#### The Limited Role for Thermoelectrics in the Climate Crisis

Cronin B. Vining ZT Services (no 'Inc.') 2203 Johns Circle, Auburn AL 36830-7113 climate@ztnews.com, Ph: +1.309.214.5316, FAX (deprecated)

Prepared at the request of the Office of Honorable Al Gore & Mrs. Tipper Gore for presentation at a Solutions Summit panel on 'Nanotechnology and New Materials' held May 1, 2008 in New York City

#### Abstract

The climate crisis presents unique and largely unprecedented social, economic, political and technical challenges. The technical challenges, though enormous, may prove the most tractable of all. Among the technical challenges is the development of energy technologies with much reduced environmental impact This note provides an overview of thermoelectric technology, a solid state 'heat engine' capable of converting heat to electricity or alternatively converting electricity into cooling. Such an overview is timely because thermoelectric technology has made significant scientific progress in recent years and its potential to reduce the environmental impact of electrical power generation has been discussed. While the science, technology and business of thermoelectrics has never been stronger than today, the opportunity for a material impact on the climate crisis appears limited. Only a single application, recovery of vehicle waste heat, appears plausible in this respect. And even that application faces stiff barriers.

#### Introduction

In the past 15 years the US, Japan and other nations have invested in advancing thermoelectric (TE) technology (Vining 2007) with some successes. In a business-as-usual world these investments can be justified by expanding the range of applications to which thermoelectric technology can be advantageously applied. The climate crisis utterly disrupts the investment calculus such that today one must first ask: can this technology contribute solutions to the climate crisis?

In response to this question the *International Thermoelectric Society*, a professional organization devoted to the science, technology and industry of thermoelectrics, adopted a new primary goal in 2007:

"To promote an understanding of the role thermoelectric technology may play in environmental impact and mitigating global climate change."

To reinforce this point I wrote in a recent review (Vining 2007):

"If thermoelectricity can contribute, it is imperative that we do so. Alternatively, if it can be determined that TE has little to offer then we must not act as advocates of thermoelectric technology. Instead, resources must re-directed to technologies that may help. The stakes are simply too high for anything less." This note represents my current thoughts on what thermoelectrics can, can't and might offer in the specific context of the climate crisis. Ten questions listed in Appendix 1 helped guide preparation of this note. The following sections provide a brief overview and status of thermoelectric technology, discussion of recent scientific advances, and applications with possible climate crisis implications.

#### **Basics of Thermoelectric Technology**

The simplest thermoelectric (TE) device is a 'thermocouple' consisting of two different electrically conducting materials. One of the two materials is n-type, meaning electricity is carried by electrons: negatively charged particles. The other material is p-type, meaning electricity is particles. carried by 'holes': positively charged Thermoelectric devices typically are in the form of a module constructed from a number of these thermocouples (Figure 1). Heat applied to one side of the module will 'push' electrons (in the n-type material) and holes (in the p-type) from the hot side to the cold. With an appropriate circuit, a current flows and electrical power can be generated. In some ways the electrons and holes act like the steam in a steam turbine, where heat causes the steam to expand and drive a turbine.



#### Figure 1: A thermoelectric device [Courtesy J. Snyder, Caltech/JPL]. (See animated version online: http://thermoelectrics.caltech.edu/demos\_page.htm)

A thermoelectric module can also be operated in reverse, as a heat pump, to produce cooling (refrigeration): apply electrical current to the module and one side will cool. Key advantages include high reliability, small size and no noise. By these measures of performance, thermoelectric technology is highly competitive. But thermoelectric technology is not known for high efficiency and much R&D has been devoted to improve efficiency by seeking better n-type and p-type 'thermoelectric' materials. Regarding efficiency, the key property is known as the 'thermoelectric figure of merit' often written as 'ZT'. ZT itself is a particular combination of three properties of a material: thermal conductivity ( $\kappa$ ), electrical resistivity ( $\rho$ ) and Seebeck coefficient (*S*):

$$ZT = \frac{S^2 T}{kr} \tag{1}.$$

The problem comes down to the materials science, physics and chemistry of semiconductors with high ZT. Figure 2 illustrates ZT values for 'Best Practice' thermoelectric materials prepared by traditional 'bulk' fabrication techniques. Four of these materials (CeFe<sub>4</sub>Sb<sub>12</sub>, Yb<sub>14</sub>MnSb<sub>11</sub>, CoSb<sub>3</sub> and La<sub>3</sub>Te<sub>4</sub>) are new, developed relatively recently, while the remainder have been known and in use for decades.



Figure 2: 'Best Practice' ZT Values For p-type (above) and n-type (below) Materials [Courtesy J. Snyder, Caltech/JPL, <u>http://thermoelectrics.caltech.edu/]</u>

Like all heat engines, a thermoelectric device operates between two temperatures:  $T_{hot}$  (the heat source temperature) and  $T_{cold}$  (the heat rejection temperature). High efficiency is achieved mainly by 1) operating over a wider temperature range and 2) using materials with the highest possible ZT. Figure 3 illustrates the effect of ZT on efficiency. Here ZT means an appropriate average over of the p-type and n-type materials and over the range of operation. It is an average ZT value that counts, not just the maximum value. Higher ZT is better but note that efficiency improves only slowly with increasing ZT. Using materials available in bulk form today efficiency is limited to perhaps 1/6 the maximum possible Carnot efficiency.



Figure 3: The effect of ZT on efficiency.

#### Space Power RTGs: Classic Thermoelectric Application

Exploration of the solar system must be counted among mankind's crowning achievements. Radioisotope Thermoelectric Generators (RTGs) have made enabling contributions to this as the only technology (so far) capable of providing electrical power for deep-space missions including Voyagers I and II, Galileo, Cassini, and the most recent New Horizons mission to Pluto shown in Figure 4. The RTG is the black, cylindrical finned object at lower left.



Figure 4: New Horizons spacecraft to Pluto with RTG (lower left) [Courtesy J.-P. Fleurial, JPL/Caltech].

This RTG consists of hundreds of individual silicongermanium (SiGe) thermocouples (Figure 5) arranged around graphite-encased plutonium. One such RTG weighs about 55 kg and produces about 240 Watts of electricity at about 7% conversion efficiency. The hot side is glowing red hot at 1300 K and even the 'cold' side is 600 K. There is no 'off' switch: the radioisotope heat source half-life is 87 years. Even in the harsh environment of space these thermocouples have accumulated more than a trillion device-hours without a single failure. NASA maintains thermoelectric expertise at the Jet Propulsion Laboratory, lead by J.-P. Fleurial and T. Caillat, to support this key space power technology.



Figure 5: The SiGe thermocouple, basis of the RTGs [Courtesy J.-P. Fleurial, JPL/Caltech]

NASA uses thermoelectrics not because they are efficient (they aren't), but because they are reliable and lightweight. More to the point, no other conversion technology has yet emerged to meet the demanding performance requirements of space. Indeed, thermoelectric technology is often selected because no other will quite fill the bill.

# **Thermoelectric Business Status**

The world wide commercial market for thermoelectric power generation is quite modest, perhaps US\$25-50M/year (for full thermoelectric generator, TEG, systems) due to the high cost and low efficiency. The leading supplier is Canada's Global Thermoelectric specializing in remote power units (Figure 6).



Figure 6: 500 Watt TEG on a natural gas pipeline in Peru [Courtesy LeSage, Global Thermoelectric]

The world market for cooling modules (not final products or systems: TE modules only) is thought to be about US\$200-250M/year. Figure 7 illustrates the diversity of applications for TE cooling modules.



### Figure 7: Market Distribution for TE Cooling Modules. [Komatsu (Hachiuma and Fukuda 2007)]

Although the benefits of improved ZT has not yet reached the marketplace, new and innovative engineering is enabling new TE cooling products. Notable are the car seat cooler/heaters introduced by Amerigon (Figure 8). About two million such units were shipped last year and revenue growth is strong (Figure 9).



Figure 8: Thermoelectric-based car seat cooler/heater [Courtesy Bell, Amerigon/BSST].



# Figure 9: Amerigon revenue: the only publicly traded company based purely on thermoelectrics.

The placement of thermoelectric technology into automobiles is significant for several reasons. First, it acts as a technology driver to improve efficiency and reduce costs. Second, it builds experience on larger scale/lower cost manufacturing. This experience reduces the barriers for introducing additional thermoelectric-based products. Finally, Amerigon estimates about a 2% reduction in fuel consumption (Bell 2008) because 1) in cooler mode the cabin air conditioner is used less and 2) in heater mode it is more efficient than the cabin heater.

Modern semiconductor manufacturing techniques are under development at two recent startups: Nextreme (US), a spin-off from the Research Triangle Institute utilizing a CVD superlattice technology (see Figure 10 and Figure 15) and Micropelt (Germany), a spin-off from an Infineon/ Fraunhofer Institute collaboration utilizing a wafer-scale device fabrication method (Figure 10). Neither technology is yet more efficient than prior art, but they offer other advantages such as faster thermal response times, higher heat pumping capacity (W/cm<sup>2</sup>), reduced size and require smaller quantities of thermoelectric materials. Both companies offer evaluation kits but are not yet in general production.



Figure 10: Nextreme (left) thin-film TE cooler and Micropelt (right) Bi<sub>2</sub>Te<sub>3</sub> 4<sup>2</sup> thin-film TE wafer.

The most recent startup is GMZ Energy, Inc. (Figure 17) which has announced plans to offer an improved p-type material. The thermoelectric business has never been better than today with new technologies and products entering the marketplace. Future prospects are also promising as costs continue to decrease, and one can hope recent efficiency (ZT) advances will eventually make their way to products.

#### **Progress in Thermoelectric Science**

Two things appeared almost simultaneously in the early 1990s: new ideas and new funding. One influential new idea was a theoretical calculation by (Hicks and Dresselhaus 1993) that indicated large improvements in ZT might be possible by making an artificial material modified on a nanometer length scale (Figure 11). Their idea, known as a 'quantum well superlattice', was important for inspiring nano-scale engineering generally to improve ZT.



Figure 11: Early MIT theory of ZT in a 'quantum well superlattice (Hicks and Dresselhaus 1993).

The other key factor was new funding. In the early 1990s DARPA and the Office of Naval Research initiated support for basic thermoelectric materials research, based in part on a remarkable conference organized by the Army Night Vision Lab (Horn 1992) in which many key new ideas were first introduced. At that time DoD was the largest user of thermoelectric coolers (for night vision, sensors, guidance systems, etc.) and it was thought even modest efficiency gains might make TE air conditioning practical in submarines (TE cooling is quiet) and enhance the existing DoD applications. With DoD backing, ZT has increased (Figure 12) and the scientific literature on thermoelectrics has grown markedly (Figure 13).



Figure 12: Impact of DoD funding on ZT.



Figure 13: Open literature publications on thermoelectrics.

# **Key Thermoelectric Developments**

The following six figures illustrate developments key to the problem of finding large ZT values. At the risk of oversimplifying, each illustrates the use of nano-scale engineering to reduce thermal conductivity of a material, which thereby enhances ZT. Oversimplifying again, lower thermal conductivity means heat is retained longer in the material and has a better chance of 'pushing' the electrons to create an electric current. If you think about everyday thermal insulation materials (styrofoam, that pink stuff in your attic, a down vest), they typically consist of loosely connected layers or particles. All those layers make it more difficult for heat to flow. These new nano-structured materials interfere with heat flow in a similar way.

Figure 14 shows a quantum dot superlattice prepared at MIT-Lincoln Labs by molecular beam epitaxy (MBE) (Harman, Taylor et al. 2000) with a reported ZT~3.5 at 575 K (Harman, Walsh et al. 2005). Larger ZT values have been reported but are probably not reliable. The MBE procedure deposits a layer of one semiconductor, then a layer of nanometer-sized dots, and repeats the process thousands of times. The image is looking 'down' on one of the layers. This MBE technique offers exquisite control but is generally thought much too expensive for production. No other group has reproduced this work and there has been no attempt at commercialization.



Figure 14: ZT~3.5 @ 575 K quantum dot superlattice (MBE) n-type, PbSeTe/PbTe [Harman, MIT-LL, J. Elec.Mat. 2000].

Figure 15 illustrates another kind of superlattice, simpler here without the 'dots', prepared at the Research Triangle Institute by chemical vapor deposition (CVD) with a reported ZT~2.4 at 300 K (ZT~2.9 at 400 K) (Venkatasubramanian, Silvola et al. 2001). The image is looking at a cross-section, a cut through the layers. This work is being commercialized by the startup Nextreme (Figure 10) using devices where the active TE materials are only a few micrometers thick. So far, the devices are no more efficient than prior art (due to internal losses) but they are small, fast and have high heat pumping capacity.



## Figure 15: ZT~2.4 @ 300 K superlattice (CVD) p-type, Bi2Te3/Sb2Te3, [Venkatasubramanian, RTI/Nextreme, 2001]

Figure 16 shows a 'natural' nano-scale dot formed in a bulk alloy of  $AgSbTe_2$ -PbTe known as a "LAST" material (an acronym of the constituent elements) with a reported ZT~2.2 at 800 K (Hsu, Loo et al. 2004). The nano-scale dot is thought to lower the thermal conductivity and increase ZT. Unlike the previous two examples, this material is prepared by essentially conventional methods. I am not aware of commercialization at this time.



Figure 16: ZT~2.2 @ 800 K bulk – 'natural' nanodots n-type, AgSbTe2-PbTe (aka 'LAST') [Kanatzidis, Northwestern, 2004].

ZT~1.4 was reported in March, 2008 for a 'fine grain' bulk bismuth-telluride material, made by grinding nanometer sized powder and pressing the powder back into a bulk solid (Figure 17) (Poudel, Hao et al. 2008). The nano-sized grains are thought to lower the thermal conductivity and improve ZT. GMZ Energy, Inc., a startup company backed by Kleiner, Perkins, Caufield and Byers, has announced intentions to produce commercial quantities.



Figure 17: ZT~1.4 @ 373 K bulk – fine grain p-type, (Bi,Sb)2Te3 [15 authors, BC/MIT/GMZ Energy/Nanjing University, 2008].

The next two results on silicon nanowires (Figure 18 and Figure 19) were published simultaneously in early 2008. This is one of those coincidences in which nearly the same idea was pursued by two different groups, (Boukai, Bunimovich et al. 2008) headed by Heath at Caltech and (Hochbaum, Chen et al. 2008) headed by Yang and Majumdar at Berkeley. The nanowires conduct heat about 100 times less than bulk silicon, resulting rather respectable ZT values. While the silicon authors point out that is very cheap, commercialization of the technique presents obvious challenges: a thousand of these nanowires laid side-by-side is still less than the diameter of a human hair. Also, the ZT values achieved are not significantly higher than known materials. The significance is not so much the ZT achieved so far, but the proof of principle these papers offer (Vining 2008).



Figure 18: ZT~1.2 @ 350 K nanowire p-type, Si [Heath, Caltech, 2008]



Figure 19: ZT~0.6 @ 300 K nanowire p-type, Si [Yang/Majumdar, Berkeley, 2008]

After 15 years of intense R&D only three efforts have produced ZT values in excess of 2: Harman's quantum-dot superlattice (Figure 14), Venkatsubramanian's superlattice (Figure 15) and Kanatizidis's 'LAST' bulk/'nanodot' material (Figure 16). In each study, only one 'type' (either nor. p-type, but not both) was reported improved. And predictive models to quantitatively explain the results have yet to emerge. Translation of these high ZT laboratory results to commercial quantities of materials and/or efficient devices does not appear imminent.

A recent review says ZT=3 is the "Holy Grail" of thermoelectrics and indicates it "appears to be within reach in the next several years" (Tritt, Böttner et al. 2008). While scientifically plausible, no clear path to do so has been identified. Engineering development is therefore limited to existing, lower ZT materials until such time as the "Holy Grail" enters the marketplace.

# **Possible TE Applications for Greentech**

The most promising thermoelectric application with Greentech implications is clearly vehicle waste heat recovery to improve fuel economy. In this concept vehicle waste heat, usually from the exhaust, is redirected to a thermoelectric generator to produce electricity (Figure 20) rather than using drive train power and an alternator. More drive train power is available to move the vehicle and electricity is still available. Under the US DoE FreedomCar program, managed by John Fairbanks and Aaron Yocum, four teams have been assembled to pursue this concept. FreedomCar targets both cars and trucks to improve overall fuel economy by 10% and aims to reach production in the 2011-2014 timeframe.

As none of the nano/high-ZT materials are yet available, development is proceeding with the best available materials. Presumably better materials technology will be employed as they become available. Most likely some improvement of ZT will be required for commercialization, but even without them the present study should provide better cost/payoff estimates.



Figure 20: BMW 530i concept with TE generator (yellow) and radiator (red/blue) [BMW]

The four thermoelectric generator teams consist of a lead organization (**bold**) combined with major vehicle/engine manufacturers, thermoelectric technology organizations, universities and others:

- **BSST** with BMW, Visteon, Marlow, Virginia Tech, Purdue, UC-Santa Cruz
- *GM* with GE, U of Michigan, U of South Florida, ORNL, RTI
- *Michigan State* with Cummins, Tellurex, NASA-JPL, Iowa State
- *United Technologies* with Pratt & Whitney, Hi-Z, Pacific Northwest National Lab., and Caterpillar

TE generators of this kind have been in field test on trucks for some years (Figure 21) and development for cars is well underway under the FreedomCar program (Figure 22).



Figure 21: 1 kW TEG on Kenworth Truck [Hi-Z].



Figure 22: 500 Watt BiTe TEG [BSST].

Significant barriers remain before deployment including: costs, heat transfer to TE modules, dedicated radiator for TEG, system weight, acceptance of change, competition with alternate conversion technologies as well as competition with all other means of increasing fuel efficiency (not all of which need be accretive).

Even for vehicle waste heat, competition from mechanical engines can be expected to be fierce. Honda, for example, has tested a system using a Rankine steam engine to generate electricity from waste heat in a Honda Stream hybrid vehicle, increasing overall engine efficiency by 3.8% (Kadota and Yamamoto 2008). BMW has for some years had a similar effort called Turbosteamer, but in their effort the added device is used to supplement the power train (rather than generate electricity) improving fuel efficiency 15%. Either project appears to beat the FreedomCar goal of 10% fuel savings today.

In 2006 the US Department of Energy's Office of Basic Energy Sciences initiated support to develop improved thermoelectric materials as part of solar energy project. The idea, described in a DoE report (Lewis and Crabtree 2005) and a Physics Today article (Crabtree and Lewis 2007), is simple enough: concentrate solar energy to create heat which a TEG turns into electricity. Engineering work has not begun, presumably because much higher ZT values are needed.

Industrial waste heat (incinerators, cement, steel mills, etc.) has also been discussed. NEDO (Japan) has invested in TE R&D for waste heat since at least 1997. Their most recent 5 year, US\$25M program completed satisfactorily in 2007 with reasonable progress toward program goals of 15% efficiency. Unlike American programs which generally cite increased security and saving money, the Japanese program is focused on reducing  $CO_2$  emissions. There is some possibility participants of the NEDO program will pursue commercialization on their own, and a follow-on project may be possible in 2009.

Other possible applications have been occasionally mentioned: geothermal, home cogeneration (fuel oil fired furnaces or gas water heaters plus TEGs), woodstoves (efficient cooking, for third world) and of course the potential 2% fuel savings from car seat cooler/heater mentioned above.

#### Efficiency of Power Plants and the Effect of Size

Particularly for large scale applications, efficiency will be paramount and future thermoelectric potential needs to be compared to currently available technologies. Figure 23 illustrates the efficiency (electrical power out/heat in) for several heat sources (geothermal, industrial waste, solar, nuclear and coal) in combination with several thermal-toelectric conversion technologies (organic Rankine, Kalina cycle, Stirling, Brayton and steam Rankine). The filled points indicate actual in-service power plants. The open circles represent design studies, but based on actual demonstrated technologies. Also plotted is the efficiency of a thermoelectric converter granted a number of small-ish but favorable assumptions (described in Appendix 2).



### 'Best Practice' vs. Thermoelectric Efficiency

Figure 23: Efficiency of 'Best Practice' mechanical heat engines compared to an optimistic thermoelectric estimate.

The systems shown here represent an estimate of 'best practice,' meaning these values are based on the actual performance of up-to-date systems. These are not 'best possible' values as each of these technologies can be expected to improve going forward. The smallest mechanical engine represented in Figure 23 is the 'Solar/Stirling' machine at 25 kW<sub>e</sub>. The others are at least 9 times larger and range up to 1600 MW<sub>e</sub> for the Nuclear/Brayton+Rankine study.

Figure 23 illustrates an important point. Existing, practical mechanical systems are far more efficient than thermoelectrics and more efficient than thermoelectrics are likely to become in the foreseeable future. After 15 years of R&D the best reported thermoelectric material: has a *maximum* (not average) value of ZT= 3.5, is n-type only (we need both) and is impossibly expensive. But set that aside and assume one can achieve: ZT=4, averaged over the entire temperature range, for both n- and p-type, in an infinitely cascaded device with no losses. Assume all that and you have the solid line labeled "ZT=4" in Figure 23, which is still less efficient than existing, commercially available technology regardless of what temperature range is of interest.

Unless some extraordinary system consideration firmly prohibits the use of mechanical engines, it seems unlikely that thermoelectric technology has anything to contribute for large scale systems. Of course, some totally unforeseen (and very large) advance in thermoelectrics could happen. But that is hardly the basis for a plan.

Size, however, can favor thermoelectric systems. Typical conversion systems become less efficient as they are scaled down to small size. Figure 24 illustrates this principle in a purely schematic way (the numbers and shape of the curves are illustrative only). Thermoelectric converters have been built which deliver reasonable efficiency at the milliwatt and even microwatt level. The efficiency of mechanical engines drops off at much higher power levels. This means there is a crossover point: below some power level thermoelectric technology will tend to be more efficient. Increasing ZT will move the crossover point to higher power levels, increasing the range of applications where thermoelectrics compete. Meanwhile mechanical engine R&D focuses on (among other goals) pushing the size down. Such is the nature of technology competition. No general value is possible as the precise crossover point will be different for each application: one value for waste heat in cars, another for geothermal.



Figure 24: Schematic illustration of efficiency vs. size

If thermoelectrics are to have some impact on the climate crisis we should look at applications which involve relatively low power levels (where TE can compete), but occur in large numbers (in order that it has an overall impact). Of the applications considered to date, only a few meet these criteria, as summarized in Table 1. Of these, vehicle waste heat appears the most promising.

 Table 1: TE applications with possible Climate Crisis

 impact

Application Type	Power Scale (kWe)	Examples	Required Device ZT	Impact on CC
Ι	> 1000s	Solar Thermal 'Engine' Replacement	> 8-20	Highly Unlikely
п	> 10s	Industrial Waste Heat Geothermal Bottoming Cycles	>4	Unlikely
III	0.5 – several	Vehicle Waste Heat Car Seat Cool/Heaters Home Co-generation (?)	> 1.5-2	TBD
IV	< 0.5	Remote Power 'Personal' Micropower All Existing Apps.	> 0.5-1	(almost) None

TBD = To Be Determined

# Summary

Thermoelectric technology has made admirable progress in recent years. *Laboratory* ZT values have increased several fold, business has grown significantly, startups have appeared (Nextreme, MicroPelt, GMZ) introducing next-generation TE technology and TE devices are now appearing in cars in significant numbers.

Yet the last 15 years of basic (ZT) R&D has hardly affected products and the nano/ZT>2 materials reported in the literature are not yet commercially available. The challenges to migrate the new TE materials to products include: understand exactly why high ZT happens, develop predictive models, capture the essential, underlying nanophysics in cost-effective materials, extend the temperature range of high ZT and establish both n- and p-type materials with high ZT.

Moreover, even if this future R&D acheives a full-fledged, device level average ZT=4 it is still probably insufficient to displace mechanical engines for large-scale applications. Of course, ZT=4 should greatly enhance the range and performance of niche applications TE technology serves so well today. But the impact on the climate crisis, even with ZT=4, seems limited to smaller scale, decentralized applications the most promising of which appears to be vehicle exhaust heat recovery. Even there, the benefit is potentially about 10% improved fuel economy assuming all the hurdles to market penetration are overcome. The opportunity for thermoelectric technology to help in the climate crisis appears limited.

# Acknowledgments

The author wishes to thank L. Bell, J. Snyder, J. Stockholm, C. Uher, B. LeSage, B. Nickerson, R. Venkatasubramanian, D. Rowe, T. Kajikawa, J-P Fleurial, T. Caillat, J. Heath, L. Whitlow, H. Böttner, E. P. Vining and many others throughout the thermoelectric community for supportive discussions and input. The opinions, errors and omissions, however, are solely the author's.

## **Appendix 1: Questions**

The following questions were provided by Office of Honorable Al Gore & Mrs. Tipper Gore and used as guidance in the preparation of this note.

- 1. Please provide a brief overview of what thermoelectrics are.
- 2. Do you they have a role to play in greentech and if so, what are the possible applications?
- 3. What are the difficulties in applying thermoelectrics to greentech?
- 4. Are there any thermoelectric applications that are close to the market?
- 5. What are the main factors that determine thermoelectric performance and cost, and how could nanotechnology play a role in improving these attributes?
- 6. What will be required for thermoelectrics to be applied in mainstream heat-to electricity conversion applications (e.g. exhaust of power plants or heat engines)?
- 7. Will thermoelectrics ever achieve higher ZT than 2?
- 8. Who are the leading researchers in thermoelectrics and how do their approaches differ?
- 9. What, if any, are the potential long-term thermoelectric technologies or processes coming down the pipeline?
- 10. Which approaches seem the most promising?

# **Appendix 2: Optimistic TE Efficiency Estimate**

In this note we are interested in the future potential for thermoelectric technology and have therefore adopted a simplified and slightly optimistic method of estimating efficiency from ZT. The following assumptions have been made:

• No device or system heat losses

- No device or system electrical losses
- Heat is rejected at 300 K
- ZT is constant over the temperature range
- The device is 'infinitely cascaded'

The 'infinitely cascaded' assumption means the device is made of an infinite number of stages, each optimized to operate at one particular temperature, with heat flowing in succession from one stage to another. Zener (Zener 1960) introduced this concept and provided the following expression for efficiency:

$$e = \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+1} \tag{2}$$

$$h = 1 - \left(\frac{T_{cold}}{T_{hot}}\right)^{e}$$
(3)

The ZT value to use in this estimate is an appropriate average over temperature and between the n- and p-type materials. Each of these assumptions tend to overestimate efficiency, but not grossly so.

# References

- Bell, L. E. (2008). Personal Communication.
- Boukai, A. I., Y. Bunimovich, et al. (2008). "Silicon nanowires as efficient thermoelectric materials." <u>Nature</u> 451(7175): 168-171.
- Crabtree, G. W. and N. S. Lewis (2007). "Solar Energy Conversion." <u>Physics Today</u> **60**(3): 37-42.
- Hachiuma, H. and K. Fukuda. (2007). "Activities and Future Vision of Komatsu Thermo modules." <u>European</u> <u>Conference on Thermoelectrics, ECT2007</u>, from <u>http://ect2007.its.org/system/files/u1/pdf/01.pdf</u>.
- Harman, T. C., P. J. Taylor, et al. (2000). "Thermoelectric quantum-dot superlattices with high ZT." <u>Journal of Electronic Materials</u> 29(1): L1-4.
- Harman, T. C., M. P. Walsh, et al. (2005). "Nanostructured thermoelectric materials." <u>Journal of Electronic Materials</u> 34(5): L19-L22.
- Hicks, L. D. and M. S. Dresselhaus (1993). "Effect of quantum-well structures on the thermoelectric figure of merit." <u>Phys. Rev. B</u> 47(19): 12727-12731.
- Hochbaum, A. I., R. Chen, et al. (2008). "Enhanced thermoelectric performance of rough silicon nanowires." <u>Nature</u> 451(7175): 163-167.
- Horn, S. B. (1992). <u>Proceedings of the 1992 1st National</u> <u>Thermogenic Cooler Conference - Attendee list</u>. Fort Belvoir, VA, Center for Night Vision and Electro-Optics (unpublished).
- Hsu, K. F., S. Loo, et al. (2004). "Cubic AgPb<sub>m</sub>SbTe<sub>2+m</sub>: Bulk Thermoelectric Materials with High Figure of Merit." <u>Science</u> **303**: 818-821.
- Kadota, M. and K. Yamamoto (2008). "Advanced Transient Simulation on Hybrid Vehicle Using Rankine Cycle System."
- Lewis, N. S. and G. W. Crabtree. (2005). "Basic Research Needs for Solar Energy Utilization: Report on the Basic Energy Sciences Workshop on Solar Energy Utilization,

April 18-21, 2005." from <u>http://www.sc.doe.gov/bes/reports/abstracts.html#SEU</u>.

- Poudel, B., Q. Hao, et al. (2008). "High-Thermoelectric Performance of Nanostructured Bismuth Antimony Telluride Bulk Alloys." <u>Science</u>: 1156446.
- Tritt, T. M., H. Böttner, et al. (2008). "Thermoelectrics: Direct Solar Thermal Energy Conversion." <u>MRS Bulletin</u> 33(4): 366-368.
- Venkatasubramanian, R., E. Silvola, et al. (2001). "Thin-film thermoelectric devices with high room-temperature figures of merit." Nature **413**(6856): 597-602.
- Vining, C. B. (2007). "ZT ~ 3.5: Fifteen Years of Progress and Things to Come." <u>European Conference on</u> <u>Thermoelectrics, ECT2007</u>, from <u>http://ect2007.its.org/system/files/u1/pdf/02.pdf</u>.
- Vining, C. B. (2008). "Materials science: Desperately seeking silicon." <u>Nature</u> 451(7175): 132-133.
- Zener, C. (1960). The Impact of Thermoelectricity upon Science and Technology. <u>Thermoelectricity</u>; including <u>the proceedings of the Conference on Thermoelectricity</u>, <u>September, 1958</u>. P. H. Egli, Wiley, New York: 3-22.