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Abstract

The development of new, more efficient, materials and devices is the key to expand the range of applications of thermoelectric generators. New potential terrestrial applications have been recently described in the literature. There exists a wide range of heat source temperatures for these applications, from low grade waste heat, at 320-350K, up to 800 to 1100K, such as in the heat recovery from a processing plant of combustible solid waste. The automobile industry has also recently developed a strong interest in a waste exhaust heat recovery power source operating in the 375-775K temperature range to supplement or replace the alternator and thus decrease fuel consumption. Because of the relatively small temperature drop across the generator and of the generator mass requirements, it is estimated that values of 1.5 to 2.0 are needed for the dimensionless thermoelectric figure of merit, ZT, in order to develop an economically viable system. Of course, there are other factors besides ZT when considering the potential use of thermoelectrics. For example, most commercial applications also require that the materials have also to be cheap enough, or environmentally friendly to make the thermoelectric power generation a viable option. Due to the need for reductions in the mass, cost and volume of radioisotope thermoelectric generators (RTGs) used to power spacecrafts for deep space missions, a search for new advanced materials with ZT values substantially higher than state-of-the-art $Si_{0.8}Ge_{0.2}$ alloys ($ZT_m \approx 0.65$ from 575 to 1275K) was initiated a few years ago at the Jet Propulsion Laboratory. Recent results on novel materials have demonstrated that ZT values significantly larger than 1.0 could be obtained in the 475 to 975K temperature range. These materials are excellent candidates to be used in terrestrial thermoelectric power generators using waste heat or liquid fuels.

INTRODUCTION

Because of their high reliability, long lifetime, and absence of moving parts and emissions, solid state thermoelectric devices have been used in a variety of cooling and power generation applications. However, the efficiency of these devices is relatively low, mainly because of the relatively low energy conversion efficiency of state-of-the-art thermoelectric materials used in these devices. The discovery and development of advanced thermoelectric materials for high performance systems is required to widen the range of applications of thermoelectric devices. Improved thermoelectric power generators could be used for a variety of applications including waste heat recovery in vehicles, remote power units in harsh environments, portable generators and space power sources,

For several of these terrestrial applications, the heat source temperature can range from 550-700K up to 850-1100K. Thermoelectric generators operating on natural gas, propane or diesel have been built with different thermoelectric alloys, depending on the maximum hot side temperature, from 525K up to 875K (Naughton, 1995). These devices are used in various industrial applications such as for cathodic protection, data acquisition and telecommunications. More recently, there has been a growing interest for thermoelectric power generation recovering waste heat from various industrial heat-generating processes such as the combustion of solid waste, geothermal energy, and power plants (Matsuura, 1993; Rowe et al., 1993; Kajikawa et al., 1994). There is currently an important effort in Japan to develop large scale waste heat recovery thermoelectric generators using state-of-the-art materials, But perhaps the automobile industry is the market with the most potential, Because of the need for cleaner, more efficient cars, car manufacturers worldwide are interested in using the waste heat generated by the vehicle exhaust to replace or supplement the alternator and thus decrease fuel consumption (Takanose and Tamakoshi, 1994; Birkholz et al., 1988; Morelli, 1996). According to some car manufacturers, the available temperature range would be from 375 to 650-800K. Because of the smaller temperature drop across the ģcncralor and of the generator mass rcquircmcnls, it is cslimalcd that ZT values of 1.5 to 2.0 will bc nccdcd to develop an economically availablc systcm.

NOVEL THERMOELECTRIC MATERIALS

The Jet Propulsion Laboratory (JPL) started in 1991 a broad search to identify and develop advanced thcrmoclcctric materials for power generation applications. Using several physical and chcmical critcria, several families of compounds were idcntificd and rctaincd for invcstigations. Among thcsc materials, skultcrudilc and 7&Nr$_3$-based materials arc particularly promising anti several of these materials arc currently being dcvclopcd and optimizcd (Caillat ct al., 1996a; Flcurial ct al., 1996; Caillat ct al., 1996b). ZT values equal to or greater than 1 were obtained for these materials over a different range of tcmpcraturcs: p-type Zn.$_4$Sb$_3$-based matcrials (375-675K), p-type Cc-bawd filled skutlcrudilc (675 -975 K), and li-type heavily doped CoSb$_3$ (525-975K). Rcccnt results obtained in these families of materials have shown that further improvements in their thcrmoclcctric performance arc possible.

The thermoclcctric figures of merit, ZT, for several p-type slalc-of-the-atl thcrmoclcctric materials as wcl 1 as for 2tn&b$_3$-based and skutlcrudilc materials arc shown in Fig 1. From room temperature to about 400K, Bi$_2$Tc$_3$ alloys have the best ZT values. in the 400 to 675K tcmpcralurc range, where state-of-the-art thcrmoclcctric materials arc not very cfficicnt, Zn$_4$Sb$_3$ and Zn$_4$Sb$_3$ alloys have the highest ZT values with a maximum of 1.4 at 675K and 525K rcspcctivcly[1].

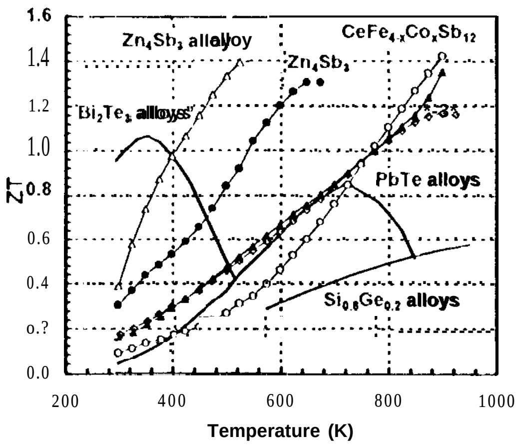

FIGURE 1: ZT values for state-of-the-arl and JPL improvcd p-type thcrmoclcctric malcrials as a function of tcmpcraturc

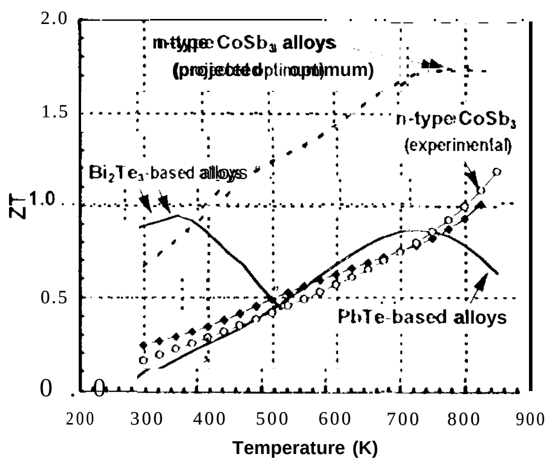

FIGURE 2: ZT values for slatc-of-thc-arl and JPL improvcd n-type thcrmoclcctric malcrials as a function of tcmpcraturc

JPL has also been working on several materials corresponding to a "filled" version of thc skultcrudilc structure. The best results obtained to date on CeFc$_{4-x}$Co$_x$Sb$_{12}$ samplcs arc shown in Figure 1, Above 725K, the propcrtics of PbTc-based alloys start to dcterioratc whcrcas thc 7,1' values of tilled skultcrudilc keep incrcasing up to 875K with a maximum of about 1.4 al this tcmpcraturc. Additional improvements in the Z']' values for filled skultcruditcs arc expected by forming solid solutions and/or introducing different transition mctal and filling clcmcnts in thc structure. Also, some of thcsc compositions might bc cvcn more rcfractory and could be used at even highcr hot-side tcmpcraturcs (over 1000K), which would results in higher overall conversion cfficicncics. Thcsc materials arc currently being dcvclopcd and optimizcd at JPL.

N-type materials

The ZT values for n-type s[atc-of-the-art and ncw thcrmoclcctric materials dcvclopcd at J} '1. arc shown in Figure 2. in the 300 to 525K temperature range, Ili$_2$3'c$_3$.based materials remain the most cfficicnt materials at low tcmpcraturcs. At higher tcmpcraturcs, the properties of heavily doped n-type CoSb$_3$ arc similar to those of PbTc alloys up to 775K. However, the properties of PbTe-based alloys start to degrade above this temperature whereas the properties of the skutterudites remain nearly constant. Heavily doped n-type $CoSb_3$ bot-pressed samples have also been reproducibly fabricated with comparable optimum thermoelectric properties. Several possibilities for improving the thermoelectric properties of skutterudites have been found (Slack et al., 1996). In particular, four different approaches have been identified and experimentally demonstrated to reduce the lattice thermal conductivity of skutterudites: 1) fill the two empty octants in the skutterudite (filled skutterudites) 2) use electron-phonon scattering in heavily doped samples 3) form ternary compounds and 4) form solid solutions. Based on experimental results obtained on lattice thermal conductivity reduction corresponding to different phonon scattering mechanisms above and also theoretical calculations, it was found that, if several of these mechanisms can operate simultaneously in one material, high ZT values could be achieved. The projected optimum values arc plotted on Figure 2 and up to 60% improvement is possible compared to current $CoSb_3$ optimized samples, The optimization of the n-type alloys is currently being pursued.

IMPROVED THERMOELECTRIC GENERATORS

The material efficiency (η) of a thermoelectric generator can be calculated by:

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

where T_H and T_C arc the temperature values for the hot-side and the cold-side, respectively, and ZT is the combined average thermoelectric figure of merit for the n-type and p-type legs over the temperature range T_H-T_C, S is the Seebeck coefficient, σ is the electrical conductivity, p is the electrical resistivity, and λ is the thermal conductivity of the thermoelectric material.

The increase in the thermal-to-clcc(ric materials conversion efficiency as a function of ZT for a thermoelectric generator operating between different temperature gradients is plotted in Figure 3. This figure shows the advantage of using more efficient thermoelectric materials and of operating the generator at larger AT values. A thermoelectric generator using segmented legs made of state-of-the-art materials, Ili~'I'c_3-based and Pb'1'c-based alloys, could operate between 300 and 845K. The schematic of such a segmented generator is reproduced in Figure 4. Using an average calculated ZT value of 0.76 (scc Figures. 1 and 2), wc calculated a material efficiency of 1 2.5% for a segmented thermoelectric generator using Bi_2Te_3- and PbTc-based thermoelectric materials and operating in the 300-845K temperature range (scc Figure 3 and Table 1). One of the obvious limitations of this generator is the maximum hot-side temperature of 84 SK imposed by using PbTc-alloys. This limits the efficiency, which is further restrained by the relatively poor performance of both p-type Bi_2Te_3- and Pbl'c-based materials in the 475 to 62SK temperature range. To develop more efficient segmented legs, the segmentation needs to bc optimized to achieve higher ZT values over the entire temperature range. Also, the hot-side temperature of the device must be increased by developing new materials capable of operating at higher temperatures than Pb'1'c-based materials,

A segmented thermoelectric generator utilizing a combination of s[atc-of-the-art thermoelectric materials and new thermoelectric materials developed at JPL could be made to operate between 300 and 975K. The p-leg would be composed of $Bi_{0.25}Sb_{0.75}Te_3$ (300 -425 K), Zn_4Sb_3 (425 -675 K), and Cc-based filled skutterudite (675-975 K), and the n-leg of $Bi_2Te_{2.7}Se_{0.3}$ (300 -525K) and heavily-doped $CoSb_3$ (525-975K). This new segmentation allows to operate the generator at higher T_H and also achieve higher average ZT values in the 300-975K temperature range (Zt_{ave} - 0.93). The corresponding increase in materials efficiency was calculated and is shown in Table 1 and Figure 3 (as "improved materials (l)"). By using these new segmented legs, the material efficiency will Significantly increase from 12.5% to 15.9%.

The usc of optimized Zn_4Sb_3-based and $CoSb_3$-based thermoelectric materials to design and fabricate segmented legs would result in a further increase in the efficiency of the con esponding thermoelectric generator. Using p-type $Bi_{0.25}Sb_{0.75}Te_3$, p-type Zn_4Sb_3-based materials, and p-type Cc-based tilled skutterudite for the p-legs, and n-type $Bi_2Te_{2.7}Se_{0.3}$ and n-type $CoSb_3$-based materials for the n-type legs, an average ZT value of 1,25 has been predicted over the 30() -975K temperature range. The segmented generator schematic is reproduced in Figure 5. With these improved legs, the material efficiency of the corresponding generator is expected to increase by about 60% compared to Bi_2Te_3- and PbTe-based generators, with a maximum thermoelectric materials conversion efficiency higher than 19% (see "Table 1 and Figure 3 "Improved Materials (2)).

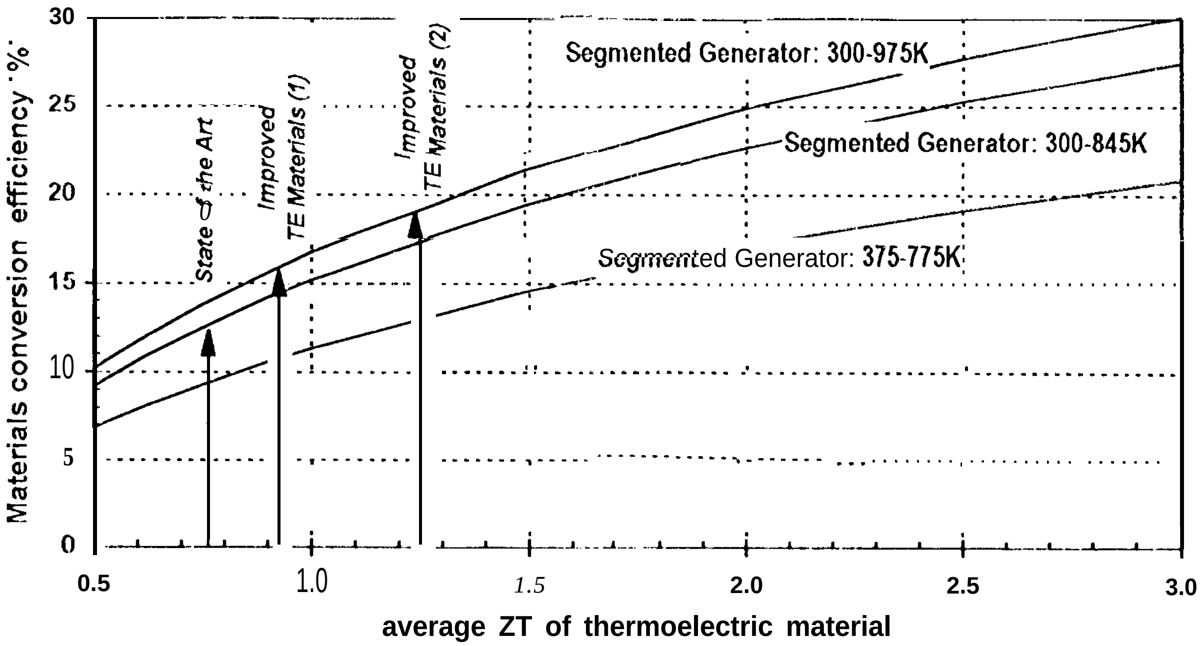

FIGURE 3: Calculated thermoelectric materials conversion efficiency as a function of ZT for various segmented generators operating at different ΔT

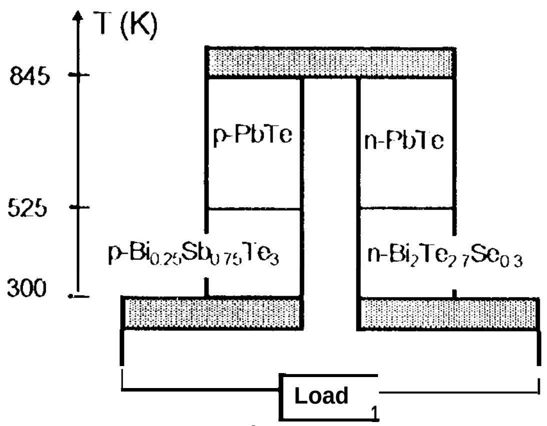

FIGURE 4: Schematic of a segmented thermoelectric generator using state-of-the-art Bi_2Te_3- and PbTe-based thermoelectric materials

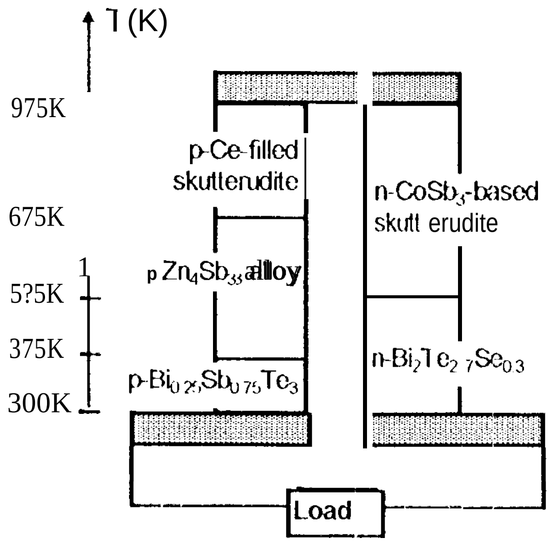

FIGURE 5: Schematic of a segmented thermoelectric generator based on improved thermoelectric materials under development at JPL

TABLE 1: Materials Conversion Efficiency Calculated for Various Segmented Legs

Configuration of segmented thermoelectric generator	Average n+p ZT	300-845K efficiency (%)	300-975K efficiency (%)
(p) Bi_2Te_3 + PbTe / (n) Bi_2Te_3 + PbTe	0,-/57	12.5	
(p) Bi_2Te_3+ Zn_4Sb_3 + $CeFe_4Sb_{12}$ /(n) Bi_2Te_3 + $CoSb_3$	0.924		15.9
(p) Bi_2Te_3 + Zn_4Sb_3-based + $CeFe_4Sb_{12}$ / (n) Bi_2Te_3 + $CoSb_3$-based	1.248		19.2

The properties of the various thermoelectric materials to be used in the fabrication of the segmented legs must be compatible with each other to prevent failure under operating conditions. In particular, the different thermoelectric materials should have similar thermal conductivity and thermal expansion coefficient values. Table 2 lists those values for the materials considered here and shows that a reasonable good match between Bi_2Te_3 and the novel Zn_4Sb_3-based and skutterudite materials will be achieved.

TABLE 2: Thermal Expansion Coefficient (α) and Thermal Conductivity (λ) at 300K

Material	Bi_2Te_3-based	PbTe-based	Zn_4Sb_3-based	Skutterudites
α (10^{-6} K^{-1})	13	19-20	15-20	6-10
λ ($Wm^{-1}K^{-1}$)	**10-15**	12-20	6-11	**14-?5**

To build such an advanced thermoelectric generator would also require the development of bonding materials to connect the different segments in the legs and to the metallic electrodes which provide the electrical current path in the device. A low contact resistance and temperature stability are the major requirements for the bonds. Specific soldering/brazing alloys are used to ensure a low electrical resistance contact between the metallic electrode and the thermoelectric materials. The composition of the alloy depends on the type of thermoelectric material used, on the maximum temperature on the hot side of the device and on the coefficient of thermal expansion mismatch. The results of initial bonding and temperature stability tests for Zn_4Sb_3 samples brazed to Cu electrodes demonstrated that low electrical contact resistance, stable, high quality bonds could be achieved (Caillat et al. 1996c). However, more work needs to done to develop suitable bonding materials for Zn_4Sb_3-based alloys and skutterudite materials.

CONCLUSION

New high efficiency thermoelectric materials with ZT values substantially larger than 1.0 have. been recently developed. The successful development of a segmented thermoelectric generator utilizing a combination of state-of-the-art thermoelectric materials and those novel thermoelectric materials could result in a high thermal-to-electric materials conversion efficiency over 1 9%. This is because the new thermoelectric materials have a higher average ZT value and the generator can be operated in a temperature range wider than possible with state-of-the-art materials. Such improved power generators could be used for a variety of applications including, waste heat recovery. This could also lead to the development of high performance thermoelectric generators operating in a relatively narrow temperature range for specific applications.

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REFERENCES

Birkholz, U., Grob, E., Stohrer, U., Voss, K, Gruden, D.O., and Wurster W, (1988) *Proceedings, 7th International Conference on Thermoelectrics*, ed. K. Rae, University of Texas at Arlington, 1:124.

Caillat T., Fleurial J.-P. and Borshchevsky A (1996a), "A Low Thermal Conductivity Compound for Thermoelectric Applications: β-Zn_4Sb_3", *Proceedings 15th International Conference on Thermoelectrics*, ed. T. Caillat, Institute of Electrical and Electronics Engineers, Inc, I: 151.

Caillat T., Fleurial J.-P. and Borshchevsky A. (1996b), "Properties of Single Crystalline Semiconducting $CoSb_3$", *J. Appl. Phys.*, 80 (8), 4442.-4449.

Caillat T. and Fleurial J.-P. (1996 c), "Zn-Sb Alloys for Thermoelectric Power Generation", *Proceedings 31st Intersociety Energy Conversion Engineering Conference*, Institute of Electrical and Electronics Engineers, inc.. 2:905.

Fleurial J.-P., Borshchevsky A., Caillat T., Morelli D.T. and Meisner G. (1996), "High Figure of Merit in Ce-Filled Skutterudites", *Proceedings 15th International Conference on Thermoelectrics, ed.* T. Caillat, Institute of Electrical and Electronics Engineers, inc., 1:91.

Kajikawa, T., Ito, M., Shibuya, E., and Hirayama, N. (1994) *Proceedings 12th International Conference on Thermoelectrics*, ed. K. Matsuura, Institute of Electrical Engineers of Japan, 1:491.

Matsuura, K. (1994) "Large Scale Thermoelectric Generators and Devices, the Future *Proceedings 12th International Conference on Thermoelectrics*,, ed. K. Matsuura, Institute of Electrical Engineers of Japan, 1:439.

Morelli, D.T., (1996), "Potential Applications of Advanced Thermoelectrics in the Automobile Industry", *Proceedings 15th International Conference on Thermoelectrics*, ed. T. Caillat, Institute of Electrical and Electronics Engineers, Inc., 1:383..

Naughton, A.G. (1995) "Commercially Available Generators,", in *CRC Handbook of Thermoelectrics*, ed. M. Rowe, CRC Press, 459.

Rowe, D.M., Matsuura, K., Koumoto, K., Tsumura, H., and Tsuyoshi, A. (1994) "Design Optimization of Thermoelectric Generator for Utilization of Geothermal Energy *Proceedings 12th International Conference on Thermoelectrics*, ed. K, Matsuura, Institut e of Electrical Engineers of Japan, 1:463,

Slack GA., Fleurial J.-P. and Caillat T. (1996), "The Thermoelectric Properties of Skutterudites", Naval *Research Reviews*, (4) 26.

Takanose, E., and Tamakoshi, H. (1994) *Proceedings 12th International Conference on Thermoelectrics, ed.* K Matsuura, Institute of Electrical Engineers of Japan, 1: 587.