PROPECTS FOR EFFICIENT THERMOELECTRIC MATERIALS IN THE NEAR TERM

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The issue of thermoelectric efficiency is examined from the standpoint of what material figures-of-merit (FOMs) will enable solid-state devices to compete with conventional electricity generators or vapor-compression refrigerators. It is estimated that FOMs of ZT ≥8 will be required. Some of the emerging new bulk materials may eventually reach that level of performance, but probably not in the near term. Multilayer thin films appear to have the best chance of attaining the requisite FOMs within the next few years.

INTRODUCTION

Despite the fact that thermoelectric devices are compact, quiet, rugged, stable, and very reliable, thermoelectrics have found only niche applications because they are also inefficient (less than 5% conversion efficiency is typical) and costly. The key to more widespread acceptance of thermoelectrics is discovery of materials that are capable of much higher conversion efficiencies than those now available.

It proves convenient to discuss the search for such materials in terms of a quality approximation or figure-of-merit (FOM) defined in units of K^{-1} as

$$Z = \alpha^2/\rho\kappa\,, \tag{1}$$

where α is $\Delta V/\Delta T$ (the Seebeck coefficient), V is voltage, T is absolute temperature, ρ is electrical resistivity, and κ is thermal conductivity. The FOM is often quoted as a dimensionless parameter ZT, which is the usage adopted here.

For more than 35 years, the best performance of thermoelectric materials has hovered around ZT ≈1, which corresponds to a conversion efficiency on the order of 5% for practical devices. Clearly, this is not good enough to compete with conventional generators and coolers. Consumers would probably pay a premium for the attributes of thermoelectricity (no moving parts, quiet operation, and reliability) only if the performance were comparable to the conventional alternatives. Lately it has been said that if materials with ZT ≥3 could be found, thermoelectric systems would have efficiencies close to that of an ideal Carnot engine and solid-

state devices could then replace commercially-available electricity generators and compressor-based refrigerators.[1-5] Our intention here is to look more closely into the issue of required FOMs and to judge the near-term prospects for discovering or developing materials that measure up to those requirements.

HOW GOOD IS GOOD ENOUGH?

For the purposes of this discussion, thermal efficiency will be the criterion for comparisons. Since efficiency considerations are somewhat different between electricity generation and refrigeration, the two applications are examined separately.

Electricity Generation

The efficiency of thermoelectric devices that depend on the Seebeck effect is expressed as[6]

$$\eta = \frac{T_{hot} - T_{cold}}{T_{hot}} \left[\frac{(1+ZT)^{1/2} - 1}{(1+ZT)^{1/2} + T_{cold}/T_{hot}} \right] \qquad (2)$$

In other words, the overall efficiency is the Carnot efficiency, $(T_{hot}-T_{cold})/T_{hot}$, degraded by the factor in brackets in Eqn. (2), which for convenience is called the Fraction of Carnot Efficiency (FCE). Whereas overall efficiency depends on the specific hot side and cold side temperatures, FCE depends only on ZT and the temperature ratio (T_{cold}/T_{hot}), which can be depicted parametrically. Fig. 1 shows the relationship among ZT, T_{cold}/T_{hot}, and FCE. Notice that for realistic temperature ratios ($T_{cold}/T_{hot} \geq 0.3$), reaching just 50% of Carnot efficiency requires ZTs in the range 4.3 to 6.3.

To be competitive, a thermoelectric generator would have to match the capability of whatever conventional machine it is intended to replace. A likely competitor for electricity generation at high temperatures is the combustion turbine with an overall efficiency of 35-37%. Just for illustration, assume that a thermoelectric generator can operate with hot side and cold side temperatures of 2000K and 900K, respectively. This equates to an ideal Carnot efficiency of 0.55. In order to match the efficiency of a combustion turbine, then, the FCE of the thermoelectric generator would have to be about 0.64, which this corresponds in Fig. 1 to a ZT of

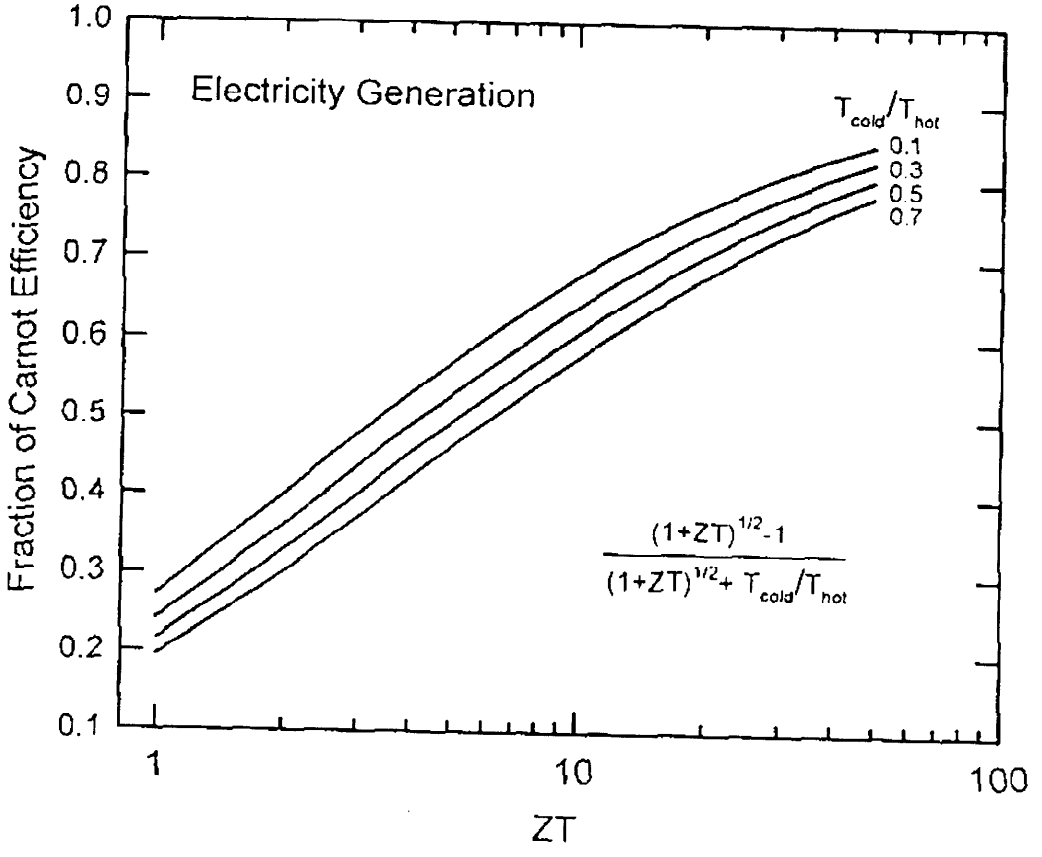

Fig. 1. Fraction of Carnot efficiency as a function of ZT and temperature ratio for thermoelectric generation.

about 12. Whether or not achieving this level of performance is even possible will be addressed later.

Topping cycles are not the only anticipated application for thermoelectric generators. Bottoming cycles, involving conversion of low-grade heat from incineration of municipal solid wastes, industrial boilers, or ground-vehicle exhaust, could also have significant impact; in these sectors the conventional competition is probably less efficient than the combustion turbine.

Refrigeration

Coolers based on the Peltier effect are even more restricted than thermoelectric generators, in part because heat must be pumped "uphill" (the Peltier flux is opposed by heat conduction) and in part because temperatures are low and ZT scales with temperature. As Sharp[7] points out, ". . . ZT = 1 at 100K is as great a challenge as ZT = 3 at 300K or ZT = 6 at 600K."

Cooling systems are characterized conventionally by a Coefficient of Performance (COP), which is the ratio of the cooling power (q_w) to the rate at which electrical energy is supplied (W). The ideal or "Carnot COP" is $T_{cold}/(T_{hot}-T_{cold})$. Inserting temperatures typical of residential refrigerators, T_{hot} = 315K and T_{cold} = 270K, gives a Carnot COP of 6.

The COP of Peltier coolers is given by[6]

$$COP = \frac{q_w}{W} = \frac{T_{cold}}{T_{hot} - T_{cold}} \left[\frac{(1+ZT)^{1/2} - T_{hot}/T_{cold}}{(1+ZT)^{1/2} + 1)} \right] \tag{3}$$

Again, the "Carnot efficiency" is degraded by the quantity in brackets (FCE), which is shown parametrically in Fig. 2. It is seen in Fig. 2 that 50% of Carnot COP for realistic temperature differences requires ZT >10.

As was the case for generators, the competitiveness of thermoelectric coolers depends on the capabilities of conventional machines, e.g., refrigerators based on the vapor compression (V-C) cycle. Lyon indicates that the efficiencies of V-C refrigerators are capacity dependent.[8] There appears to be no *thermodynamic* reason why the V-C cycle should be capacity dependent; apparently "extraneous" features (such as insulation quality, seals, circulation fans, etc.) are responsible, and it is hard to quantify those effects. Instead, we estimate the factors that might

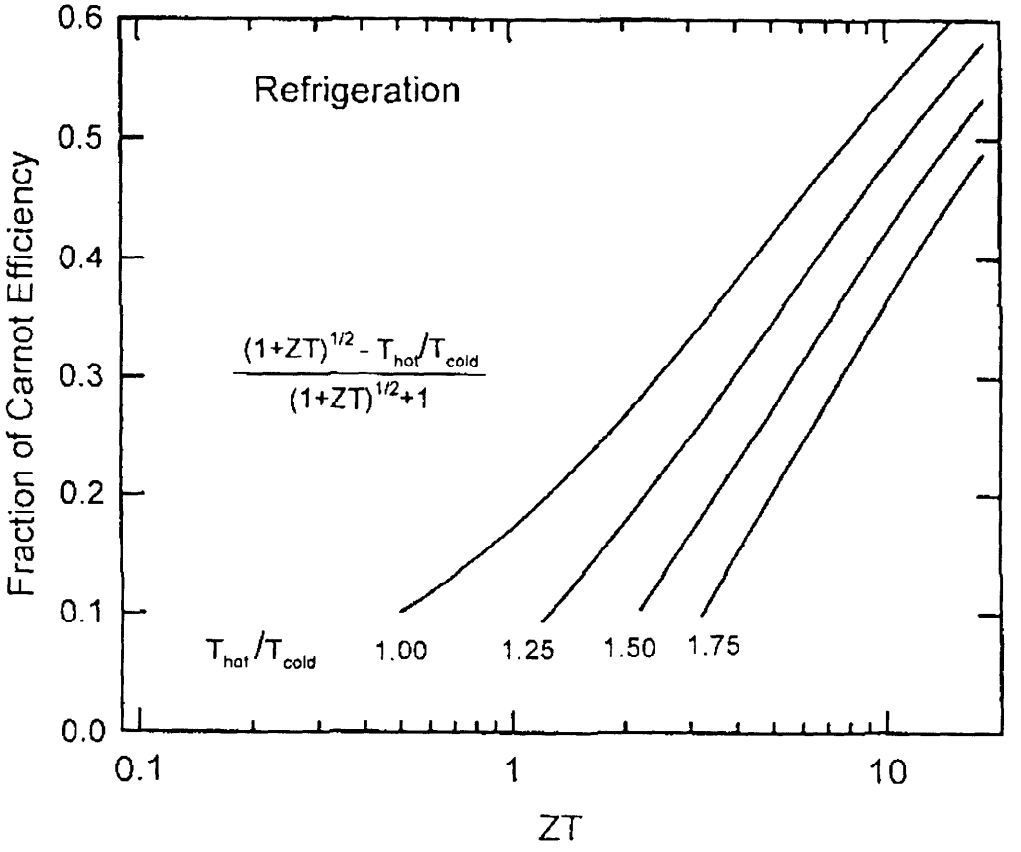

Fig. 2. Fraction of Carnot efficiency as a function of ZT and temperature ratio for Peltier cooling.

affect the COP of the V-C cycle: evaporating and condensing temperatures (ΔT); compressor efficiency; and drive motor efficiency. Typical values for the first two factors are 0.82 (for ΔT of 45K) and 0.8 for a low-pressure reciprocating compressor.[9] Further, assume an efficiency of 0.7 for a fractional-horsepower electric motor in typical household appliances, which results in an FCE of (0.82)(0.8)(0.7) = 0.46. Referring to Fig. 2, an FCE of 0.46 at a T_{hot}/T_{cold} ratio of 1.17 corresponds to a ZT of about 8, which might be considered as a lower bound for thermoelectric materials in order for Peltier coolers to compete successfully with modest-size V-C refrigerators.

THE PACE OF PROGRESS

In the preceding section, it was argued that thermoelectric FOMs required for competitiveness in either electricity generation or refrigeration are of the order of ZT $\geq$8, which is higher than is usually implied in the current literature. If these higher target levels are true, a reevaluation of where thermoelectrics are now and how fast they are changing may be worthwhile.

Recent research has brought about incremental improvements (FOMs between 1 and 2) in several material categories, and theoretical prescriptions of where and how to look for new bulk materials with ZT >1 have identified interesting avenues for exploration. Nevertheless, if ZTs for old and new materials are plotted against the dates they were announced, as in Figs. 3 and 4, and the extrapolations are compared with the requirements for competitiveness, it appears that at the present rate of improvement it would be many years before bulk-material thermoelectrics could replace conventional electricity generators or refrigerators.

What are the prospects for markedly increasing the improvement rate of bulk thermoelectrics in the near term? Not bright, for two reasons. In the first place, the avenues suggested by theory, however meritorious, cannot be explored quickly. Systematic, experimental searches must be conducted, for example, for mixed-valence rare-earth compounds[10] or for ternary systems with voids in the crystal structures (clathrates or cryptoclathrates) in which "guest" atoms can be loosely trapped.[11] In the second place, it is not certain that the requisite high Seebeck coefficient (α), low electrical resistivity (ρ), and low thermal conductivity (κ) are even achievable simultaneously in a real bulk material. Normally, an increase in α implies an increase in ρ (owing to carrier density considerations), and a decrease in ρ implies an increase in

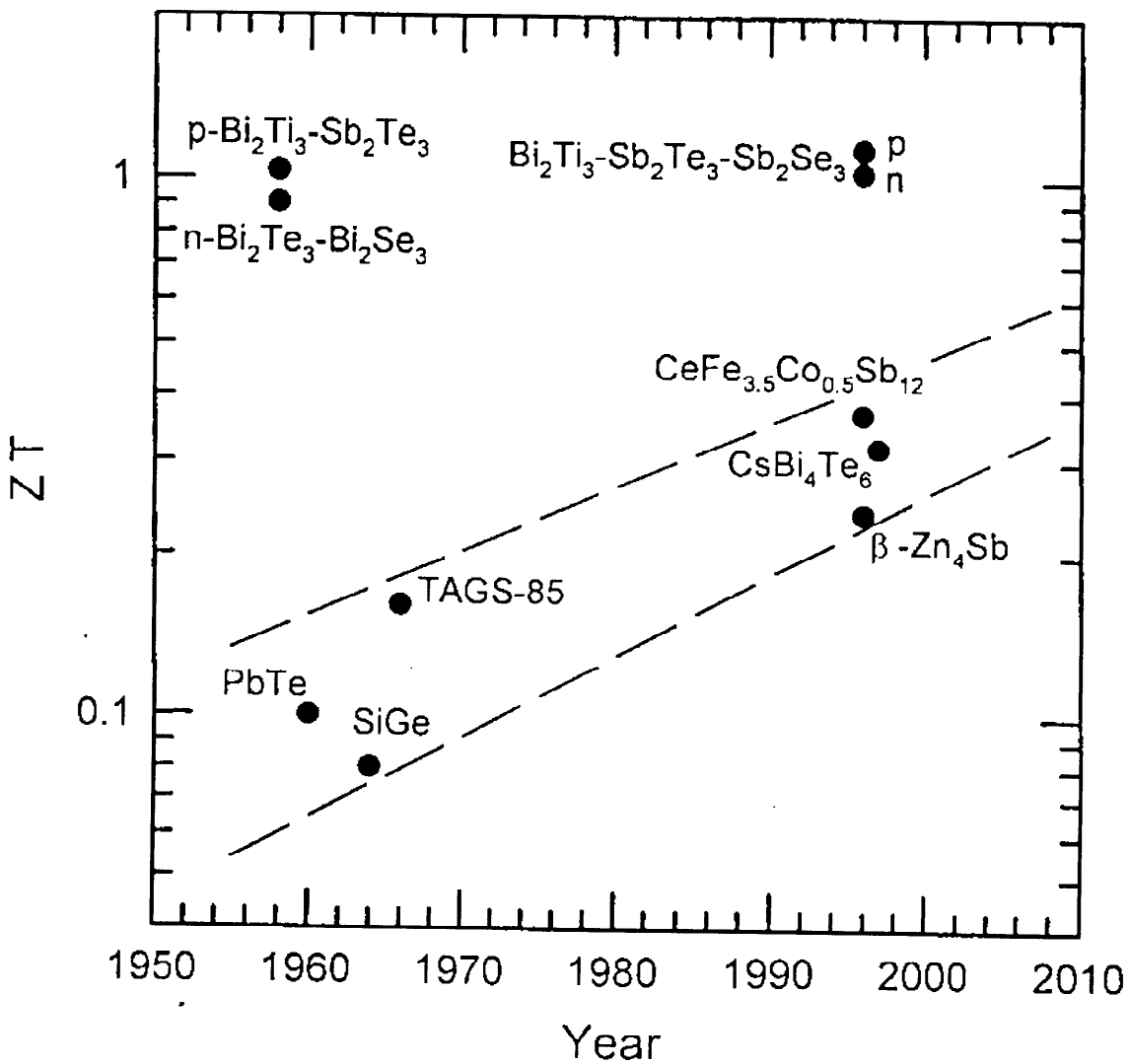

Fig. 3. Historical trend of ZT at 300K for bulk thermoelectric materials

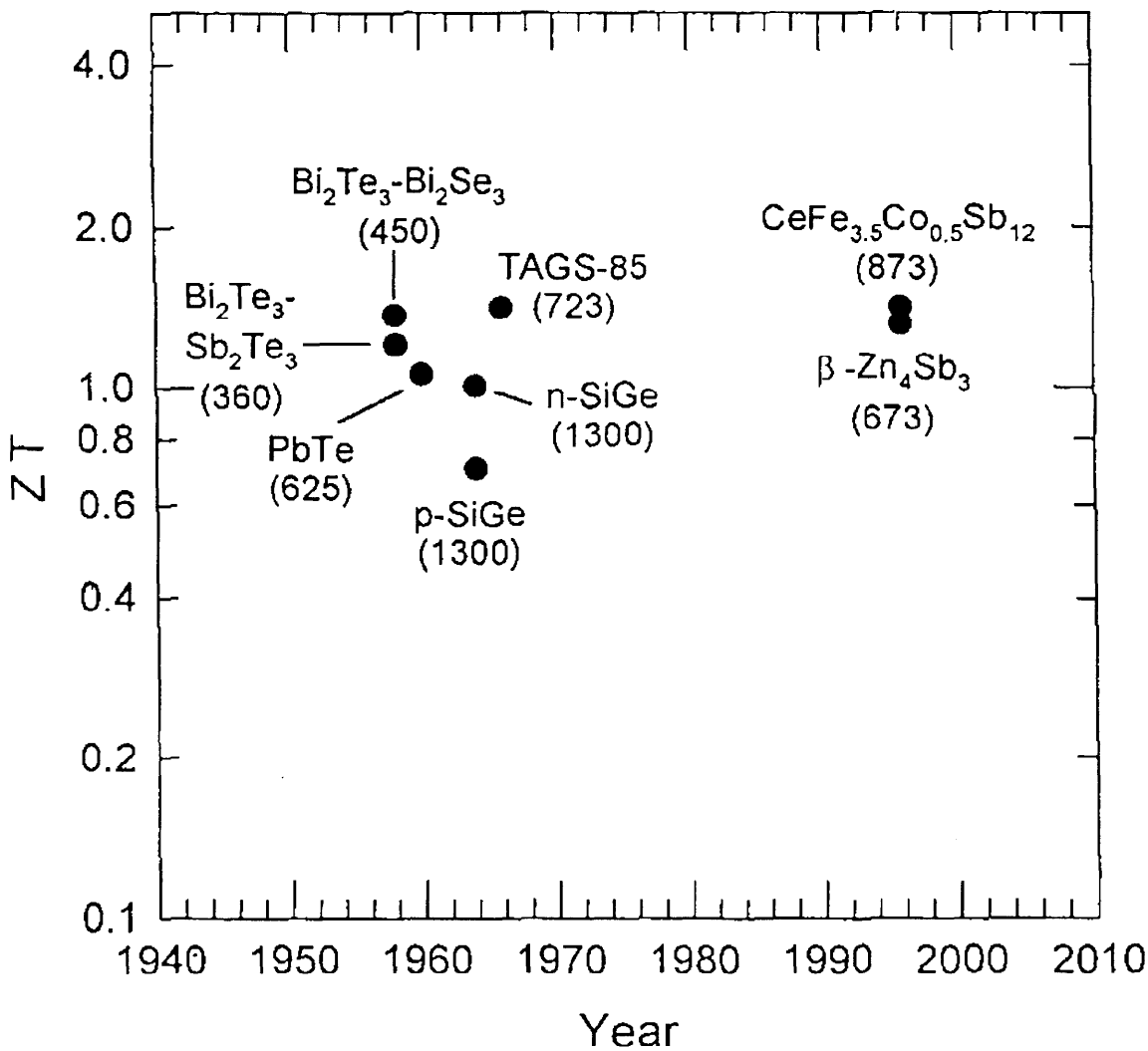

Fig. 4. Historical trend of ZT at elevated temperatures for bulk thermoelectric materials; numbers in parentheses are the temperatures in degrees Kelvin at which the properties were measured.

the electronic component of κ (the Wiedemann-Franz law). Similar considerations have led Goldsmid to suppose that ZT will never be greater than about 2 for any bulk conductor.[12]

ALTERNATIVES TO BULK MATERIALS

In a nutshell, then, the problem with bulk thermoelectrics is that the constituents of ZT (α, ρ, and κ) are not independent. In order to increase ZT significantly, the contributing parameters must be uncoupled from each other to some degree. Compositionally-modulated thin films are a way to accomplish uncoupling. One category of compositionally-modulated structures is the two-dimensional quantum well (2DQW)[13]: a nanometers-thick layer of a smaller bandgap semiconductor sandwiched between thin barrier layers with a larger bandgap. If the layers are thin enough (less than the de Broglie wavelengths of the charge carriers), and the difference in bandgaps is large enough, then all the mobile charge carriers will be in the layer with the smaller bandgap and all the charge carriers will be confined to motion in two dimensions instead of three. In other words, the charge carriers will be in a "quantum well."

The consequences of restricting electrical conduction to two dimensions are approximately as follows[14]: interaction among the charge carriers (overlap of wave functions) is reduced because one dimension of interaction is eliminated; owing in large part to the reduced interaction, the energy ranges of the charge carriers are narrowed (quantization of energy levels), which is reflected as an increase in the number of charge carriers per unit of mass (density of states at the Fermi level), which in turn increases the thermopower (α). At the same time, electrical conductivity in the plane of the active layer does not suffer (ρ does not increase) since confining the charge carriers to two dimensions means that they cannot scatter off the interfaces between layers, while their mobility parallel to the layers is unchanged. Finally, thermal conductivity (κ) is lowered because the carriers of heat (phonons) are not restricted to two dimensions and they do scatter off the interfaces. The net effect is that the ZT parameters are uncoupled from each other, at least in part, and ZT is increased.

A second strategy for enhancing ZT is by way of short-period superlattices[15] (SPSLs). Alternate layers, nanometers thick, are built up much as they are in 2DQWs, except that the bandgap differences are smaller (less than thermal activation). Instead, the acoustic mismatch between the superlattice components is exploited to exert a profound effect on phonon transport,

resulting in phonon-blocking but electron-transmitting structures.[16] In 2DQW heterostructures, the current flow and heat flow are in the plane of the thin films; the barrier layers do not contribute to either the Seebeck current flow or to the Peltier heat flow. In contrast, both kinds of layers contribute to thermoelectric performance of SPSLs. Moreover, current and heat flow are perpendicular to the SPSL layers, which should be advantageous for constructing practical thermoelectric modules.[15]

Some recent results for 2DQWs and SPSLs are summarized in Table 1 and Fig. 5. Although the points plotted in the figure are based on experimental measurements, it is emphasized that most of the points are really estimates. At the time the investigations were published, thermal conductivities could not be measured reliably in the plane of the thin films and power factors (α^2/ρ) could not be measured perpendicular to the film plane. Nevertheless, even worst-case assumptions suggest that thermoelectrics based on 2DQWs or SPSLs could reach competitive performance levels in the near term.

An Illustration of One Strategy

A good example of an approach to practical thermoelectrics for electricity generation is the work on boron carbide layered structures reported by Ghamaty and co-workers.[17, 19] The thermoelectric properties of boron carbides seem ot be of the "right"kind[20-22]: Large Seebeck coefficients that *increase* with temperature, small thermal conductivities that *decrease* with temperature, thermally-activated electrical conductivity (polaron hopping), and stability at high temperatures. Ghamaty, *et al.*,[17, 19] took advantage of these property trends by assembling thermoelectric devices from B_4C/B_9C multilayers grown by MBE as p-type legs and either bulk or layered $Si_{0.8}Ge_{0.2}$ or bulk Bi_2Te_3 as the n-type legs. Device efficiencies are claimed to be in the range 15% to 26% with n-Bi_2Te_3 operating between T_{cold} = 523K, and up to 40% with n-SiGe operating between T_{cold} = 323K and T_{hot} = 1273K. Again, it should be borne in mind that the quoted efficiencies are only estimates because thermal conductivity of the multilayers was assumed to be the same as bulk B_4C and corrections were calculated for contributions of the substrate silicon wafer to both the Seebeck coefficients and resistivities. Moreover, electrical connections were made to the multilayers by wrapping nickel wire around the specimens and bonding the wires to the surfaces with silver paint.[17,19] Such connections are a far cry from the

Table 1. FOMs for 2DQWs and SPSLs

System	T, °K	ZT (estimated)	Date	Ref.
Bi_2Te_3-Sb_2Te_3 SPSL	300	3-4 from power-factor parallel and κ perpendicular	1996	15
n-PbTe/$Pb_{1-x}Eu_xTe$ 2DQW	300	1.2 from measured power factor and bulk κ	1996	13
n-PbTe/$PbSe_{0.98}Te_{0.02}$ 2DQW	300	0.88 from measured power factor and calculated κ	1999	18
	550	2 from measured power factor and calculated κ		
n-Si/Ge SPSL	300	0.4 from power factor parallel and κ perpendicular	1997	15
B_4C/B_9C Multilayer thin film (2DQW)	300	3.06 from κ for bulk	1996	17
	1273	48.6 from κ for bulk	1996	17
B_4C/B_9C-n-Bi_2Te_3 2DQW bulk	T_{cold} = 313 T_{hot} = 363	4.95 bulk κ assumed	1999	19
	T_{cold} = 323 T_{hot} = 523	3.2-18.7 depending on κ assumptions		

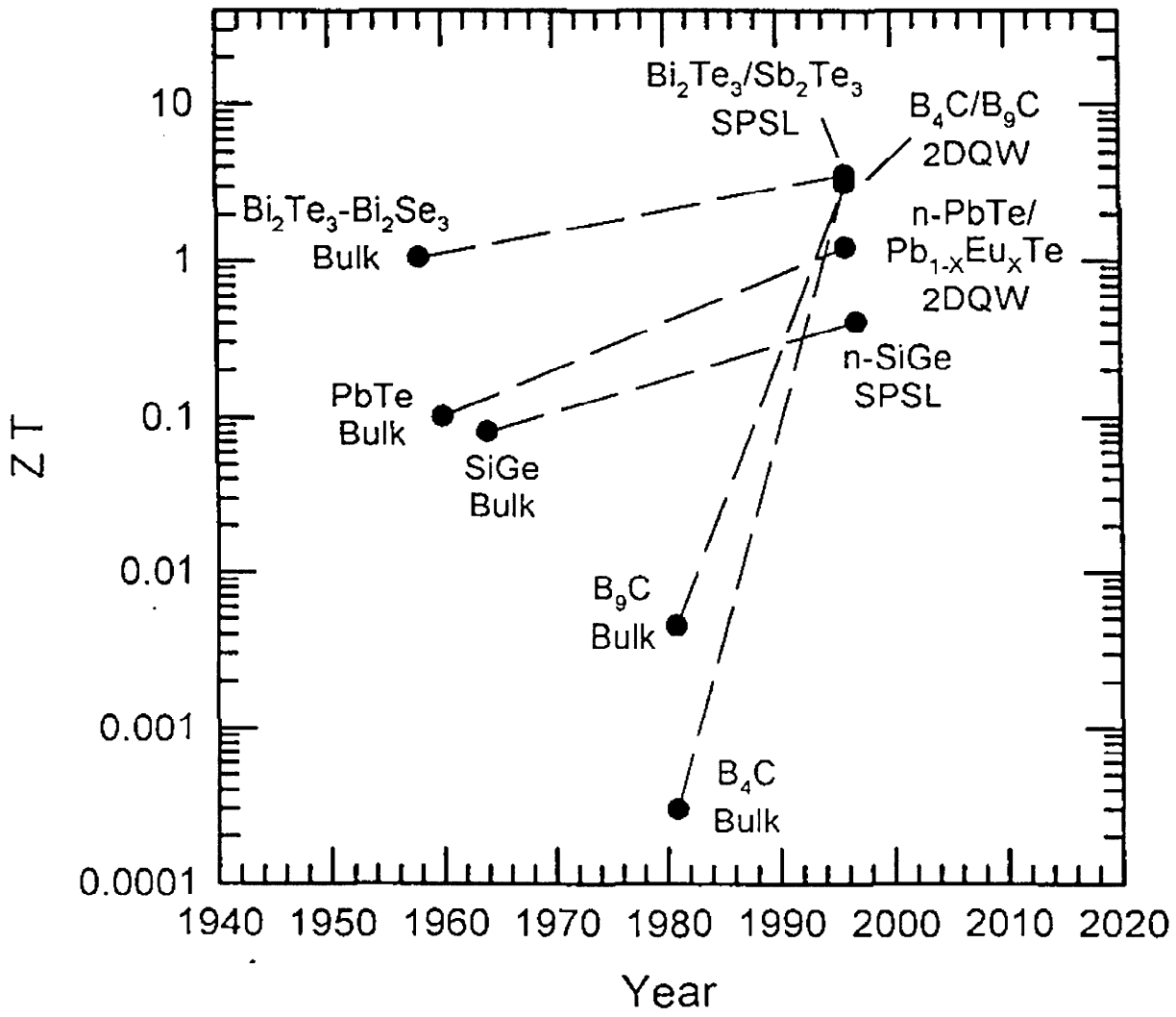

Fig. 5. ZTs at 300K compared for bulk thermoelectrics and multilayer thin films; connecting lines suggest progress trends

quality required for commercial devices. Nevertheless, these glimpses of unprecedentedly high FOMs lend credence to the multilayer approach to competitive thermoelectics.

THERMOELECTRICS AND THE POWER INDUSTRY

Naturally, the power industry would be very interested if thermoelectrics could be developed for electricity generation at very high temperatures, i.e., topping cycles. However, the megawatt scale required for such devices makes it very unlikely that multilayer heterostructures could be made large enough to fulfill that function, at least in the foreseeable future. By the same reasoning, replacement of the boilers and turbomachinery associated with Rankine cycle generation of electricity seems equally unlikely. In contrast, demand-side applications, particularly residential refrigeration and air conditioning, represent an immense consumption of electricity by modest-size machines. It is in this sector that thermoelectrics can have an impact on the electric power industry.

SUMMARY

The quality of a thermoelectric material is approximated by a dimensionless figure-of-merit (FOM), ZT. Established thermoelectric materials were all developed in the 1960s and all are characterized by $ZT \leq 1$, which corresponds to conversion efficiencies of about 5% for practical devices. Although many materials have been investigated in the last 30 years or so, thermoelectric efficiencies have not improved very much. More efficient materials would make feasible the widespread use of thermoelectric converters in everyday applications.

A common rule of thumb suggests that a value of $ZT \approx 3$ would make thermoelectric devices economically competitive for both electricity generation and refrigeration. It is shown here that much higher FOMs will be required; depending on the competition, $ZT \approx 8$ for refrigeration and $ZT \approx 12$-20 for electricity generation are probably reasonable estimates.

Achievement of the requisite FOMs in the near term is judged unlikely for bulk materials. However, layered thin-film structures based on two-dimensional quantum wells and short-period superlattices appear to have the qualities that will enable fairly rapid attainment of FOMs that signal economic competitiveness.

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