HIGH EFFICIENCY THERMOELECTRIC GENERATORS USING NEW VERY HIGH PERFORMANCE MATERIALS

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Abstract

Extensive theoretical and experimental studies have resulted in reasonable performance improvements (from an average ZT of 0.62 up to 0.7S) of the state of the art high temperature SiGe thermoelectric materials in the last 5 years. However, significantly higher material conversion efficiencies are needed to make thermoelectrics competitive and economically attractive. A new approach that looks at radically different compounds and alloys was recently started at JPL and a new family of materials with great potential has been discovered. A real breakthrough was achieved when maximum ZT values of 2.0 were obtained to date on one of these materials in the 300-400C temperature range. initial analysis of various experimental tests have confirmed its good mechanical and physico-chemical properties. Substantial increases in conversion efficiency and specific power are predicted (60-90%) by incorporating this new material into state of the art space nuclear power systems such as Radioisotope Thermoelectric Generators (RTG).

INTRODUCTION

To reduce mass, cost and volume of radioisotope thermoelectric generators used to power spacecrafts for deep space missions, it is necessary to increase their energy conversion efficiency. Extensive theoretical and experimental studies have resulted in the last 5 years in significant performance improvements of the state of the art high temperature thermoelectric $Si_{80}Ge_{20}$ alloys, from ZT≈ 0.62 10 ZT≈ 0.75 in the 300-1000C temperature range (Vining and Fleurial, 1991). Although thermoelectric devices have been used for their simplicity, reliability, small size and long lifetime, current ZT values severely limit performance (5 to 8°A conversion efficiency) and restrict more and more their range of applications. Requirements for the next generation of space power systems call for conversion efficiency of at least 13Y0. No fundamental principle limits ZT, a combination of various electrical and thermal transport properties, to such low values. But in 35 years of research, sometimes intensive, on thermoelectrics, no one material has ever clearly broken the ZT = 1 barrier. As the final stages of the SiGe optimization process are in sight, it has become critical to the future of thermoelectrics to initiate new research efforts. One of these approaches was to look at radically different compounds and alloys with the potential to be high ZT thermoelectric materials. Such a program has been carrying out a broad investigation to identify new candidates for high temperature thermoelectric energy conversion applications (Caillat et al., 1992a). These materials would replace the heavily doped $Si_{80}Ge_{20}$ alloys currently used in or scheduled for space missions using Radioisotope Thermoelectric Generators (RTGs) or the SP-1 00 power system.

RESULTS AND DISCUSSION

The search for new high temperature thermoelectric materials with high ZT values was guided by a certain number of criteria, and included; a) semiconducting properties, from lightly degenerated (low temperatures) to semimetallic behavior (high temperatures); b) large Seebeck coefficient, S, (related to the band structure: heavy effective masses, presence of d bands. ..); c) low lattice thermal conductivity (related to complex crystal structure, heavy mean atomic masses, possibility to introduce lattice defects..,); d) large carrier mobility, low electrical resistivity, p (linked to small electronegativity difference, covalent bonding between the various atoms. ,.); c) existence of a bandgap large enough to minimize minority conduction effects in the temperature range of usefulness; f) high melting point and chemical stability relatively to the temperature range of usefulness; g) opportunity to make solid solutions with isostructural compounds to expand range of optimization of the transport properties; h) possibility to obtain both n-type and p-type conductivity materials.

Following this process, several new families of Ge, Sb and Bi compounds with transition metal or rare earth elements were selected for further investigation. An array of crystal growth and powder metallurgy techniques was used to quickly investigate bulk samples of quality good enough for measurements of their thermoelectric properties. Some of these compounds, such as $IrSb_3$, have shown great potential (Caillat et al., 1992b). A combination of theoretical and experimental efforts succeeded in optimizing the thermoelectric properties of $IrSb_3$. The thermoelectric properties of several optimized samples of $IrSb_3$ were fully characterized from 25C to 900C. A maximum ZT value of 2 has been achieved to date in the 300-400C temperature range, These results, displayed on Figure 1, are much higher than for any other state of the art materials (p-type or n-type). Thermogravimetric Analysis showed that unoptimized $IrSb_3$ samples did not dissociate at all even at 500C. Moreover, the possibility to optimize this new material by forming solid solutions with isostructural compounds is very interesting. N-type samples have also been successfully prepared and, if their thermoelectric properties are good enough (ZT of at least 0.9),could replace current state of the art n-type alloys,

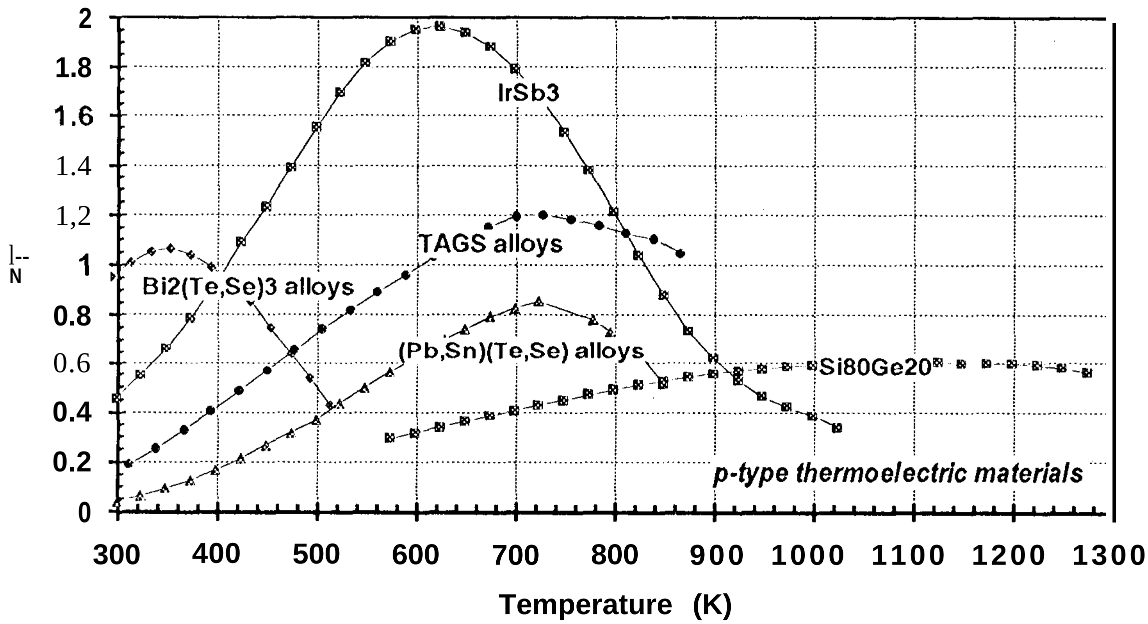

FIGURE 1: Dimensionless Figure of Merit ZT as a Function of Temperature for $IrSb_3$ Compared with ZT Values for Current State of the Art p-Type Thermoelectric Materials.

The following discussion intends to illustrate the impact of this new materials on the economics of thermoelectric energy conversion technology. The efficiency η of a thermoelectric generator is calculated from the following expression:

$$\eta = \frac{T_h - T_c}{T_h} \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+\frac{T_c}{T_h}} \quad \text{where} \quad ZT = \frac{S^2\sigma T}{\lambda} = \frac{S^2 T}{\rho\lambda}$$

where Th and Tc are respectively the temperature values for the hot side and cold side of the thermoelectric generator or cooler and ZT corresponds to an integrated average over the T_h-T_c temperature range. The dimensionless figure of merit ZT is a function of all three transport properties, electrical resistivity ρ [or electrical conductivity σ), Seebeck coefficient S and thermal conductivity λ.

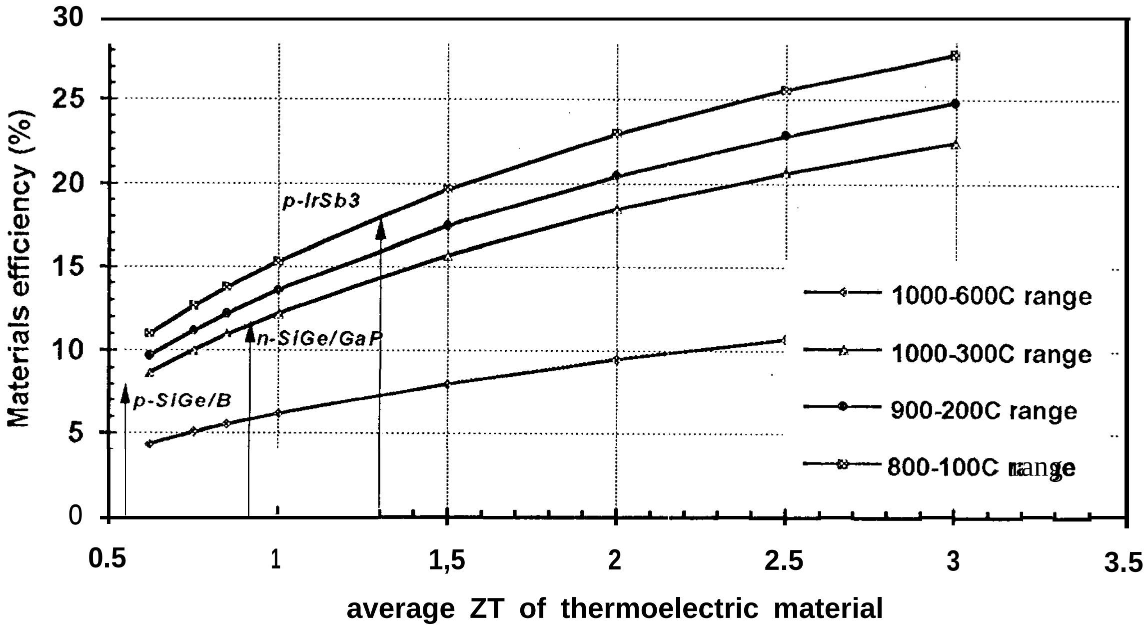

FIGURE 2: Materials Conversion Efficiency as a Function of Average ZT (in Various Temperature Ranges)

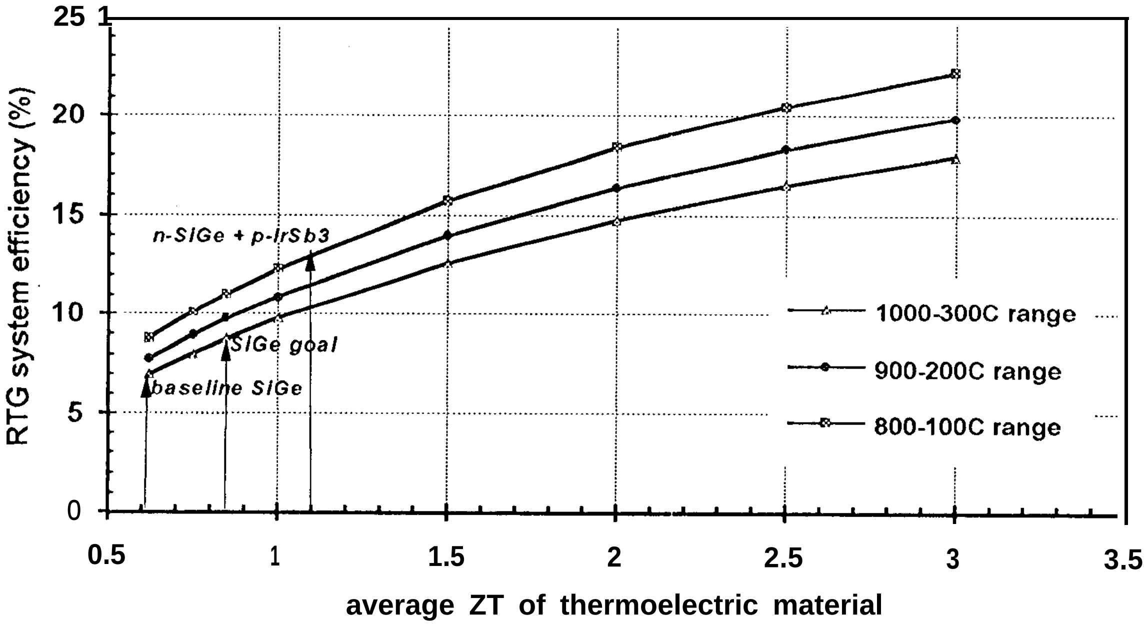

FIGURE 3: Radioisotope Thermoelectric Generator (RTG) System Efficiency as a Function of Average ZT (in Corresponding Temperature Range). Coupling p-Type $IrSb_3$ with n-Type SiGe Alloy in 800-1 00C Temperature Range Would Double System Efficiency over Current State of the Art p-Type and n-Type SiGe Alloys in 1000 C-300C Temperature Range.

Radioisotope Thermoelectric Generators (RTGs) have been used to power spacecraft instrumentation in deep space missions (Voyager 1 and 2, Galileo, Ulysses, Cassini...). Despite their low conversion efficiency (about 6.5%), the high reliability and lifetime of these solid state devices has insured the success of these programs. I lo~t'ever, ncw projects arc calling for much higher efficiencies (at least 13%) that current state of the art materials, even after optimization of their properties will never attain. It is thus critical for Thermoelectrics to develop new materials 10 challenge these high temperature energy conversion technologies.

Figure 2 describes the increase in materials conversion efficiency with increasing ZT and for various temperature ranges. Performance for opt imized slate of the art $Si_{80}Ge_{20}$ alloys and p-type $IrSb_3$ is indicated. In the 1OO-8OOC temperature range, p-type $IrSb_3$ reaches 18'% conversion efficiency, twice as much as p-type $Si_{80}Ge_{20}$ in the 300-1000C temperature range. The RTG system efficiency is calculated from the materials efficiency by multiplying by a factor of 0.8 taking into account thermal and electrical losses in the device. Figure 3 shows that by coupling current p-type $IrSb_3$ material with n-type SiGe alloy in a 800-1 OOC temperature range would double RTG system efficiency over present slate of the art p-type and n-type SiGe alloys in 1000-300C temperature range. Such a 14°/0 efficient RTG would result in substantial mass and cost savings, 'I'his is illustrated on Figure 4 where the system specific power (number of wat ts produced per kilogram of RTG) is plotted versus the same average ZT values. Keeping the same temperature difference and decreasing the cold side temperature brings higher efficiency for a thermoelectric generator. However it also increases the mass of the heat rejection system (radiator) and the corresponding jump in overall system mass must be taken into account, Based on calculations already done in technologies trade-off studies at JPL, the RTG mass increased from S4 kgs (1000-300C) to 56 kgs (900 -200C) and up to 64 kgs (800- 100C). Still, specific power would dramatically increase by 70°/0, from 5.6 W/kg Up to 9.5 W/kg.

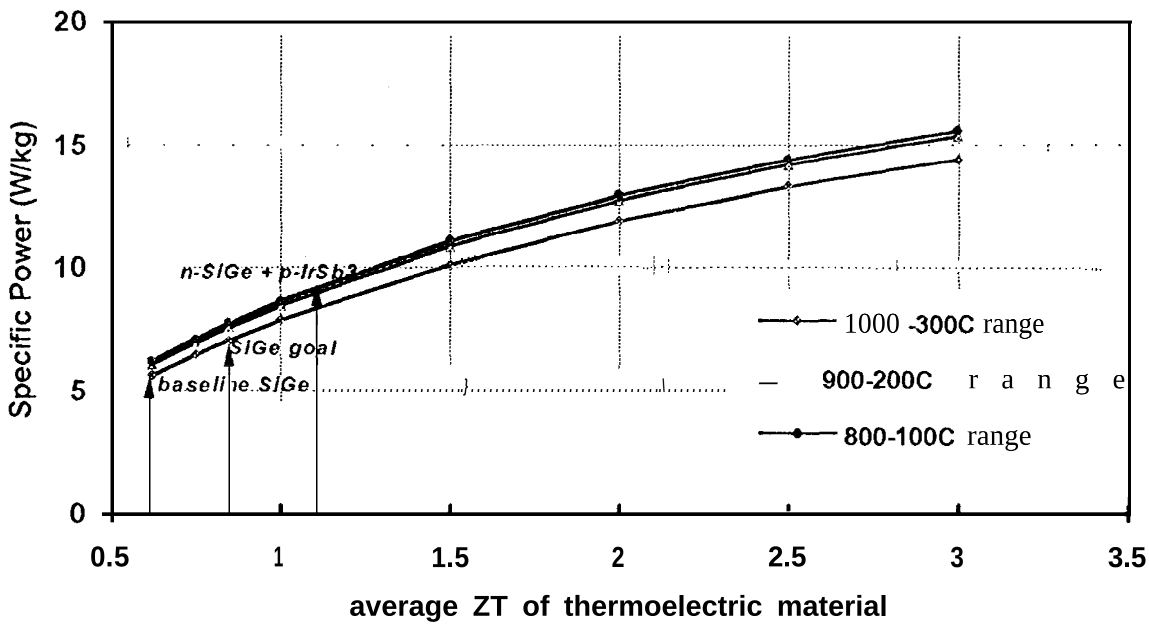

FIGURE 4: Radioisotope Thermoelectric Generator (RTG) Specific Power as a Function of Average ZT (in Corresponding Temperature Range). Coupling p-Type $IrSb_3$ with n-Type SiGe Alloy in 8OO-1OOC Temperature Range Would Double System Efficiency over Current State of the Art p-Type and n-Type SiGe Alloys in 1000C-300C Temperature Range. Increase in Radiator Weight to Accommodate Lower Cold Side Temperature was Taken into Account.

'1'here arc other potential applications for space power systems. Onc of them is a hybrid two-stage thermionic-thermoelect ric converter (Allen, 1993) which could run at more than 21 % efficiency for the Pluto mission. A terrestrial version is also possible (Nikolacv ct al., 1992). Another onc consists of a 15V0 cfficicnt solar thcrmoclcctric systcm in carth orbit (Suitor, 1993) using solar concentrators and a thermal mass to keep thc hot side in tcmpcraturc (about 600-700 C). Waste heat applications (solid waste, geothermal, power plants, automobi Its...) arc also of interest, confirmed by the recent very important cfforts by the Japanese science and industry (Bass and Elsncr, 1992; Kajikawa et al., 1992). The power capacity of these systems ranges from 10 to 10000 kW and the introduction of a ZT=2 material such as $IrSb_3$ ideally suited to the 1OO-6OOC temperature range (scc Table 2) would make such "en\'irol~]l~c]~tally friendly" dcviccs more affordable as break-even times are sharply reduced,

TABLE 2: Average ZT and Corresponding Materials Conversion Efficicncics for Various Temperature Rangc

Tcmpcraturc range (K)	Materials combinations	Average ZT	Materials conversion cfficicncy
373-673	p-$IrSb_3$	1,59	12.6
400-700	p-$IrSb_3$	1.68	13.7
473-873	p-$IrSb_3$	1.59	13.0
373-873	p-$IrSb_3$	1.49	16.5
373-673	p-$IrSb_3$ + n-PbTc	1.3	11.1
400-700	p-$IrSb_3$ +n-PbTc	1.3	11.8
473-873	p-$IrSb_3$ +n-PbTe	1.3	11.5
373-873	p-$IrSb_3$ + n-PbTe	1.3	15.2

CONCLUSION

By carrying out a broad literature investigation and looking at radically different compounds and alloys with the potcntial 10 bc high ZT thcrmoclcctric materials, several ncw families of Gc, Sb and Bi compounds with transition mctal or rare carth clcmcnts were sclcctcd. An array of crystal growth and powder metallurgy techniques was used to quickly i nvcstigatc bulk samples of quality good enough for mcasurcmcnts of their thcrmoclcctric propert its. Several of these new materials have shown exceptional transport propcrtics. A combination of cxpcrimcntal and thcorctical cfforts resulted in the optimization of p-type samples of the $IrSb_3$ compound. ZT values of up to 2, much highcr than ever found on any other thermoelectric material, have been obtained around 400C. Even better rcsults arc prcdictcd by alloying $IrSb_3$ with isostructural compounds as thermal conductivity values are substantially lower in these solid solutions. By combining the properties of current p-type $IrSb_3$ material with thosc of statc of the art n-typc $Si_{80}Ge_{20}$, the systcm cfficicncy of a Radioisotope Thcrmoclcctric Generator (RTG) in thc 300- 1000C tcmpcraturc range would double from about 7°/0 for current $Si_{80}Ge_{20}$-only dcviccs to more than 14%. A significant reduction in mass would bc achicvcd as the spccific power would increase from about 5.6 W/kg to more than 10 W/kg. Because of the very high performance of thcse materials in the 1OO-8OOC tcmpcraturc range, thcy have expanded the range and scope of a variety of thcrmoclcctric dcviccs in space and terrestrial power applications,

Acknowledgments

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