USING THE COMPATIBILITY FACTOR TO DESIGN HIGH EFFICIENCY SEGMENTED THERMOELECTRIC GENERATORS

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ABSTRACT

Using thermoelectric compatibility, efficient thermoelectric generators are rationally designed. With examples, compatible and incompatible systems are explained and materials proposed for targeted development. The compatibility factor explains why segmentation of TAGS with SnTe or PbTe produces little extra power, while filled skutterudite increases the efficiency from 10.5% to 13.6%. High efficiency generators are designed with compatible n-type La_2Te_3, and similar p-type material, while incompatible SiGe alloys actually reduce the efficiency. A refractory metal with high p-type thermopower (> 100 μV/K) is required for development. The Chevrel compound $Cu_4Mo_6Se_8$ is a compatible p-type metal that provides a modest increase in efficiency. A fully segmented generator using Bi_2Te_3-type, PbTe, TAGS, Zn_4Sb_3, skutterudite, La_2Te_3, and Chevrel compounds between 25° C and 1000° C will achieve 18.1% conversion efficiency.

INTRODUCTION

The efficiency of a thermoelectric generator is governed by the thermoelectric properties of the generator materials and the temperature drop across the generator. The temperature difference, ΔT between the hot side (T_h) and the cold side (T_c) sets the upper limit of efficiency through the Carnot efficiency $\eta_C = \frac{\Delta T}{T_H}$. The thermoelectric material governs how close the efficiency can be to Carnot primarily through the thermoelectric figure of merit, z, defined by $z = \frac{\alpha^2}{\kappa\rho}$. The relevant materials properties are the Seebeck coefficient α, the thermal conductivity κ, and electrical resistivity ρ, which all vary with temperature.

Thus to achieve high efficiency, both large temperature differences and high figure of merit materials are desired. Since the material thermoelectric properties (α, ρ, κ) vary with temperature it is not desirable or even possible to use the same material throughout an entire, large temperature drop. Ideally, different materials can be *segmented* together (Figure 1) such that a material with high efficiency at high temperature is segmented with a different material with high efficiency at low temperature. In this way both materials are operating only in their most efficient temperature range.

We have shown [1] that for the exact calculation of thermoelectric efficiency, the thermoelectric compatibility must also be considered. The maximum efficiency (determined by z) is only achieved [1] when the relative current density u, (ratio of the electrical current density to the heat flux by conduction: $u = \frac{J}{\kappa \nabla T}$) is equal to the compatibility factor $s = \frac{\sqrt{1+zT}-1}{\alpha T}$.

In an efficient generator the relative current density is roughly a constant throughout a segmented element (typically u changes by less than 20%). Thus the goal is to select high figure

of merit materials that have similar compatibility factors. If the compatibility factors differ by a factor of two or more, a given u can not be suitable for both materials and segmentation will not be efficient. Compatibility is most important for segmented generators because the thermoelectric material properties may change dramatically from one segment to another. Other factors (not considered here) may also affect the selection such as: thermal and chemical stability, heat losses, coefficient of thermal expansion, processing requirements, availability and cost. For this analysis, we consider only the thermoelectric properties in the 1-dimensional heat flow problem.

The following examples demonstrate how the materials selection can be made rational by considering both z and s.

CALCULATION OF EFFICIENCY

To provide quantitative results that are easy to compare, the single element (n- or p-type) efficiencies were calculated following [2]. The overall efficiency is close to the average of the n- and p- single element efficiencies. To calculate the variation of $u(T)$ with temperature, the differential equation,

$$\frac{d(1/u)}{dT} = -\frac{1}{u^2}\frac{du}{dT} = -T\frac{d\alpha}{dT} - u\rho\kappa$$

derived from the heat equation, must be solved. For computation, this can be approximated by combining the zero Thomson effect ($d\alpha/dT = 0$) solution with the zero resistance ($\rho\kappa = 0$) solution.

$$\frac{1}{u_2} = \frac{1}{u_1}\sqrt{1 - 2u_1^2\overline{\rho\kappa}\Delta T} - \overline{T}\Delta\alpha$$

where $\Delta\alpha = \alpha(T_2) - \alpha(T_1)$ and $\overline{\rho\kappa}$ denotes the average of $\rho\kappa$ between T_1 and T_2.

The above equation is also valid to calculate the change in u at the interface between segmented materials where α is discontinuous ($\Delta T = 0$, $\Delta\alpha \neq 0$).

Once $u(T)$ is known, the efficiency of a single thermoelectric element (n- or p-type) can be calculated from

$$\eta = 1 - \frac{\alpha_c T_c + 1/u_c}{\alpha_h T_h + 1/u_h}$$

The subscripts h and c denote the value at the thermoelectric hot or cold side (T_h = hot side temperature, $\alpha_h = \alpha(T_h)$).

RESULTS

Improved Segmented PbTe-TAGS

As the first example, consider the TAGS-SnTe segmented p-type thermoelectric generator element that has been used successfully on several NASA space missions [3]. The TAGS material ($(AgSbTe_2)_{0.15}(GeTe)_{0.85}$) must be maintained below 525° C (or lower for long term applications), while the PbTe n-type element can operate to 600°C. To achieve a 600° C system, a segment of another p-type material is added to the TAGS p-leg between 525° C and 600° C.

From zT (Figure 2), it appears that p-type PbTe would be a better choice than SnTe for the 525° C to 600° C segment. However, the compatibility factor (Figure 2) for p-PbTe drops much lower than that of TAGS, and segmentation actually results in a decrease in efficiency (Table 1). SnTe has a closer compatibility factor to TAGS (higher is also beneficial), and thus produces a higher efficiency segmented generator despite the lower zT compared to PbTe. By alloying PbTe and SnTe a more compatible material is produced with acceptable zT, and this is used in actual TAGS generators.

A compatible and high efficiency material to segment with TAGS is p-type filled skutterudite such as $Ce_{0.85}Fe_{3.5}Co_{0.5}Sb_{12}$ ("$CeFe_4Sb_{12}$" in Figures 2 and 3). Filled skutterudite produces over twice the increase in efficiency (Table 1) compared to SnTe.

Further increases in efficiency of PbTe/TAGS generators can be achieved by segmenting with both *p*- and *n*-type skutterudite ($CeFe_4Sb_{12}$ and $CoSb_3$) and increasing the hot side temperature (*e.g.* to 700°C in Table 1).

Table 1. Maximum Single element efficiencies for Thermoelectric generators. $u(T_c)$ is the relative current density that gives the maximum efficiency.

Material	Efficiency (%)	T_c (C)	$T_{Interface}$ (C)	T_h (C)	$u(T_c)$ (V^{-1})
p-TAGS	10.45	100		525	2.97
p-TAGS/PbTe	10.33	100	525	600	2.33
p-TAGS/SnTe	11.09	100	525	600	2.84
p-TAGS/$CeFe_4Sb_{12}$	11.87	100	525	600	2.94
p-TAGS/$CeFe_4Sb_{12}$	13.56	100	525	700	2.88
p-SiGe	4.23	525		1000	0.85
p-TAGS/SiGe	9.89	100	525	1000	1.12
p-$Cu_4Mo_6Se_8$	4.00	525		1000	1.78
p-TAGS/$Cu_4Mo_6Se_8$	11.48	100	525	1000	2.77
n-PbTe	9.87	100		600	-2.00
n-PbTe/$CoSb_3$	11.30	100	600	700	-1.96
n-PbTe/SiGe	13.76	100	600	1000	-1.46
n-PbTe/La_2Te_3	15.56	100	600	1000	-1.80
n-SiGe	5.44	600		1000	-1.29
p-Bi_2Te_3/Zn_4Sb_3 /TAGS/$CeFe_4Sb_{12}$ /$Cu_4Mo_6Se_8$	18.57	25	170/400 525/700	1000	2.94
n-Bi_2Te_3/PbTe /$CoSb_3$/La_2Te_3	17.83	25	190/480 600	1000	-2.01

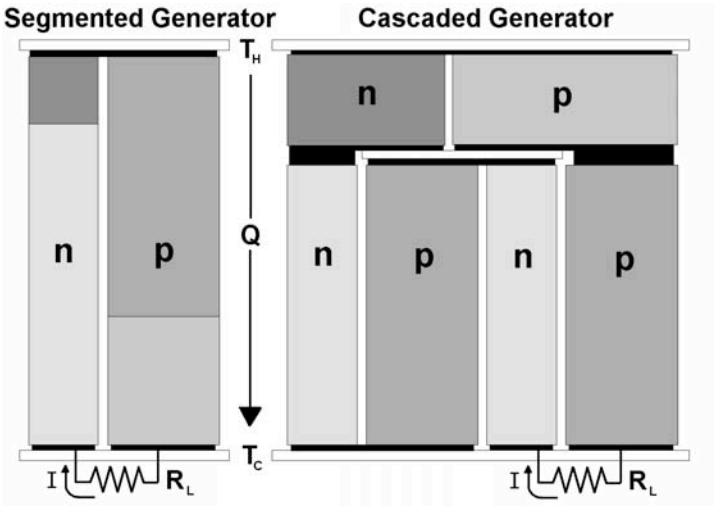

Figure 1. Schematic diagram comparing segmented and cascaded thermoelectric generators.

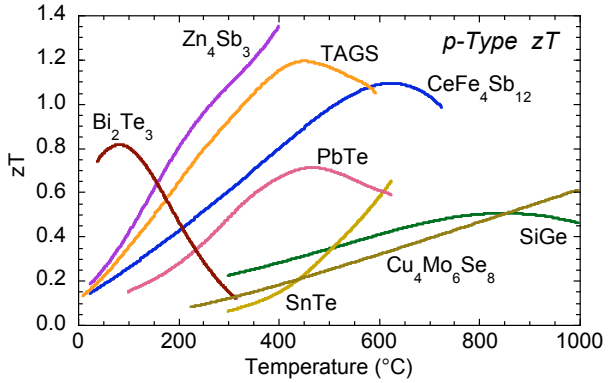

Figure 2. Figure of merit (*zT*) for p-type materials.

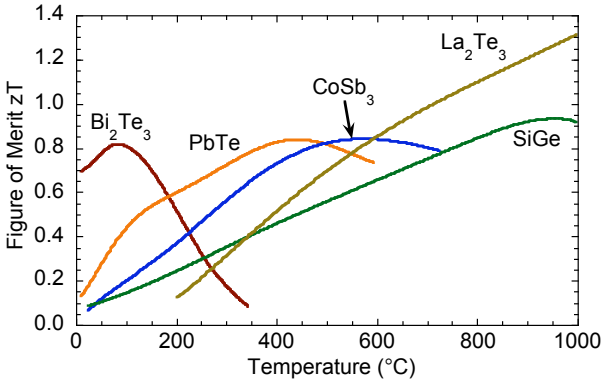

Figure 4. Figure of merit (*zT*) for n-type materials.

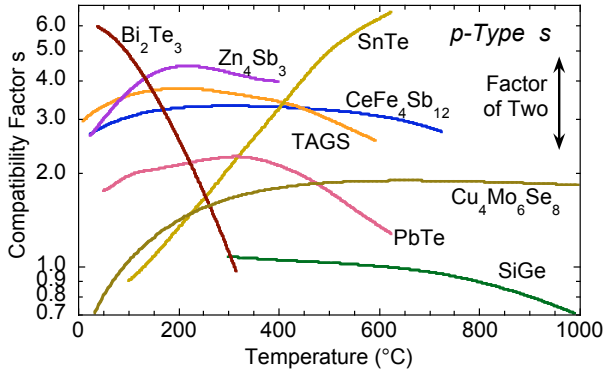

Figure 3. Compatibility factor (*s*) for p-type materials.

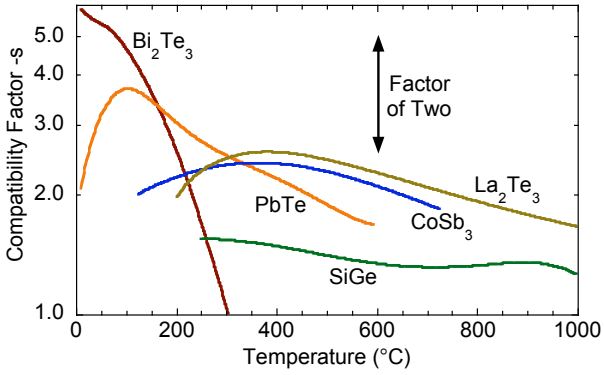

Figure 5. Compatibility factor (*s*) for n-type materials (negative).

High Efficiency Segmented Generators

For the highest efficiency, it is necessary to use the highest temperature difference possible because of the Carnot factor. The thermoelectric hot side in a thermoelectric generator used for space applications can achieve 1000° C. Many of the refractory materials with high *zT* such as SiGe or Boron Carbide [4]) have low electrical conductivity with high Seebeck coefficient and therefore low compatibility factors (SiGe Figures 2–5). The low compatibility factors reduce their suitability for segmentation with PbTe, TAGS or Skutterudite materials. P-type SiGe is so incompatible that a decrease in efficiency would actually occur (Table 1).

The rare earth chalcogenides [4], in particular La_2Te_3 [5-7] have not only high *zT* but also have higher *s* compatible with PbTe and Skutterudite thermoelectric materials. Segmenting PbTe with La_2Te_3 results in an increase in efficiency from 9.9 % to 15.6 %.

Materials Specification for Development

For the high temperature p-type element, a high *zT* material that is also compatible with PbTe, TAGS or Skutterudite has not been identified. To utilize La_2Te_3 in the n-element, some high temperature p-type material must be used. Even if the material has low $zT \approx 0.5$, it will produce some power, *as long as it is compatible*. For a material with a low *zT* to be compatible with

PbTe, TAGS or Skutterudite it must have $s > 1.5$ V^{-1}, ideally $s \approx 3$ V^{-1}. Since $s \approx z/2\alpha$, the $zT \approx 0.5$ material can not be a high Seebeck coefficient band or polaron semiconductor.

Materials with high z and s have thermoelectric properties typical of high α metals. In a metal, the thermal conductivity is dominated by the electronic contribution given by the Wiedemann-Franz law $\kappa_\varepsilon = LT/\rho$ where $L \approx 2.4 \times 10^{-8}$ V^2/K^2. The compatibility factor $s \approx \alpha/(2\kappa\rho) \approx \alpha/(2LT)$ would then be appropriate if α is greater than 100 μV/K at 1000 K.

Thus the material that is most necessary for development of high efficiency thermoelectric generators is a refractory p-type metal with a reasonably high Seebeck coefficient, much like a p-type version of La_2Te_3 which has α and ρ increasing linearly with T.

Chevrel High Temperature p-type

An example of a compatible, high temperature p-type material is the copper intercalated Chevrel phase $Cu_4Mo_6Se_8$. Such Chevrel phases contain clusters of Mo_6X_8 (X = S or Se), packed in such a way as to provide many sites for intercalation atoms which are expected to disrupt phonon heat transport, resulting in the low observed thermal conductivities [8, 9]. In a study on $Cu_{4-x}Mo_6S_8$, it was found that the copper atoms are positioned on multiple disordered sites [10](Figure 6).

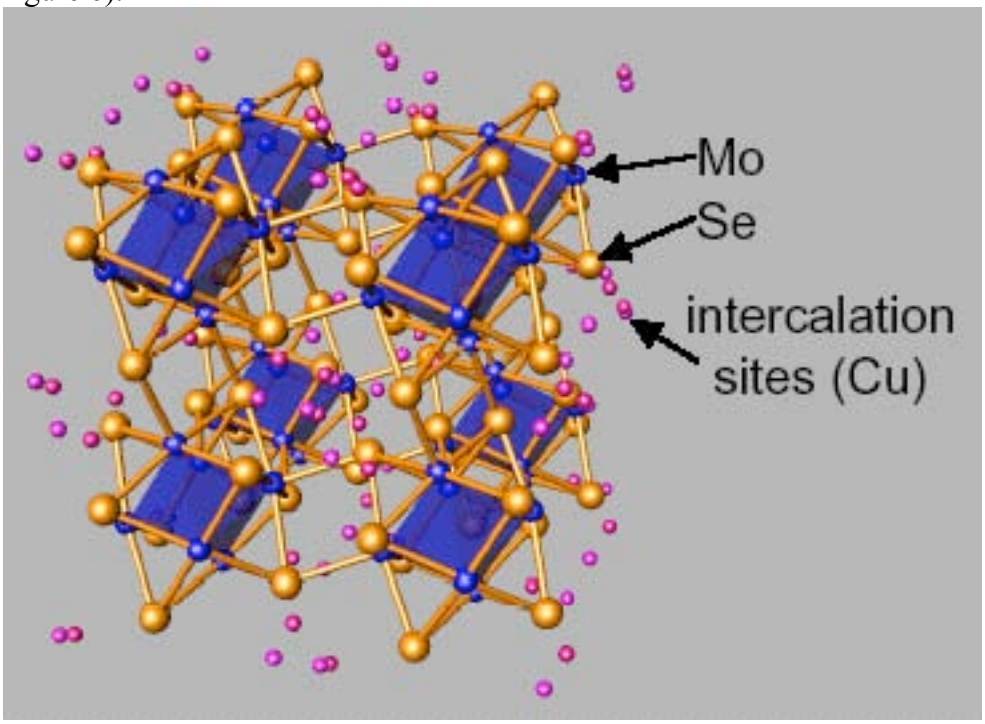

Figure 6. Structure of Chevrel phase with intercalation atoms based on $Cu_{4-x}Mo_6S_8$ [10].

A sample of $Cu_4Mo_6Se_8$ was prepared and analyzed according to [8, 9], with preliminary results of thermoelectric measurements (on heating and cooling) given in Figure 7. $Cu_4Mo_6Se_8$ has a zT similar to that of p-SiGe (Figure 2) but a dramatically larger compatibility factor s (Figure 3). This is due to the lower Seebeck and higher electrical conductivity (more characteristic of a metal) and lower thermal conductivity compared to p-SiGe. By itself, $Cu_4Mo_6Se_8$ has a slightly lower efficiency than p-SiGe (4.0% compared to 4.2% – Table 1). Nevertheless, because it is much more compatible with TAGS than p-SiGe (Figure 3), segmentation of $Cu_4Mo_6Se_8$ with TAGS results in 1% efficiency gain (compared to TAGS alone) as opposed to 0.5% efficiency decrease for p-SiGe/TAGS (Table 1). An increase in α for $Cu_4Mo_6Se_8$, will improve the efficiency not only by increasing z but also by increasing s.

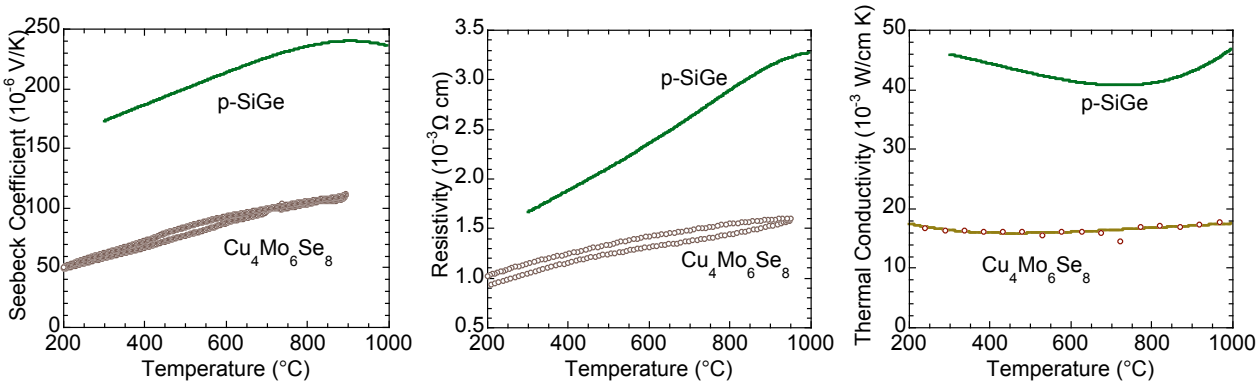

Figure 7. Thermoelectric Properties for $Cu_4Mo_6Se_8$ compared to p-SiGe.

Fully Segmented Generator

By combining all the highest *zT* thermoelectric materials that have compatible *s*, The highest efficiency is produced. For the large temperature difference 25° C to 1000° C, a fully segmented thermoelectric generator can have a total efficiency of 18.14% (Table 1). This generator uses p-$(Bi,Sb)_2Te_3$ up to 170° C, then Zn_4Sb_3 to 400° C, then $CeFe_4Sb_{12}$ to 700° C and finally $Cu_4Mo_6Se_8$ to 1000° C for the p-leg. The n-leg uses n-Bi_2Te_3 up to 190° C, then PbTe to 480° C, then $CoSb_3$ to 600° C and finally La_2Te_3 to 1000° C.

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