported by several investigators (Fleuriel 1993 and Cook 1994a) through compositional and processing refinements. Figures-of-merit of $0.9 \times 10^{-3} \text{ K}^{-1}$ and $0.6 \times 10^{-3} \text{ K}^{-1}$ have been reported for n- and p-type SiGe, respectively, based on measurements of small, laboratory-scale specimens. For the p-type alloy, the improvements have been easily obtained by increasing the amount of boron added as a dopant, and by improving the homogeneity of the material. For the n-type alloy, however, the solubility of phosphorus is limited to a value less than optimum. However, it has been shown that the addition of gallium can enhance the solubility of phosphorus in these materials through a III-V ion pairing interaction. In addition to these compositional changes, the use of mechanical alloying has been shown (Cook 1993) to be a viable method of preparing large, production-scale compacts. In order to more accurately predict the performance that can be realized with these materials in an actual converter, the materials will be used to fabricate unicouples, eighteen of which will then be assembled into a small-scale test module to compare with previous results (Kelly 1994 and Nakahara 1995).

MATERIAL PREPARATION

Improved P-Type Alloy

As shown in Figure 1, the p-type improved material was produced by a process of melting, chill-casting, pulverizing, and hot pressing (Loughin 1993). Three initial castings were prepared. For each casting, the crucible was loaded with 266.9 g Si, 172.4 g Ge, and 0.6453 g B. The furnace was evacuated and the charge was inductively heated to $1723 \pm 20 \text{ K}$. After 1-2 minutes, the temperature was allowed to decrease slightly to $1693 \pm 5 \text{ K}$, and the melt was poured into a water-chilled copper mold previously coated with amorphous graphite (AquaDAG) as a mold release. The resulting ingots were rectangular prisms, $12.5 \times 91.3 \times 127.0 \text{ mm}$. These were crushed and ball milled to produce three lots of powder, with median grain sizes of 5.0, 6.3, and 5.8 μm , respectively.

Each lot was vacuum-hot-pressed following the schedule shown in Table 1. This resulted in three compacts which were subsequently recrushed and remilled to obtain three lots of powder with median grain sizes of 5.5, 5.2, and 5.4 μm , respectively. The powders were blended to produce a master lot of 1.19 kg of powder with a median grain size of 5.4 μm . Mold charges of 397 grams were drawn from this master lot, and pressed into three compacts following the schedule shown in Table 1. Each compact weighed about 394 grams and about 2.8 cm thick by 7.6 cm in diameter. The first of these compacts, designated CAS4882B-1, was machined to obtain the samples for material characterization as presented here.

MASTER

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resistivity, thermal conductivity as a function of temperature. The integrated average (573-1273 K) figures-of-merit for the improved material are $0.58 \times 10^{-3} \text{ K}^{-1}$ and $0.86 \times 10^{-3} \text{ K}^{-1}$ for the p-type and n-type alloys, respectively. We must compare these values with $0.52 \times 10^{-3} \text{ K}^{-1}$ and $0.76 \times 10^{-3} \text{ K}^{-1}$ for p-type and n-type standard Cassini alloys, respectively. This represents an improvement of 11% for the p-type alloy and 13% for the n-type alloy. Figure 8 presents a comparison of the improved figures-of-merit with those of standard Cassini materials.

TABLE 2. Room Temperature Hall Effect Measurements for the Cassini Materials.

Sample	Treatment	$n (\times 10^{26} \text{ m}^{-3})$	$\rho (\times 10^{-5} \Omega \cdot \text{m})$	$\mu (\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1})$
n-type	as pressed	1.36	0.78	59.4
n-type	20 min/1323 K	1.64	0.66	57.4
p-type, disk 2	as pressed	1.64	0.98	38.8
p-type, disk 1	20 min/1323 K	1.59	0.98	40.2
p-type, disk 2	4 hrs /1273 K	1.73	0.98	36.9

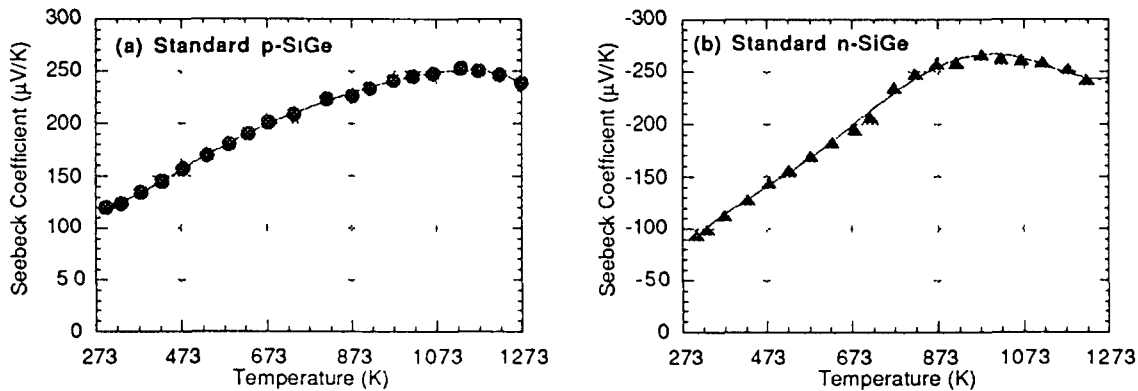


FIGURE 5. Seebeck Coefficient of Standard Cassini P-Type SiGe (a) and N-Type SiGe (b).

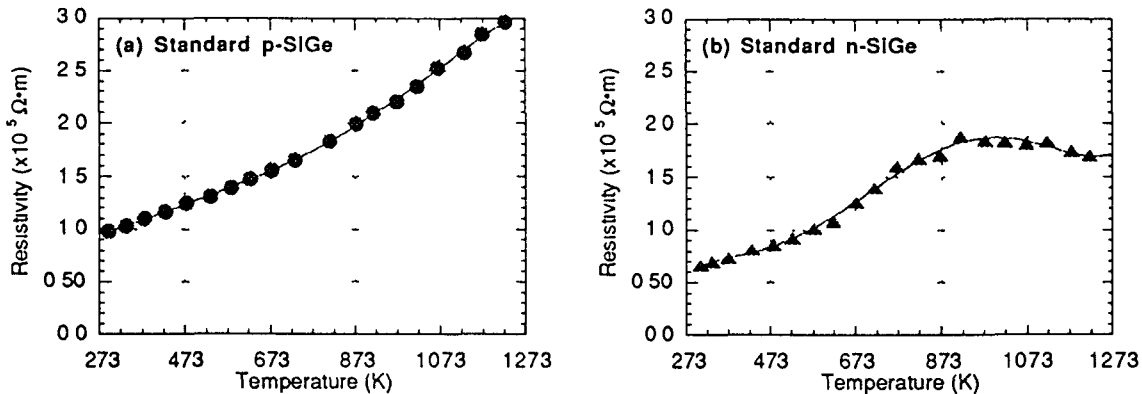


FIGURE 6. Electrical Resistivity of Standard Cassini P-Type SiGe (a) and N-Type SiGe (b).

Improved and Standard Materials Post-Fabrication

Obviously, a measured improvement in the as-fabricated state does not guarantee that the improvement will be retained in the finished devices. The devices are subjected to several high temperature cycles during assembly and these may affect the thermoelectric properties. To assess how much of the improvement is retained in the final device, we fabricated actual devices then removed the thermoelectric material for characterization. The measurements were made without further heat treatment, that is no "reset" was applied. Only the power factor, S^2/ρ , was measured since the geometry of the thermoelectric elements in the actual device precludes the measurement of thermal conductivity. The integrated averages of the Seebeck coefficient, electrical resistivity, and power factor, over the temperature range 573-1273 K, are compared in Table 3.

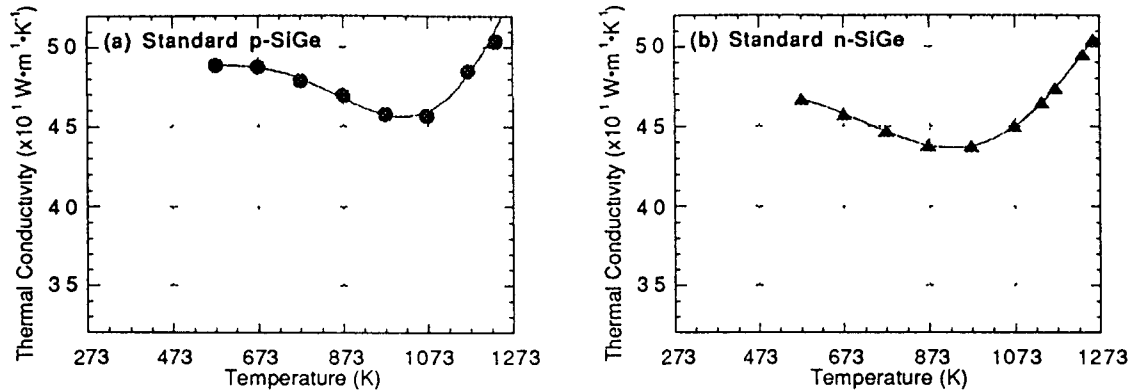


FIGURE 7. Thermal Conductivity of Standard Cassini P-Type SiGe (a) and N-Type SiGe (b).

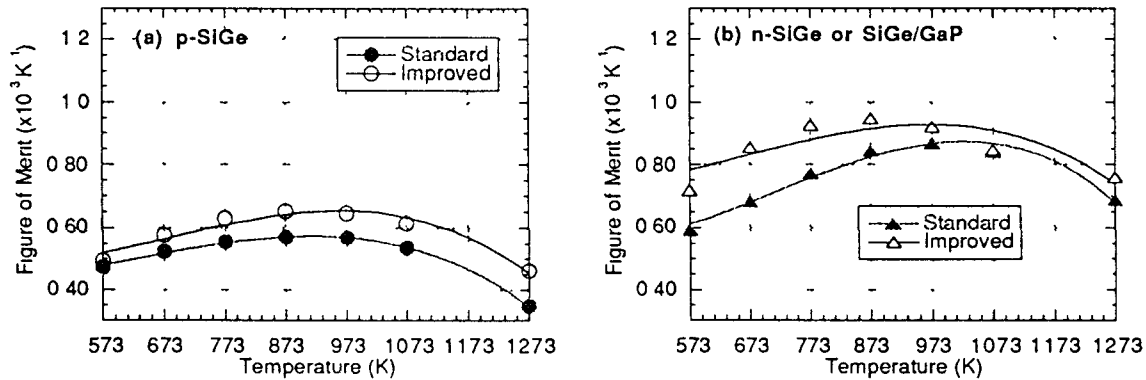


FIGURE 8. Figures-of-Merit of the Improved Materials and Standard Cassini Materials Compared for P-Type SiGe (a) and N-Type SiGe and SiGe/GaP (b).

TABLE 3. Comparison of Integrated Average (573-1273 K) Power Factors for Improved SiGe and Standard Cassini SiGe Alloys Removed from Unicouples after Fabrication.

Material	Seebeck ($\mu\text{V}/\text{K}$)	Resistivity ($\times 10^{-5} \Omega \cdot \text{m}$)	Power Factor ($\mu\text{W}/\text{cm} \cdot \text{K}^2$)
p-SiGe Std. Cassini	220.6	2.34	20.8
p-SiGe "Improved"	174.6	1.53	19.9
n-SiGe Std. Cassini	-249.3	2.05	30.3
n-SiGe "Improved"	-215.9	1.51	30.9

Because of the configuration of uncouple thermoelectric elements, we were unable to characterize the thermal conductivity changes occurring during fabrication. However, if we assume that the only change in thermal conductivity is in the electronic component, $\Lambda_e = \mathcal{L}_0 \sigma T$, then, using calculated values (Vining 1991a and 1991b) for the Lorentz factor, \mathcal{L}_0 , we can estimate the post fabrication thermal conductivities. Using these values, we expect that the improved n-type material will retain a significant advantage over the standard n-type material after device fabrication. This may be due, in part, to the fact that the presence of GaP will suppress the precipitation of phosphorus. However, the improved p-leg material may offer only a modest advantage, because the dopant precipitation effects in both the improved and standard materials will be fairly similar.

CONCLUSIONS

In conclusion, we have demonstrated that improved $\text{Si}_{0.78}\text{Ge}_{0.22}$ thermoelectric alloys can be fabricated in production-scale quantities sufficient to support production of an 18-couple test module. The improved p-type material was found to have an integrated average (573-1273 K) figure-of-merit of $0.59 \times 10^{-3} \text{ K}^{-1}$, compared with a value of $0.52 \times 10^{-3} \text{ K}^{-1}$ for the baseline material. Over the same temperature range, the integrated average figure-of-

merit of the improved n-type material ranged from 0.84×10^{-3} to $0.86 \times 10^{-3} \text{ K}^{-1}$, compared with a value of $0.76 \times 10^{-3} \text{ K}^{-1}$ for the baseline material. Judging by the measured power factor of baseline and improved materials taken from completed devices, these improvements are largely retained through the fabrication process. This conjecture will be tested in future work, once the 18-couple module fabrication and test are completed. Also, the hot isostatic pressing method employed to produce the n-type material is a new and distinctly different consolidation process. Some small-scale samples prepared by this technique had figures-of-merit as high as $0.92 \times 10^{-3} \text{ K}^{-1}$, thus encouraging us to expect further improvements in the n-type figure-of-merit for production-scale compacts as this new technique is further optimized and refined.

Acknowledgments

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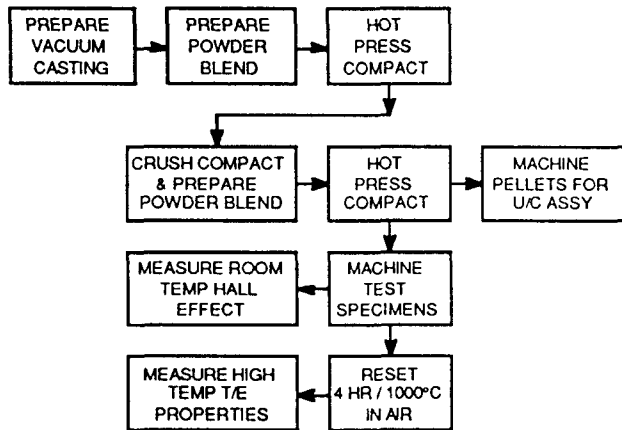
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TABLE 1. Temperature / Pressure Profile for Vacuum Hot Pressing of Improved P-Type SiGe Compacts.

Elapsed Time (minutes)	Heat / Cool Rate (K/min)	Soak Temperature (K)	Applied Pressure (MPa)	Operation
0	34	–	140	Heat Up
40	–	1633	140	Soak
130	–	1633	0	Begin to Extrude
136	23	–	0	Vacuum Cool
156	15	–	0	Rapid Gas Cool

(a) Improved p-type $\text{Si}_{0.796}\text{Ge}_{0.199}\text{B}_{0.005}$



(b) Improved n-type $\text{Si}_{0.784}\text{Ge}_{0.197}\text{Ga}_{0.005}\text{P}_{0.015}$

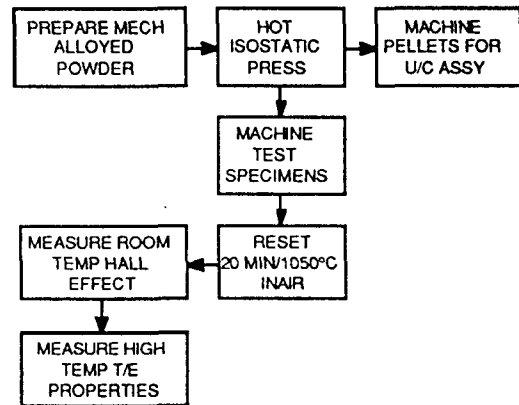


FIGURE 1. Fabrication Process for Improved P-Type SiGe (a) and N-Type SiGe/GaP (b) Alloys.

Improved N-Type Alloy

As shown in Figure 1, the n-type SiGe/GaP material was prepared by mechanically alloying (Maurice 1990) the elements to a fine powder, then consolidating the powder by hot isostatic pressing. A nominal composition of $\text{Si}_{0.784}\text{Ge}_{0.197}\text{Ga}_{0.005}\text{P}_{0.015}$ was selected based on previous results obtained on small-scale samples. The elements were weighed out in a He-filled glove box to form 20 gram charges, loaded into steel vials along with a number of hardened steel balls, and first mechanically milled for 2 hours to produce a uniform particle size, then mechanically alloyed for 6 hours in a He atmosphere. Alloy formation was verified by x-ray diffraction.

The alloy powder was stored in an inert atmosphere until 60 to 75 grams of powder were accumulated. In order to consolidate the powder, it was loaded into a 50.8 mm diameter, by either 25.4 or 38.1 mm high canister fabricated from 0.508 mm thick Ta foil, the interior surface of which was lined with graphite-foil. A tantalum cover was placed on the canister, and the assembly was transferred in a sealed, helium-filled bag, to an e-beam welder where the cover was welded to the canister under a vacuum of 10^{-5} torr. The sealed canister was loaded into the hot isostatic press, and heated to 1403 K, then the pressure was increased over 45 minute period to 138 MPa (20 ksi), after which both pressure and temperature were maintained for 45 minutes. The final dimensions of the compact, upon removal from the tantalum canister, were approximately 42 mm diameter by 13-19 mm thick (center versus edge). Samples were machined for room temperature Hall effect measurement and high temperature thermoelectric property evaluation.

RESULTS AND DISCUSSION

Improved Materials

The improved alloys were evaluated to determine their thermoelectric properties. For the improved n- and p-type alloys, Figures 2, 3, and 4 show the Seebeck coefficient, S ; the electrical resistivity, ρ ; and the thermal conductivity, Λ ; respectively. For the p-type material, the properties were measured on samples from compact CAS4882B-1, with a 1273 K/4 hour heat treatment, or "reset", applied. For the n-type material, each of these properties was measured on samples from two compacts, HIP-15 and HIP-17, with a 1323 K/20 minute reset applied.

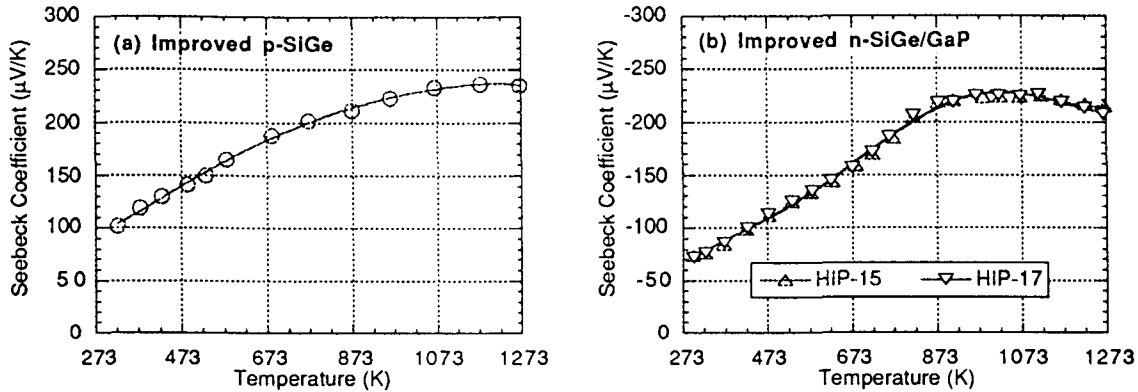


FIGURE 2. Seebeck Coefficient of Improved P-Type SiGe (a) and N-Type SiGe/GaP (b).

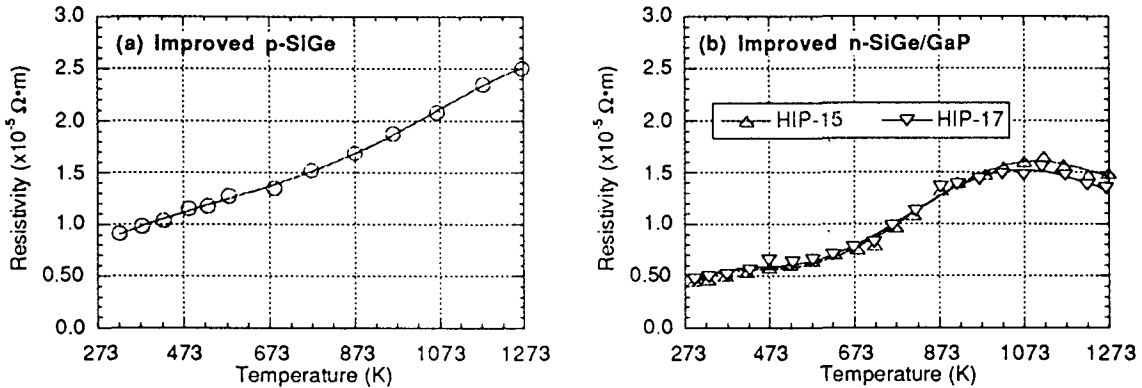


FIGURE 3. Electrical Resistivity of Improved P-Type SiGe (a) and N-Type SiGe/GaP (b).

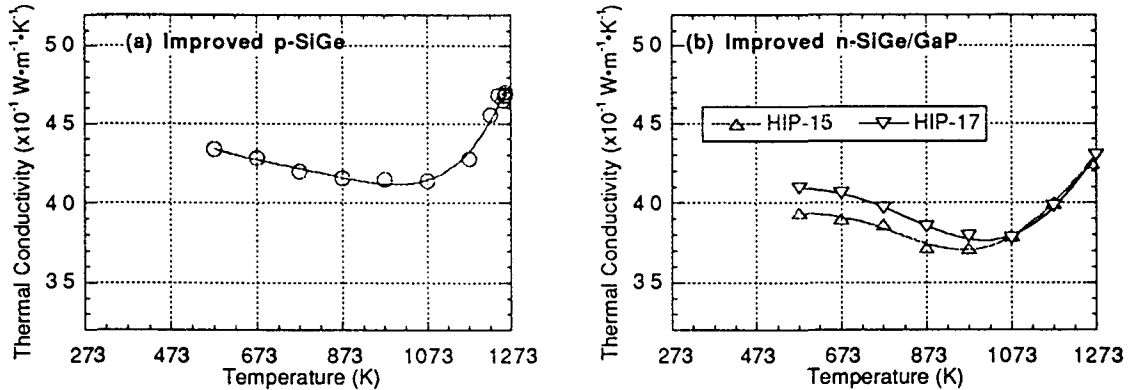


FIGURE 4. Thermal Conductivity of Improved P-Type SiGe (a) and N-Type SiGe/GaP (b).

Standard Cassini Alloys

Ultimately, the performance of any improved material must be evaluated with respect to the material it is intended to replace, preferably employing the same measurement techniques and apparatus for both. For this purpose, samples of the coarse-grain, $\text{Si}_{0.78}\text{Ge}_{0.22}$, thermoelectric material prepared under the Cassini RTG Contract (U.S. DOE 1991) were obtained. Four samples each, of the n-type material and p-type material were provided -- two 12.7 mm diameter disks and two rectangular prisms of each material. Room temperature Hall effect results are shown in Table 2 for these materials with various heat treatments (Cook 1994b). Because of dopant precipitation, these alloys are sensitive to prior thermal cycling. The applied heat treatments provide a means of redissolving precipitate phases, providing a more uniform thermodynamic condition from which to begin the measurements.

The Seebeck coefficient, electrical resistivity and thermal conductivity were measured over the temperature range 573-1273 K. For the n- and p-type Cassini materials, Figures 5, 6 and 7, present the Seebeck coefficients, electrical