1. Introduction

The performance of a thermoelectric energy converter, either as a heat pump or a generator, can be expressed in terms of the hot and cold junction temperatures and a quantity known as the figure of merit, $zT$. During the second half of the twentieth century the figure of merit has gradually improved. This has come about through the selection of semiconductor materials with improved electronic properties and a small lattice thermal conductivity. Further advancements have been achieved by enhancing the scattering of phonons. There is also the possibility of improving the so-called power factor, that is the part of the figure of merit that contains the Seebeck coefficient and the electrical conductivity. However, it appears that it will be increasingly difficult to make further advances because of the manner in which these quantities vary with the Fermi energy. It is shown that this may set a practical limit on $zT$. Nevertheless, it may be possible to reach an efficiency or COP of about 40% of that of an ideal thermodynamic machine.

We suppose that the temperature difference, $\Delta T$, between the junctions is much smaller than the absolute temperature, $T$. Then, if the device is used as a generator, the efficiency is

$$\eta = \frac{\Delta T (M - 1)}{T (M + 1)}$$

(2)

where $M$ is equal to $(1 + ZT)^{1/2}$. Likewise, the coefficient of performance in the heat pump mode is

$$\phi = \frac{T (M - 1)}{\Delta T (M + 1)}$$

(3)

under the same condition $\Delta T \ll T$.

It is common practice to make use of a figure of merit $zT$ for a single material defined as $\alpha^2\sigma/\lambda$. The
The magnitude of the Seebeck coefficient is a measure of the energy difference between the Fermi levels of the two branches of a thermocouple. It is given by the formula $S = \frac{\Delta V}{\Delta T}$, where $\Delta V$ is the voltage difference and $\Delta T$ is the temperature difference between the two branches.

In general, the Seebeck coefficient is positive for materials that have a lattice that is more ordered, and negative for materials that have a more disordered lattice. However, for materials that have a mixed lattice, such as skutterudites, the Seebeck coefficient can be both positive and negative, depending on the orientation of the crystal.

The Seebeck coefficient is also influenced by the size of the crystal and the material properties. In general, larger crystals tend to have a lower Seebeck coefficient, while materials with lower atomic weights tend to have a higher Seebeck coefficient.

The Seebeck coefficient is also affected by the doping level of the material. For example, p-type silicon has a higher Seebeck coefficient than n-type silicon, due to the presence of holes as the majority carriers.

In conclusion, the Seebeck coefficient is a valuable property for materials used in thermoelectric devices, as it determines the efficiency of energy conversion. By understanding the factors that influence the Seebeck coefficient, researchers can design materials with optimized thermoelectric performance.
4. The electronic properties

The value of $\mu (m^*/m)^{3/2}$ for p-type bismuth telluride at room temperature is 560 cm$^2$/V s. This is approached in few other materials, though it is equal to 2200 cm$^2$/V s for electrons in pure silicon. [A table of semiconductor properties is to be found in the CRC Handbook of Chemistry and Physics, 91st Edition, 2010–2011]. One might expect, then, that the power factor should be four times larger for silicon than for bismuth telluride. However, this turns out not to be the case. The electron mobility falls rapidly as impurities are added to silicon in order to optimize the carrier concentration. Ionized-impurity scattering is less noticeable in bismuth telluride because its much larger dielectric constant shields the electrons. It is just possible that a high electron mobility might be maintained in heavily-doped silicon if the necessary impurities are present as charged nanoparticles rather than as ions [9].

Hicks and Dresselhaus [10] actually proposed that nanostructured thermoelectrics would have an improved power factor compared with that of bulk material. This has prompted studies of nanostructured material and indeed a figure of merit $ZT$ as large as 2.4 was reported for a nanostructured bismuth telluride alloy [11]. However, this large value has yet to be confirmed. In any case, even if the improvement is real, it is due to a reduction of the lattice thermal conductivity rather than any change in the electronic properties. Nevertheless, the adoption of nanostructures does offer the prospect of improving $ZT$ in the future.

It is now realized that the relationship between the Seebeck coefficient and the electrical conductivity in any given semiconductor is not unique. Thus, one of Ioffe’s suggestions was the deliberate introduction of ionized impurities to scatter preferentially the low energy carriers [1]. The reduction in mobility could be more than compensated by an increase in the Seebeck coefficient. This effect is likely to be of only marginal significance for most materials but it could be important when the energy gap is small or even negative as it is for bismuth. Bismuth would have a value of $zT$ in excess of unity if conduction by positive carriers could be suppressed or if the low energy carriers could be preferentially scattered. It is quite possible that bismuth and bismuth-antimony will come into prominence as thermoelectric materials at ordinary temperatures through some such effect. A considerable enhancement of the figure of merit in bismuth has been reported for samples produced by a chemical exfoliation – spark plasma sintering process [12].

5. A barrier to further improvement

In selecting thermoelectric materials many workers use a dimensionless quantity $\beta$ [13] that is given by

$$\beta = \left(\frac{k}{\sigma}\right)^2 \frac{\sigma_0 T}{\lambda L}$$

where $k$ is Boltzmann’s constant and $\sigma_0$ depends on the mobility and effective mass according to

$$\sigma_0 = 2e\mu \left(\frac{2\pi m^* kT}{\hbar^2}\right)^{3/2}$$

$\beta$ has a value of 0.4 for a bismuth telluride alloy with $ZT$ then equal to about 1. $\beta$ would be equal to about 3.2 for a material with $\mu (m^*/m)^{3/2}$ equal to its value for pure silicon combined with a glass-like lattice thermal conductivity. Such a material with an optimized carrier concentration should have $ZT$ equal to about 4 and a Seebeck coefficient approaching ±400 $\mu$V/K. This would seem to be the best that one might hope for in the near future.

In fact, even if larger values of $\beta$ are forthcoming, it may still be difficult to obtain much greater values of $ZT$. The problem is that the Seebeck coefficient varies more or less linearly with the Fermi energy whereas the carrier concentration has a near exponential dependence. As $\beta$ increases, the optimum Seebeck coefficient becomes somewhat larger but the carrier concentration becomes much smaller. Figure 1 shows how $zT$ is expected to vary with $\beta$. Once $zT$ becomes greater than unity, further improvement requires much larger values of $\beta$. $\beta$ is equal to about 0.4 for a bismuth telluride alloy with $zT = 1$ and has to rise to about 3.2 for $zT$ to reach 4. A further doubling of $\beta$ only allows $zT$ to climb to about 5.

At the present time there are a few materials with $zT$ close to unity near room temperature. This allows us to make single-stage thermoelectric refrigerators that cool to about 90° below room temperature. A thermoelectric heat pump operating with a temperature difference between the source and sink of 30 degrees has a coefficient of performance of about 1. With $zT = 4$ the coefficient of performance would rise to about 3 for the same hot and cold junction temperatures. This would make thermoelectric heat pumps very attractive but even now they can be a viable alternative to conventional devices. One of the most convincing demonstrations of the virtues of thermoelectric air conditioning was a long-running trial on the French railways [14]. A 20 kW unit was installed in a train operating a regular service out of Paris. The unit worked perfectly with no failures over a period of ten years.

Perhaps the most important potential application is electrical generation from a low grade heat source. If $ZT$ were equal to 4 the efficiency would be nearly 40% of that of an ideal machine. It is remarkable that this could be achieved with a system having no moving parts and capable of operating over a wide temperature range.
6. Conclusions

In summary, following the significant improvements in materials during the second half of the twentieth century it should now be possible to make thermoelectric generators and heat pumps that can compete with conventional devices. However, because of the manner in which the Seebeck coefficient and the electrical conductivity depend on the charge carrier concentration, it will be increasingly difficult to attain further improvements in the figure of merit $ZT$. Nevertheless, with this quantity rising to about 4, thermoelectric energy converters should still find widespread application.

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Disclosure statement

No potential conflict of interest was reported by the author.

Notes on contributor

Prof. H. Julian Goldsmid received his PhD in 1958 from the University of London. From 1969 he was Professor of Experimental Physics at the University of New South Wales, and Emeritus Professor from 1988 to the present. In 1954 he developed the first viable thermoelectric refrigerator using bismuth telluride thermoelements under the guidance of his group leader R. W. Douglas. For this work Goldsmid is widely regarded as the father of modern thermoelectricity, though he would dispute this claim. Bismuth telluride alloys are still the preferred thermoelectric materials with sufficiently high energy conversion efficiency near room temperature today. In addition to his work on bismuth telluride-based materials, he has made significant discoveries relating to thermal and electrical transport solids. He was the first to demonstrate bipolar heat conduction, a phenomenon of great practical as well as theoretical significance. His ideas are still the inspiration for work on the development of new and improved thermoelectric materials. He received NIMS Award 2020 for his pioneering work in thermoelectric materials.

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