Thermoelectric Current Generation: Thermodynamic Limits, Scientific Confusion and Practical Achievements

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Thermoelectricity was discovered and is known since over a century ago. In 1823 the German physicist Seebeck discovered that a voltage was developed in a loop containing two dissimilar metals, provided the two junctions maintained at different temperatures. A decade later, French scientist Peltier found that electrons moving through a solid could carry heat from one side of the material to the other side. The ratio of heat flow to current for a particular material is known as Peltier coefficient, Π. Its value is closely related to another intrinsic property, the Seebeck (S) coefficient. Thomson (Lord Kelvin) established a relationship between the Seebeck and Peltier coefficients and predicted the third thermoelectric effect, the Thomson effect. This effect relates to the heating or cooling in a single homogenous conductor when a current passes along it in the presence of a temperature gradient.

These three effects are connected to each other by a simple relationship: $S = \Pi / T$. All three effects are the simple consequence of the fact that electrons, besides possessing an electrical charge, also carry a certain amount of entropy. Therefore every charge flow (electrical current I=dQ/dt) due to electron movement will also be coupled to an entropy flow (J=dS/dt). In a more modern thermodynamic treatment this can be seen as a directly coupled entropy and charge flux, so that an electrical potential gradient (an applied voltage) besides causing an electrical current flow will also lead to an entropy flux in the same way as a thermal gradient (a temperature difference) will additionally lead to an electrical current.

From this it is easy to determine the thermodynamic limit for thermal generation of an electrical current as well as for the electrical generation of a heat flux. It turns out that this limit is used in many publications as a “figure of merit, ZT”. Thermodynamically the upper limit of this value would be unity. However, in a practical device not only a high voltage (or temperature difference) must be produced, but a high power output (i.e. U*I or T*J, respectively). Here, loss mechanisms such as the electrical or thermal resistance of the devices come into play, so that for an Ohmic device the upper limit of the power output even decreases a maximum achievable figure of merit to 0.25. In addition, using the generated voltage by allowing current flow in an outer circuit also leads to an entropy flux in the outer circuit and thereby creates an additional loss of thermal energy.

All this seems to be relatively trivial. However, recent publications (1) claim to have achieved figures of merit of above 2. Therefore the main aim of this talk will be to discuss this discrepancy.

In our own investigations we also performed a few measurements in order to determine the additional heat losses in practical devices due to the heat flux in the outer circuit. Here a certain amount of entropy can be determined as carried by every electron. It should be discussed if this might be an universal value and on Which conditions this amount should be depending.

Also the economic aspects of using thermoelectric generators to generate electrical current from "waste" heat sources were investigated (2). Featured with no moving parts, being small in size and light in weight, environmentally friendly with no additional exhaust gases and no noise production, the thermoelectric modules seem to be ideal systems.

However, by analyzing the economical key figures it became apparent, that a cost effective thermoelectric energy conversion is not yet possible on an industrial level, even if realistic possibilities of improving these types of elements exist.

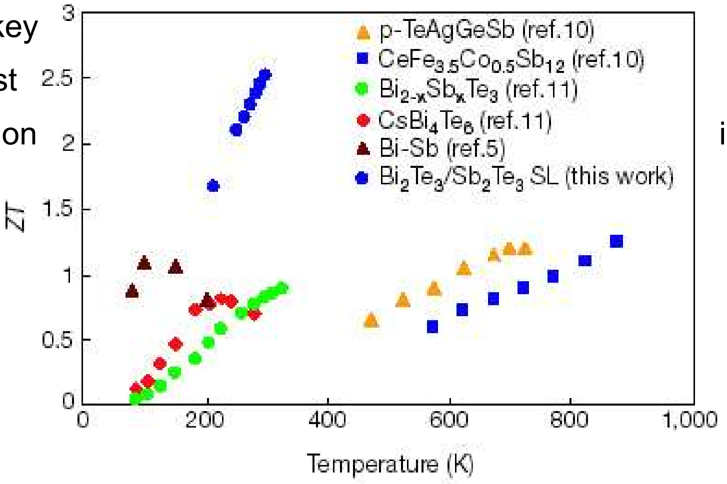

Figure 3 Temperature dependence of ZT of 10Å/50Å p-type Bi_2Te_3/Sb_2Te_3 superlattice compared to those of several recently reported materials.

Figures of Merit as published in (1) Nature 413

References:
[1] R. Venkatasubramanian et al., Nature 413 (2001), 597, B. Vining, (2001), 577 and Nature 423 (2001), 391

[2] Michael Schneiderbauer: “Wirkungsgrad und Wirtschaftlichkeit thermoelektrischer Energiewandlung”, Diplomarbeit, Department of Energy Engineering, UA University of Applied Sciences, Wels, 2005