Chapter 11
Thermoelectric Cooling Through Thermoelectric Materials

Abstract Thermoelectric (TE) cooling has been used for thermal management of high-power-dissipating electrical components, with silent, compact, reliable, and durable characteristics and being modulated to maintain a fixed temperature. However, TE coolers currently in use have a coefficient of performance (COP) of only about 0.5. This is quite a low value compared with COPs of other cooling approaches such as air conditioners and refrigerators at levels of 3.0–5.0. With increasing demands for high performance thermoelectric coolers, advanced emerging TE materials provide probability for improving their efficiency. These emerging materials include new families of advanced bulk TE materials based on crystal structures that contain weakly bound atoms or molecules with large vibrational amplitudes at partially filled structural sites acting as effective phonon scatterers, such as skutterudites, clathrates, and oxides; low dimensional materials systems, such as quantum well superlattices, quantum wires, quantum dots, thin film or band engineering structures; as well as nanocomposites, which demonstrates much higher *ZT* values than that of their bulk counterparts. The nanocomposites can be fabricated inexpensively, quickly, and in a form that is compatible with existing TE device configurations. Further research in this field will allow TE cooling to play a significant role in any future thermal management solution. This chapter will review the principle, design, and application of the TE cooling, as well as the effects of the emerging novel TE materials on its efficiency. The main contents include TE effects, design methodology and multistage architecture of TE cooling devices, and advanced TE materials and future development trends.

Introduction

Thermoelectric cooling uses the Peltier effect to form a solid state heat pump, and works in conjunction with a heat sink to dissipate heat from an electronic packing system. A modern TE cooler is a semiconductor-based electronic component that functions as a small heat pump. By applying a low voltage DC power source to a TE module, heat will be moved through the module from one side to the other. One module face, therefore, will be cooled while the opposite face simultaneously is

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heated. This phenomenon may be reversed, whereby a change in the polarity (plus and minus) of the applied DC voltage will cause heat to be moved in the opposite direction. Therefore, a thermoelectric module may be used for both heating and cooling thereby making it highly suitable for precise temperature control applications (Ferrotec 2010).

In electronic packaging, as shown in Figure 11.1, if a typical single-stage TE module was placed on a heat sink that was maintained at room temperature and the module was then connected to a suitable battery or other DC power source, the cold side of the module would cool down to Δ, for instance −40°C. At this point, the module would be pumping almost no heat and would have reached its maximum rated temperature difference (ΔT). If heat was gradually added to the cold side of the module, the cold side temperature would increase progressively until it eventually equaled the heat sink temperature. At this point the TE cooler would have attained its maximum rated heat pumping capacity ($Q_{\max}$). Actually, TE coolers work principally in a similar fashion to mechanical refrigerators. In a mechanical refrigeration unit, a compressor raises the pressure of a liquid and circulates the refrigerant through the system. In the evaporator or freezer area the refrigerant boils and, in the process of changing to a vapor, the refrigerant absorbs heat causing the freezer to become cold. The heat absorbed in the freezer area is moved to the

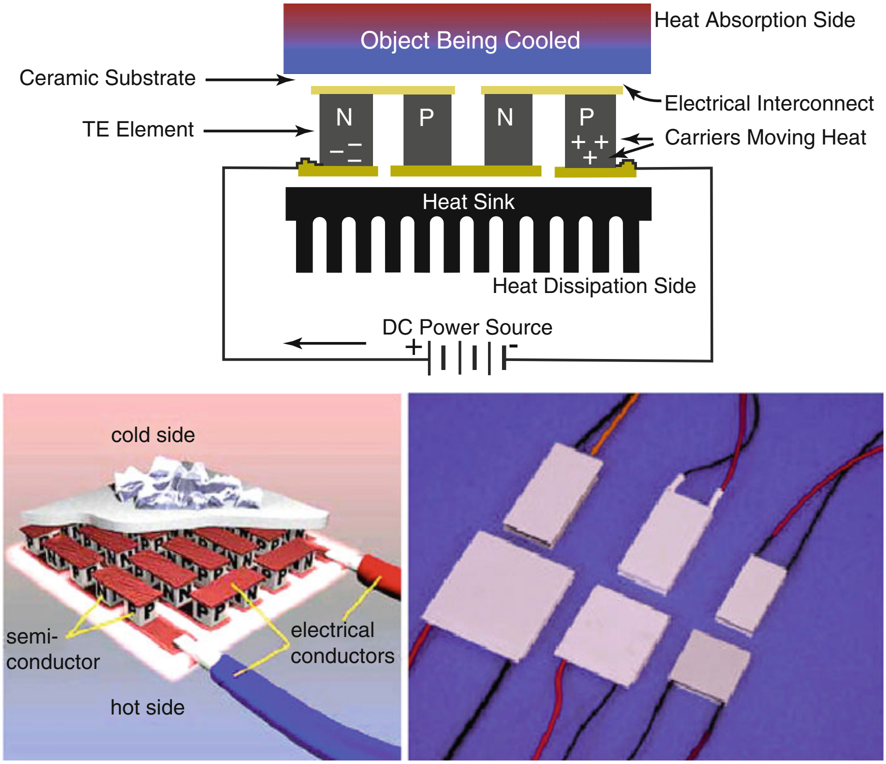

Fig. 11.1 Schematic of thermoelectric cooling device

condenser where it is transferred to the environment from the condensing refrigerant. In a TE cooling system, a doped semiconductor material essentially takes the place of the liquid refrigerant, the condenser is replaced by a finned heat sink or a liquid cooling system, and the compressor is replaced by a DC power source. The application of DC power to the TE module causes electrons to move through the semiconductor material. At the cold end (or freezer side) of the semiconductor material, heat is absorbed by the electron movement, moved through the material, and expelled at the hot end. Because the hot end of the material is physically attached to a heat sink, the heat is passed from the material to the heat sink and then, in turn, transferred to the environment (Ferrotec 2010).

The physical principles upon which modern TE coolers are based actually date back to the early 1800s, although commercial TE modules were not available until almost 1960. The first important discovery relating to thermoelectricity occurred in 1821 when Thomas Seebeck, a German scientist, found that an electric current would flow continuously in a closed circuit made up of two dissimilar metals provided that the junctions of the metals were maintained at two different temperatures. Seebeck did not actually comprehend the scientific basis for his discovery, however, and falsely assumed that flowing heat produced the same effect as flowing electric current. In 1834, Jean Peltier, a French watchmaker and part time physicist, while investigating the Seebeck effect, found that there was an opposite phenomenon whereby thermal energy could be absorbed at one dissimilar metal junction and discharged at the other junction when an electric current flowed within the closed circuit. Twenty years later, William Thomson issued a comprehensive explanation of the Seebeck and Peltier effects and described their interrelationship. At the time, however, these phenomena were still considered to be mere laboratory curiosities and were without practical application. In the 1930s, Russian scientists began studying some of the earlier TE work in an effort to construct power generators for use at remote locations throughout the country. This Russian interest in thermoelectricity eventually caught the attention of the rest of the world and inspired the development of practical TE modules. Currently, TE coolers make use of modern semiconductor technology whereby doped semiconductor material takes the place of dissimilar metals used in early TE experiments (Ferrotec 2010).

Its applications have been limited because of the low values of efficiency that are inherent in current thermoelectric coolers (TECs). A TEC requires relatively large amounts of electrical power in order to produce a cooling effect. In fact, more conventional vapor compression refrigeration systems have as much as a 3 to 1 advantage in efficiency over TEs. In addition, when using the TEC in a system for cooling, the total heat that generated and needed to be removed from the system might be even more than without the TEC. However, TECs can be useful in certain applications where the advantages outweigh the disadvantages. Actually, TECs have no moving parts and do not require the use of chlorofluorocarbons; therefore, they are safe for the environment, inherently reliable, and virtually maintenance free. They can be operated in any orientation and are ideal for cooling devices that might be sensitive to mechanical vibration. Their compact size also makes them ideal for applications that are size or weight limited where even the smallest compressor would have excess capacity. Their ability to heat and cool by a simple reversal of current flow is useful for applications where both heating and cooling is necessary or where precise temperature control is critical. Despite their small size, TEC devices can all create temperature differences of around 70°C. They can also be stacked on top of each other to create even larger temperature differences (up to 130°C). Because of their small size, TECs can be used for localized cooling, where only a small part of the system needs to be cooled. TECs are also useful as active temperature control devices. A simple feedback loop can be used to implement a TEC in a system where a specific temperature is required, because the temperature of one side of the TEC is directly proportional to the input power. The cold side of the device can be either cooled or heated to the proper temperature, depending on the direction of the electrical current. As long as the temperature variation is within the range of the TEC's capability, and a proper heat sink/heat source is used on the other side, the temperature can be controlled quite accurately. Some of the specific features of TE modules include (Ferrotec 2010):

1. *No Moving Parts*: A TE module works electrically without any moving parts so they are virtually maintenance free.
2. *Small Size and Weight*: The overall TE cooling system is much smaller and lighter than a comparable mechanical system. In addition, a variety of standard and special sizes and configurations are available to meet strict application requirements.
3. *Ability to Cool Below Ambient*: Unlike a conventional heat sink where the temperature necessarily must rise above ambient, a TE cooler attached to that same heat sink has the ability to reduce the temperature below the ambient value.
4. *Ability to Heat and Cool with the Same Module*: TE coolers will either heat or cool depending upon the polarity of the applied DC power. This feature eliminates the necessity of providing separate heating and cooling functions within a given system.
5. *Precise Temperature Control*: With an appropriate closed-loop temperature control circuit, TE coolers can control temperatures to better than ±0.1°C.
6. *High Reliability*: TE modules exhibit very high reliability due to their solid state construction. Although reliability is somewhat application dependent, the life of typical TE coolers is greater than 200,000 h.
7. *Electrically "Quiet" Operation*: Unlike a mechanical refrigeration system, TE modules generate virtually no electrical noise and can be used in conjunction with sensitive electronic sensors. They are also acoustically silent.
8. *Operation in Any Orientation*: TEs can be used in any orientation and in zero gravity environments. Thus they are popular in many aerospace applications.
9. *Convenient Power Supply*: TE modules operate directly from a DC power source. Modules having a wide range of input voltages and currents are available. Pulse width modulation may be used in many applications.
10. *Spot Cooling*: With a TE cooler it is possible to cool one specific component or area only, thereby often making it unnecessary to cool an entire package or enclosure.

11. *Ability to Generate Electrical Power*: When used in-reverse by applying a temperature differential across the faces of a TE cooler, it is possible to generate a small amount of DC power.
12. *Environmentally Friendly*: Conventional refrigeration systems cannot be fabricated without using chlorofluorocarbons or other chemicals that may be harmful to the environment. TE devices do not use or generate gases of any kind.

More exotic TEC devices are being developed that could result in better performance such as superlattice structures, quantum wires and quantum wells, thin films using SiGe/Si, and thermionic cooling.

Thermoelectric Effects

The TE effect is the direct conversion of temperature differences to electric voltage and vice versa at the junctions of two different conductors. Traditionally, the TE effect encompasses three separately identified effects, the Seebeck effect, the Peltier effect, and the Thomson effect. These three effects, together with several other phenomena, form the basis of functional TE modules.

Seebeck Effect

The Seebeck effect is the conversion of temperature differences directly into electricity. In 1822, Seebeck discovered that a compass needle would be deflected when a closed loop was formed of two metals joined in two places with a temperature difference between the junctions. This is because the metals respond differently to the temperature difference, which creates a current loop, which produces a magnetic field. However, at this time Seebeck did not recognize there was an electric current involved, so he called the phenomenon the thermomagnetic effect, thinking that the two metals became magnetically polarized by the temperature gradient. The Danish physicist Hans Christian Ørsted played a vital role in explaining and conceiving the term thermoelectricity. The Seebeck effect is then used to describe that a voltage is created in the presence of a temperature difference between two different metals or semiconductors. This causes a continuous current in the conductors if they form a complete loop. The voltage developed can be derived from (Ferrotec 2010):

$$V = \int_{T_1}^{T_2} (S_{\mathrm{B}} - S_{\mathrm{A}})\mathrm{d}T. \tag{11.1}$$

S_{A} and S_{B} are the Seebeck coefficients (also called TE power or thermopower) of the materials A and B as a function of temperature, and T_1 and T_2 are the temperatures of the two junctions. The Seebeck coefficients are nonlinear as a function of temperature, and depend on absolute temperature, material, and molecular structure of the conductors. The Seebeck effect is the principle at work behind thermal diodes and TE generators which are used for creating power from heat differentials. Seebeck coefficient of a material, represented by $S = E_x/(\mathrm{d}T/\mathrm{d}x)$, where E_x is electric field, measures the magnitude of an induced TE voltage in response to a temperature difference across that material. It has units of (V/K), though in practice it is more common to use microvolts per kelvin. Values in the hundreds of μV/K, negative or positive, are typical of good TE materials. The Seebeck effect of a material depends on the material's temperature and crystal structure. Metals typically have small thermopowers because most have half-filled bands. Electrons (negative charges) and holes (positive charges) both contribute to the induced TE voltage thus canceling each other's contribution to that voltage and making it small. In contrast, semiconductors can be doped with excess electrons or holes, and thus can have large positive or negative values of the Seebeck coefficient depending on the charge of the excess carriers.

Peltier Effect

Peltier effect is the reverse of the Seebeck effect, which was discovered by Jean Charles Athanase Peltier in 1834. That is, an applied voltage could create a temperature difference between the two dissimilar metals. Although Peltier is generally credited with the discovery of TE cooling, he did not fully understand the physics of the phenomenon. The full explanation was given four years later by Emil Lenz, who showed that a drop of water on a bismuth-antimony junction would freeze when electrical current was applied one way, and melt again when the current was reversed. As knowledge of TEs increased, the most important discoveries were related to material properties. In 1911, Altenkirch derived the TE efficiency, also called the TE figure of merit Z, which is given as (Mann 2006)

$$Z = \frac{S^2\sigma}{\kappa}, \tag{11.2}$$

where S is the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity. This expression indicates that ideal TE materials would have a high electrical conductivity to minimize Joule heating and a low thermal conductivity to prevent the backflow of heat from the hot side to the cool side. The TE efficiency can be nondimensionalized by multiplying by the average temperature T $[(T_1 + T_2)/2]$, which yields the most common form of TE efficiency, ZT, also known as the dimensionless figure of merit.

Early work in TEs resulted in very small values of Z because the materials being used were mostly metals, which did not possess ideal TE properties. Most traditional materials have a correlation between electrical and thermal conductivity.

That is, a material that conducts electricity well, such as a metal, will also conduct heat well, and a material that insulates heat, such as glass or ceramic, also insulates electricity. Beginning in the late 1930s and continuing into the 1970s, there was a surge of discoveries that showed semiconductors exhibited the best TE properties. Until that time, metals such as bismuth and antimony alloys were the state of the art with a *ZT* value of around 0.1 at room temperature. The implementation of semiconductors such as bismuth telluride (Bi_2Te_3) helped to increase that number by tenfold because semiconductors are moderate conductors of heat and electricity. However, a *ZT* value of roughly 3 is needed in order for TE cooling systems to compete with vapor compression refrigerators. A new class of TE materials has been developed and categorized as low-dimensional TEs and they have the potential to greatly increase *ZT* value. These are superlattice thin-films, also called quantum wells, which are structures built up by depositing multiple layers of alternating semiconductor materials with differing electronic band gaps to a thickness in the range of 10–100 Å, on a substrate material. This type of structure provides decoupling of the thermal and electrical conductivities of the material, and further tailoring of the layer materials can yield a higher *ZT* value up to 3 or 4 (Bass et al. 2004).

A typical TE cooling component is an n- or p-type semiconductor (bismuth telluride) sandwiched between two conductors, usually copper. The semiconductor is used because they can be optimized for pumping heat and because the type of charge carriers within them can be chosen. When an electronic field is applied to two ends of the n-type (doped with electrons) semiconductor, the electrons move towards the positive end to release heat, while the negative end absorbs heat. Therefore, the heat is transported in the direction of current flow. When a p-type semiconductor (doped with holes) is used instead, the holes move in a direction opposite the current flow. The heat is also transported in a direction opposite the current flow and in the direction of the holes. Essentially, the charge carriers dictate the direction of heat flow. Electrons can travel freely in the copper conductors but not so freely in the semiconductor. As the electrons leave the copper and enter the hot-side of the p-type, they must fill a hole in order to move through the p-type. When the electrons fill a hole, they drop down to a lower energy level and release heat in the process. Then, as the electrons move from the p-type into the copper conductor on the cold side, the electrons are bumped back to a higher energy level and absorb heat in the process. Next, the electrons move freely through the copper until they reach the cold side of the n-type semiconductor. When the electrons move into the n-type, they must bump up an energy level in order to move through the semiconductor. Heat is absorbed when this occurs. Finally, when the electrons leave the hot-side of the n-type, they can move freely in the copper. They drop down to a lower energy level and release heat in the process. To increase heat transport, several p type or n type TE components can be hooked up in parallel. However, the device requires low voltage and therefore, a large current which is too great to be commercially practical. The TE components can be put in series but the heat transport abilities are diminished because the interconnectings between the semiconductor creates thermal shorting.

The most efficient configuration is where a p and n TE component is put electrically in series but thermally in parallel. This kind of device is called a couple for electronic cooling. When assembling it into an electronic package, one side is attached to a heat source and the other a heat sink that convects the heat away. The side facing the heat source is considered the cold side and the side facing the heat sink the hot side. There must be an electrical insulator between the heat generating device and the conductor to prevent an electrical short circuit between the module and the heat source. The electrical insulator must also have a high thermal conductivity so that the temperature gradient between the source and the conductor is small. Ceramics such as alumina are generally used for this purpose. The most common devices use 254 alternating p and n type TE devices. The devices can operate at 12–16 V at 4–5 A. These values are much more practical for real-life operations.

Thomson Effect

The Thomson effect is a combination of the Seebeck and Peltier effects which was the phenomenon discovered by William Thomson in 1854, later called Lord Kelvin. It was found that there occurs a reversible transverse heat flow into or out of a conductor of a particular metal, the direction depending upon whether a longitudinal electric current flows from colder to warmer metal or from warmer to colder. Any temperature gradient previously existing in the conductor is thus modified if a current is turned on. Any current-carrying conductor (except for a superconductor) with a temperature difference between two points, will either absorb or emit heat, depending on the material. The Thomson effect does not occur in a current-carrying conductor which is initially at uniform temperature. If a current density J is passed through a homogeneous conductor, heat production per unit volume is (Roberts 1977):

$$q = \rho J^2 - \mu J \frac{\mathrm{d}T}{\mathrm{d}x}, \tag{11.3}$$

where ρ is the resistivity of the material, $\mathrm{d}T/\mathrm{d}x$ is the temperature gradient along the wire, μ is the Thomson coefficient. The first term ρJ^2 is simply the Joule heating, which is not reversible. The second term is the Thomson heat, which changes sign when J changes direction.

In metals such as zinc and copper, which have a hotter end at a higher potential and a cooler end at a lower potential, when current moves from the hotter end to the colder end, it is moving from a high to a low potential, so there is an evolution of heat. This is called the positive Thomson effect. In metals such as cobalt, nickel, and iron, which have a cooler end at a higher potential and a hotter end at a lower potential, when current moves from the hotter end to the colder end, it is moving from a low to a high potential, there is absorption of heat. This is called the negative

Thomson effect. It is commonly asserted that lead has a zero Thomson effect. While it is true that the TE coefficients of lead are small, they are in general nonzero. The Thomson coefficient of lead has been measured over a wide temperature range and has been integrated to calculate the absolute Seebeck coefficient of lead as a function of temperature. Unlike lead, the TE coefficients of all known superconductors are zero.

Thomson's theoretical treatment of thermoelectricity is remarkable in the fact that it is probably the first attempt to develop a reasonable theory of irreversible thermodynamics (nonequilibrium thermodynamics). This phenomenon is of interest in respect to the principles involved but plays a negligible role in the operation of practical TE modules. For this reason, it is ignored (Ferrotec 2010).

Application of Thermoelectric Effects to Thermoelectric Cooling

The TE semiconductor material used most often in current TE coolers is an alloy of bismuth telluride that has been suitably doped to provide individual blocks or elements having distinct "n" and "p" characteristics. TE materials most often are fabricated by either directional crystallization from a melt or pressed powder metallurgy. Each manufacturing method has its own particular advantage, but directionally grown materials are most common. In addition to bismuth telluride (Bi_2Te_3), there are other TE materials including lead telluride (PbTe), silicon germanium (SiGe), and bismuth-antimony (Bi-Sb) alloys that may be used in specific situations. From these materials, bismuth telluride (Bi_2Te_3) has highest figure of merit ZT (from 0.8 to 1) within a temperature range of around 50–100°C, and is best suited for most current cooling applications. This is attributed to its specific crystal structure. Bi_2Te_3 is highly anisotropic in nature, which results in its electrical resistivity being approximately four times greater parallel to the axis of crystal growth (C-axis) than in the perpendicular orientation. In addition, thermal conductivity is about two times greater parallel to the C-axis than in the perpendicular direction. Because the anisotropic behavior of resistivity is greater than that of thermal conductivity, the maximum performance or figure-of-merit occurs in the parallel orientation. Because of this anisotropy, TE elements must be assembled into a cooling module so that the crystal growth axis is parallel to the length or height of each element and, therefore, perpendicular to the ceramic substrates. In addition, Bi_2Te_3 crystals are made up of hexagonal layers of similar atoms. While layers of bismuth and tellurium are held together by strong covalent bonds, weak van der Waals bonds link the adjoining [Te^1] layers. As a result, crystalline bismuth telluride cleaves readily along these [Te^1][Te^1] layers, with the behavior being very similar to that of Mica sheets. Fortunately, the cleavage planes generally run parallel to the C-axis and the material is quite strong when assembled into a thermoelectric cooling module (Ferrotec 2010).

Bismuth telluride material, when produced by directional crystallization from a melt, typically is fabricated in ingot or boule form and then sliced into wafers of various thicknesses. After the wafer's surfaces have been properly prepared, the wafer is then diced into blocks that may be assembled into TE cooling modules. The blocks of bismuth telluride material, which usually are called elements or dice, also may be manufactured by a pressed powder metallurgy process. A practical TE cooler consists of two or more elements of semiconductor material that are connected electrically in series and thermally in parallel, as shown in Figure 11.1. These TE elements and their electrical interconnects typically are mounted between two ceramic substrates. The substrates serve to hold the overall structure together mechanically and to insulate the individual elements electrically from one another and from external mounting surfaces. After integrating the various component parts into a module, TE modules ranging in size from approximately 2.5 to 50 mm (0.1–2.0 in) square and 2.5 to 5 mm (0.1–0.2 in) in height may be constructed (Ferrotec 2010).

Both n-type and p-type bismuth telluride TE materials are used in a TE cooler. This arrangement causes heat to move through the cooler in one direction only while the electrical current moves back and forth alternately between the top and bottom substrates through each n and p element. N-type material is doped so that it will have an excess of electrons (more electrons than needed to complete a perfect molecular lattice structure) and p-type material is doped so that it will have a deficiency of electrons (fewer electrons than are necessary to complete a perfect lattice structure). The extra electrons in the n material and the "holes" resulting from the deficiency of electrons in the p material are the carriers which move the heat energy through the TE material (Ferrotec 2010).

Figure 11.1 shows a kind of typical TE module. The module consists of pairs of p-type and n-type semiconductor thermoelements forming thermocouples which are connected electrically in series and thermally in parallel. In cooling mode, an electrical current is supplied to the module. Heat is pumped from one side to the other (Peltier effect), the result is that one side of the module becomes cold. In generating mode conversely, a temperature gradient is maintained across the module. The heat flux passing through the module is converted into electrical power (Seebeck effect). TE cooling uses the Peltier effect to create heat flux between the junctions of two different types of materials. A Peltier cooler, heater, or TE heat pump is a solid-state active heat pump which transfers heat from one side of the device to the other side against the temperature gradient (from cold to hot), with consumption of electrical energy. Such an instrument is also called a Peltier device, Peltier diode, cooling diode, Peltier heat pump, solid state refrigerator, or TEC. Because heating can be achieved more easily and economically by many other methods, Peltier devices are mostly used for the cases that a single device is to be used for both heating and cooling. However, with the advent of more and more effective TE materials, the applications of the TEC are increasing. Peltier devices have been commonly used in camping and portable coolers and for cooling electronic components and small instruments. Some electronic equipment intended for military use in the field is thermoelectrically cooled. The cooling effect of Peltier heat pumps can also be used to extract water from the air in dehumidifiers. Peltier elements are a common component in thermal cyclers, used for the synthesis of DNA by polymerase chain reaction, which is a common molecular biological technique which requires the rapid heating and cooling of the reaction mixture for denaturation, primer annealing, and enzymatic synthesis cycles. The effect is also used in satellites and spacecraft to counter the effect of direct sunlight on one side of a craft by dissipating the heat over the cold shaded side, whereupon the heat is dissipated by thermal radiation into space. Photon detectors such as charge-coupled devices in astronomical telescopes or very high-end digital cameras are often cooled down with Peltier elements. This reduces dark counts due to thermal noise. A dark count is the event that a pixel gives a signal although it has not received a photon but rather mistook a thermal fluctuation for one. On digital photos taken at low light these occur as speckles or pixel noise (Kim and Ferreira 2008). In electronic packaging, TECs would be used to cool computer components to keep temperatures within design limits without the noise of a fan, or to maintain stable functioning when overclocking. A Peltier cooler with a heat sink or waterblock can cool a chip to well below ambient temperature.

Design and Architecture of Thermoelectric Cooling Devices

A basic architecture of a TEC with heat being moved as a result of an applied electrical current (I) is shown in Figure 11.1. Most TEC modules are fabricated with an equal number of n-type and p-type elements where one n and p element pair form a TE couple. Heat flux (heat actively pumped through the TE module) is proportional to the magnitude of the applied DC electric current. By varying the input current from zero to maximum, it is possible to adjust and control the heat flow and temperature.

Design Methodology

Peltier TEC performance is a function of ambient temperature, hot and cold side heat exchanger (heat sink) performance, thermal load, Peltier module (thermopile) geometry, and Peltier electrical parameters. Specifically, the performance of a TEC device depends on the following factors: (1) the temperature of the cold (T_{c}) and hot (T_{h}) sides; (2) thermal and electrical conductivities of the device's materials; (3) contact resistance between the TE device and heat source/heat sink; and (4) thermal resistance of the heat sink. The TE performance is usually characterized by COP. The current yielding the maximum COP is given by (Goldsmid 1986):

$$I_{\phi} = \frac{(S_{\mathrm{p}} - S_{\mathrm{n}})(T_{\mathrm{h}} - T_{\mathrm{c}})}{R\left[(1 + ZT_{\mathrm{m}})^{1/2} - 1\right]}. \qquad (11.3)$$

The maximum COP is

$$\phi_{\max} = \frac{Q_c}{W_{\text{in}}} = \frac{T_1[(1 + ZT_m)^{1/2} - T_2/T_1]}{(T_2 - T_1)[(1 + ZT_m)^{1/2} + 1]}, \tag{11.4}$$

where $T_m = (T_H + T_C)/2$. The maximum efficiency of a TE device for electricity generation is given by $\eta_{\max}$, defined as

$$\eta_{\max} = \frac{T_H - T_C}{T_H} \frac{\sqrt{1 + Z\overline{T}} - 1}{\sqrt{1 + Z\overline{T}} + \frac{T_C}{T_H}}, \tag{11.5}$$

where T_H is the temperature at the hot junction and T_C is the temperature at the surface being cooled. $Z\overline{T}$ is the modified dimensionless figure of merit which now takes into consideration the TE capacity of both TE materials being used in the power generating device, and is defined as (Goldsmid 1986)

$$Z\overline{T} = \frac{(S_p - S_n)^2 \overline{T}}{[(\rho_n k_n)^{1/2} + (\rho_p k_p)^{1/2}]^2}, \tag{11.6}$$

where ρ is the electrical resistivity, $\overline{T}$ is the average temperature between the hot and cold surfaces, and the subscripts n and p denote properties related to the n- and p-type semiconducting TE materials, respectively. It is worthwhile to note that the efficiency of a TE device is limited by the Carnot efficiency (hence the T_H and T_C terms in $\Phi_{\max}$), because TE devices are still inherently heat engines.

The COP of current commercial TE refrigerators ranges from 0.3 to 0.7, only about one-sixth the value of traditional vapor-compression refrigerators (approximately 3). A simplified way of determining the voltage and the heat load are given by (Buit 1980):

$$Q_c = (\alpha_p - \alpha_n) I T_c - K(T_H - T_c) - 1/2 I^2 R, \tag{11.7}$$

$$V = 2N\left[\alpha(T_h - T_c)\frac{IRL}{A}\right], \tag{11.8}$$

where V is the voltage and Q_c is the heat load, N is the number of couples, and L is the element height.

There are various ways to design a TEC; and different methodology has been used to design one that meets a given specification. Typically, the first step in the design of a TEC system involves making an analysis of the system's overall thermal characteristics. This analysis may be quite simple for some applications or highly complex in other cases, which must never be neglected if a satisfactory and efficient design is to be realized. The active heat load is the actual heat generated by the component to be cooled. For most applications, the active load will be equal to the electrical power input to the article being cooled (Watts = Volts × Amps) but in other situations the load may be more difficult to determine. The passive heat load (sometimes called heat leak or parasitic heat load) is that heat energy which is lost or gained by the article being cooled as a result of conduction, convection, and/or radiation. Passive heat losses may occur through any heat-conductive path including air, insulation, and electrical wiring. In applications where there is no active heat generation, the passive heat leak will represent the entire heat load on the TEC. Determination of the total heat leak within a cooling system is a relatively complicated issue but a reasonable estimate of these losses often can be made by means of some basic heat transfer calculations, however, several fundamental heat transfer equations can be used in evaluating some of the thermal aspects of a design or system. The following equation can be used for estimating heat losses due to convection and conduction of an enclosure (Marlow 1998).

$$Q_{\text{passive}} = (A\Delta T)/(x/k + 1/h), \tag{11.9}$$

where: Q_{passive} = heat load (W); A = total external surface area of enclosure (m^2); x = thickness of insulation (m); k = thermal conductivity of insulation (W/m °C); h = convective heat transfer coefficient (W/m^2 °C); ΔT = Temperature change (°C). Some designs require a set amount of time to reach the desired temperature. The following equation may be used to estimate the time required (Marlow 1998):

$$t = [(\rho)(V)(C_p)(T_1 - T_2)]/Q, \tag{11.10}$$

where: t = time (seconds); ρ = density (g/cm^3); V = volume (cm^3); C_p = specific heat (J/g °C); $T_1 - T_2$ = temperature change (°C); $Q = (Q_{\text{to}} + Q_{\text{tt}})/2$ (J/s; Note: 1 J/s = 1 W); Q_{to} is the initial heat pumping capacity when the temperature difference across the cooler is zero. Q_{tt} is the heat pumping capacity when the desired temperature difference is reached and heat pumping capacity is decreased. Q_{to} and Q_{tt} are used to obtain an average value.

Before the cooler or heat sink can be selected, the cooling requirements must be defined. This includes determining the amount of heat to be pumped. Minimizing the heat load allows the cooler to achieve colder temperatures or reduces the power required to reach the defined cooling level. The following describes the techniques used to estimate active and passive heat loads and applies only to steady state heat loads. The heat load may consist of two types; active or passive, or a combination of the two. An active load is the heat dissipated by the device being cooled. It generally equals the input power to the device. Passive heat loads are parasitic in nature and may consist of radiation, convection, or conduction. The general equation for active heat load dissipation is (Marlow 1998):

$$Q_{\text{active}} = V^2/R = VI = I^2R, \tag{11.11}$$

where: Q_{active} = active heat load (W); V = voltage applied to the device being cooled (V); R = device resistance (Ω); I = current through the device (A). When two objects at different temperatures come within proximity of each other, heat is exchanged. This occurs through electromagnetic radiation emitted from one object and absorbed by the other. The hot object will experience a net heat loss and the cold object a net heat gain as a result of the temperature difference. This is called thermal radiation. Radiation heat loads are usually considered insignificant when the system is operated in a gaseous environment since the other passive heat loads are typically much greater in magnitude. Radiation loading is usually significant in systems with small active loads and large temperature differences, especially when operating in a vacuum environment. The fundamental equation for radiation loading is (Marlow 1998):

$$Q_{\text{rad}} = FesA({T_{\text{amb}}}^4 - {T_{\text{c}}}^4), \tag{11.12}$$

where: Q_{rad} = radiation heat load (W); F = shape factor (worst case value = 1); e = emissivity (worst case value = 1); s = Stefan–Boltzmann constant (5.667×10^{-8} W/m^{2}K^4); A = area of cooled surface (m^2); T_{amb} = Ambient temperature (K); T_{c} = TEC cold ceramic temperature (K).

When the temperature of a fluid (in this case, a gas) flowing over an object differs from that of the object, heat transfer occurs. The amount of heat transfer varies depending on the fluid flow rate. Convective heat loads on TECs are generally a result of natural (or free) convection. This is the case when gas flow is not artificially induced as with a fan or pump, but rather occurs naturally from the varying density in the gas caused by the temperature difference between the object being cooled and the gas. The convective loading on a system is a function of the exposed area and the difference in temperature between this area and the surrounding gas. Convective loading is usually most significant in systems operating in a gaseous environment with small active loads or large temperature differences. The fundamental equation which describes convective loading is (Marlow 1998):

$$Q_{\text{conv}} = hA(T_{\text{air}} - T_{\text{c}}), \tag{11.13}$$

where: Q_{conv} = convective heat load (W); h = convective heat transfer coefficient (W/m^2 °C) (typical value for a flat, horizontal plate in air at 1 atm = 21.7 W/m^2 °C; A = exposed surface area (m^2); T_{air} = temperature of surrounding air (°C); T_{c} = temperature of cold surface (°C).

Conductive heat transfer occurs when energy exchange takes place by direct impact of molecules moving from a high temperature region to a low temperature region. Conductive heat loading on a system may occur through lead wires, mounting screws, etc., which form a thermal path from the device being cooled to the heat sink or ambient environment. The fundamental equation which describes conductive loading is Marlow 1998):

$$Q_{\text{cond}} = kA\Delta T/L, \tag{11.14}$$

where: Q_{cond} = conductive heat load (W); k = thermal conductivity of the material (W/m °C); A = cross-sectional area of the material (m^2); L = length of the heat path (m); ΔT = temperature difference across the heat path (°C) (usually ambient or heat sink temperature minus cold side temperature).

Heat loading may occur through one or more of four modes: active, radiation, convection, or conduction. By utilizing these equations heat loads can estimated. The resulting information can then be used to select a suitable TEC for specific application.

TECs are mounted using one of three methods: adhesive bonding, compression using thermal grease, or solder. In general, for a TEC with a ceramic base of 19 mm or less, solder or adhesive bond can be used without fear of failure due to thermal stresses. If the TEC base is larger than 19 mm, the compression method is recommended because thermal grease is not rigid and does not transfer thermal stresses. A thin layer of copper metallization on the hot and/or cold ceramic allows soldering as a means of attachment. Adhesives and greases are prone to outgassing, therefore, they are not as appropriate for use in a vacuum package (Marlow 1998).

Surface preparation is important when using any of the assembly methods. No matter which method is used, the mounting surface should be flat to less than 0.08 mm over the TEC mounting area. In addition, the surface should be clean and free from oil, nicks, and burrs. When multiple TECs are placed in parallel thermally between common plates, the TEC thicknesses should vary no more than 0.05 mm. An adhesive bonding mounting method should be used when it is necessary to permanently attach the TEC to the heat sink, when mounting with solder is not an option, when the TECs need to be lapped to the same height after mounting, or when moderate thermal conductivity is required. A compression mounting method is needed when a permanent bond is not desired, when multiple TECs are used, or when the TEC is larger than 19 mm. The soldering mounting method is necessary when minimal outgassing is needed, when the TEC is smaller than 19 mm, when need a high-strength junction, or when high thermal conductivity is required.

In general, techniques used to install TE modules in a cooling system are extremely important. Failure to observe certain basic principles may result in unsatisfactory performance or reliability. Some of the factors to be considered in system design and module installation include the following (Marlow 1998): (1) TE modules have high mechanical strength in the compression mode but shear strength is relatively low. As a result, a TEC should not be designed into a system where it serves as a significant supporting member of the mechanical structure. (2) All interfaces between system components must be flat, parallel, and clean to minimize thermal resistance. High conductivity thermal interface material is often used to ensure good contact between surfaces. (3) The “hot” and “cold” sides of standard TE modules may be identified by the position of the wire leads. Wires are attached to the hot side of the module, which is the module face that is in contact with the heat sink. For modules having insulated wire leads, when the red and black leads are connected to the respective positive and negative terminals of a DC power supply, heat will be pumped from the module's cold side, through the module, and into the heat sink. Note that for TE modules having bare wire leads, the positive connection is on the right side and the negative connection is on the left when the leads are facing toward the viewer and the substrate with the leads attached presented on the bottom. (4) When cooling below ambient, the object being cooled should be insulated as much as possible in order to minimize heat loss to the ambient air. To reduce convective losses, fans should not be positioned so that air is blowing directly at the cooled object. Conductive losses may also be minimized by limiting direct contact between the cooled object and external structural members. (5) When cooling below the dew point, moisture or frost will tend to form on exposed cooled surfaces. To prevent moisture from entering a TE module and severely reducing its thermal performance, an effective moisture seal should be installed. This seal should be formed between the heat sink and cooled object in the area surrounding the TE module(s). Flexible foam insulating tape or sheet material and/or silicone rubber RTV (Room-Temperature Vulcanization) are relatively easy to install and make an effective moisture seal. Several methods for mounting TE modules are available and the specific product application often dictates the method to be used.

TECs operate directly from DC power suitable power sources can range from batteries to simple unregulated "brute force" DC power supplies to extremely sophisticated closed-loop temperature control systems. A TEC module is a low-impedance semiconductor device that presents a resistive load to its power source. Due to the nature of the bismuth telluride material, modules exhibit a positive resistance temperature coefficient of approximately 0.5% per °C based on average module temperature. For many noncritical applications, a lightly filtered conventional battery charger may provide adequate power for a TEC provided that the AC ripple is not excessive. Simple temperature control may be obtained through the use of a standard thermostat or by means of a variable-output DC power supply used to adjust the input power level to the TE device. In applications where the thermal load is reasonably constant, a manually adjustable DC power supply often will provide temperature control on the order of ±1°C over a period of several hours or more. Where precise temperature control is required, a closed-loop (feedback) system generally is used whereby the input current level or duty cycle of the TE device is automatically controlled. With such a system, temperature control to ±0.1°C may be readily achieved and much tighter control is not unusual (Chein and Huang 2004).

Multistage Architecture

Multistage cooling and low-level signal detection are two applications which may require lower values of power supply ripple. In the case of multistage TE devices, achieving a large temperature differential is the typical goal, and a ripple component of less than 2% may be necessary to maximize module performance. In situations where very low level signals must be detected and/or measured, even though the TE module itself is electrically quiet, the presence of an AC ripple signal within the module and wire leads may be unsatisfactory. The acceptable level of power supply ripple for such applications will have to be determined on a case-by-case basis (Ferrotec 2010).

TEC modules are considered to be highly reliable components due to their solid-state construction. For most applications they will provide long, trouble-free service. There have been many instances where TE modules have been used continuously for 20 or more years and the life of a module often exceeds the life of the associated equipment. The specific reliability of TE devices tends to be difficult to define, however, because failure rates are highly dependent upon the particular application. For applications involving relatively steady-state cooling where DC power is being applied to the module on more-or-less continuous and uniform basis, TE module reliability is extremely high. Mean time between failures (MTBFs) in excess of 200,000 h are not uncommon in such cases and this MTBF value generally is considered to be an industry standard. On the other hand, applications involving thermal cycling show significantly worse MTBFs, especially when TE modules are cycled up to a high temperature. It is important that modules are installed in accordance with general requirements in order to minimize the possibility of premature module failure due to faulty assembly techniques. Temperature control methods also have an impact on TE module reliability. Linear or proportional control should always be chosen over ON/OFF techniques when prolonging the life of the module is required (Ferrotec 2010).

Various methods have been used to improve the performance of TECs which are its major drawback. Thin film coolers or multistage (bulk) coolers are two typical examples. Thin films are material layers of about 1 μm thickness. Alternating layers of Sb_2Te_3 and Bi_2Te_3 are used to produce thin film TECs. As shown in Figure 11.2, the highest power components are mounted on a diamond substrate which would be the top or cold side substrate of a thin film TEC. Power densities were reported to be above 100 W/cm^2. Thin film coolers considerably reduce the size of TE devices. Because the cooling density of a Peltier cooler is inversely proportional to its length, scaling to smaller size is desirable.

When the desired temperature differential between the cold and hot side cannot be obtained with a single-stage module, or when the cold side temperature must be lower than a one-stage cooler will allow, a multistage module may need to be applied. Multistage modules are essentially single-stage modules stacked up in a vertical pyramid-shaped array, as shown in Figure 11.3 (Simons 2001; Bar-Cohen et al. 2005). As the number of stages increases, the minimum cold side temperature will decrease. Also, increasing the number of stages increases the COP for a given cold side temperature (Nolas et al. 2001a, b). The COP of N number of multistage module is given by (Goldsmid 1986):

$$\phi = \left[(1 + \frac{1}{\phi'})^N - 1 \right]^{-1}, \tag{11.15}$$

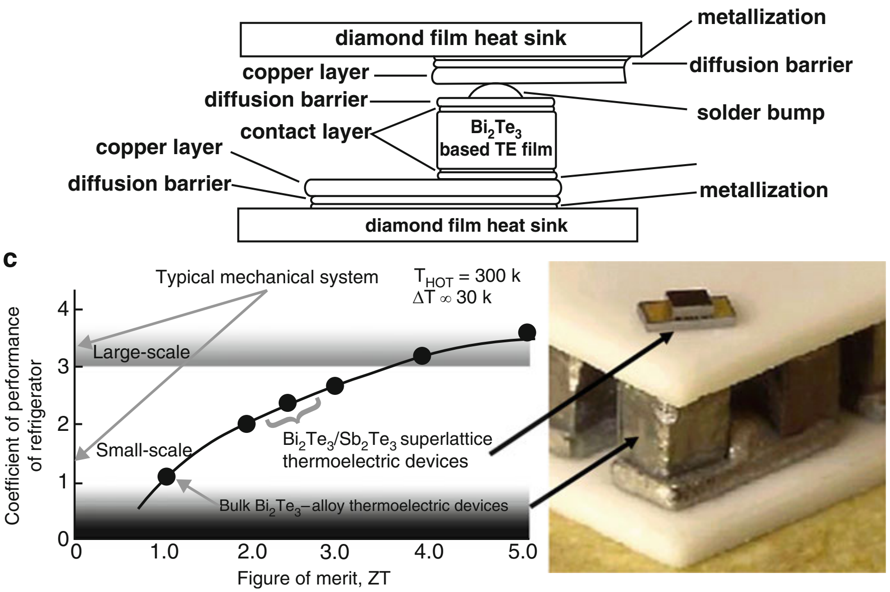

Fig. 11.2 Thin film cooler

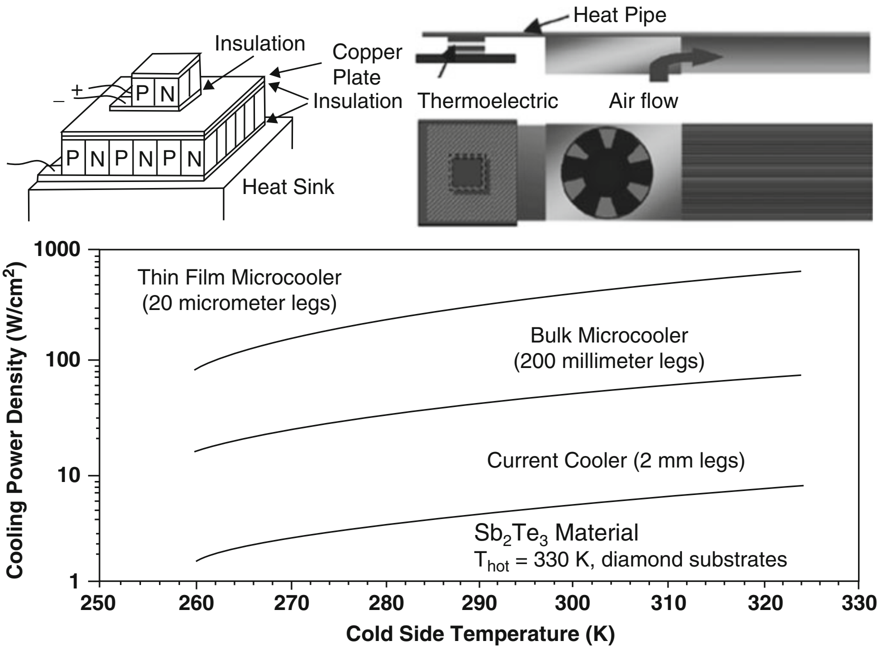

Fig. 11.3 Multistage thermoelectric cooler and cooling density of different size coolers

where ϕ' is the COP of one stage of the module and N is the number of stages. Figure 11.3 also compares the three types of coolers: bulk (multistage), thin film, and current (Simons and Chu 2000). More exotic TE devices are being researched that could result in better performance such as, superlattice structures, quantum wires and quantum wells, thin films using SiGe/Si, and thermionic cooling. Some alternative methods of TEC have been considered, such as (1) the heat produced by a computer chip can be used to provide the electricity to run a fan that cools the chip. The fan uses a TE device operating on the Seebeck effect to convert the heat to electricity. (2) When a laptop is running on batteries, the electricity used to power the fan comes from the battery. Therefore, to conserve battery life, a TE power generator is a good alternative (Bar-Cohen et al. 2005).

Thermoelectric Materials and Future Development Trends

TECs in use today have a COP of only about 0.5. This is quite a low value compared with COPs of larger scale machines, such as air conditioners and refrigerators at levels of 3.0–5.0. For electronic component cooling, advanced emerging TE materials provide probability for improved efficiency or TECs.

As the fundamental theory of thermoelectricity became well established, the important role of heavily doped semiconductors as good TE materials had been accepted, and the TE material bismuth telluride was discovered and developed for commercialization, the effectiveness of a TE material in terms of the dimensionless TE figure of merit (ZT) was established, and the TE industry was launched. From 1960 to 1990, only incremental gains were made in increasing ZT, with Bi_2Te_3 remaining the best commercial material today, with $ZT \sim 1$. During this three decade period, the thermoelectrics field received little attention from the worldwide scientific research community. Nevertheless, the TE industry grew slowly but steadily by finding niche applications for space missions, laboratory equipment, and medical applications where cost and energy efficiency were not as important as energy availability, reliability, and predictability (Dresselhaus et al. 2007).

In the early 1990s, the US Department of Defense became interested in the potential of TEs for new types of applications, encouraging the research community to reexamine research opportunities for advancing TE materials to the point they could be used more competitively for cooling and power conversion applications. This attempt was successful in stimulating the research community to once again become active in this field and to find new research directions that would have an impact on future developments and would lead to TE materials with better performance. As a result of this stimulation, two different research approaches were taken for developing the next generation of new TE materials: one using new families of advanced bulk TE materials based on crystal structures that contain weakly bound atoms or molecules with large vibrational amplitudes at partially filled structural sites acting as effective phonon scatterers, such as skutterudites, clathrates, and oxides; and the other using low dimensional materials systems, such as quantum well superlattices, quantum wires, quantum dots, thin film or band engineering structures. During the 1990s these two approaches developed independently and mostly along different directions. And then the two approaches seem to be coming together again as the most successful new bulk TE materials are host materials containing nanoscale inclusions that are prepared by chemical approaches (Dresselhaus et al. 2005). Low-dimensional materials systems are now being assembled as nanocomposites containing a coupled assembly of nanoclusters showing short-range low dimensionality embedded in a host material, thereby producing a bulk material with nanostructures and many interfaces that scatter phonons more effectively than electrons (Dresselhaus et al. 2007).

Fermi Energy in Thermoelectric Materials

The Fermi energy, of a substance is a result of the Pauli exclusion principle when the temperature of a material is lowered to absolute zero. By this principle, only one electron can inhabit a given energy state at a given time. At the temperature of absolute zero, all electrons in the solid attempt to get into the lowest available energy level. As a result, they form a sea of energy states known as the Fermi sea. The highest energy level of this sea is called the Fermi energy or Fermi level. At absolute zero no electrons have enough energy to occupy any energy levels above the Fermi level. In metals the Fermi level sits between the valence and conduction bands. The size of the band gap between the Fermi level and the conduction band determines if the metal is a conductor, insulator or semiconductor. Once the temperature of the material is raised above absolute zero the Fermi energy can be used to determine the probability of an electron having a particular energy level. The probability that an energy state will be filled is given by Femi distribution function (Nolas et al. 2001a, b):

$$f_0(E) = \frac{1}{e^{(E-E_f)/(k_B T)} + 1}, \tag{11.6}$$

where E_f is the Fermi energy, T is the absolute temperature, and k_B is Boltzmann's constant. $k_B T$ is also proportional to the thermal energy of the particles. At a temperature of absolute zero, Fermi energy has the value $E_{f_0} = (h^2/2m)(3n/8\pi)^{2/3}$, where n is the total number of free electrons per unit volume, m is the mass of a free electron, h is Planck's constant. As the temperature rises the probability of electrons with energy greater than the Fermi energy increases. These electrons take part in electric conduction which is an important application of the Fermi energy. There is a finite probability for electrons to exist in the band gap between Fermi level and the conduction band, but there is no energy state in the band gap because the density of state is zero. The Fermi energy is important to both electrical and thermal conductivities. Increased temperature leads to increased numbers of electrons jumping into the conduction band from the Fermi level. The electrons in the conduction band bump into each other causing electrical current, and heat from the collisions. With more electrons available, more current, and heat, can flow. Hence, the Fermi energy is intrinsic to both of these properties. For metals, the Fermi energy actually lies within the conduction band; hence, it takes relatively little energy to bump these electrons into the band gap, which is why metals are typically good conductors of both electricity and heat. For semiconductors, the Fermi energy lies between the valence band and conduction band, and more energy is required to excite the electrons sufficiently, and thus both electrical and thermal conductivity are lower than for metals. For insulators, the Fermi energy is considerably below the conduction band, which means that it takes an incredible amount of energy to raise an electron to the conduction band, and thus few electrons do; therefore, heat flow and electrical current are reduced significantly, in some cases to near zero. However, that the correlation between thermal and electrical conductivity is only valid for certain substances, specifically metals and metalloids. Diamond, for instance, has an incredibly high thermal conductivity but very low electrical conductivity. These differences are due to differences in structure, which makes the Fermi energy less important than other properties.

The Fermi energy represents certain minimum “zero-point” energy (the absolute minimum that can be reached) and a “zero-point” pressure. This pressure is due to the electrons moving around, even at 0 K. At high temperatures and low densities, classical pressure dominates. But at low temperatures and incredibly high densities, the Fermi energy and pressure become radically more important. The concept of Fermi energy has been widely used in explanation and development of TE materials.

Optimization Criteria of the Thermoelectric Materials

Because the TE effect was discovered in the 18th century, it had taken many years to find useful applications and materials for this discovery. In the 1950s, Abraham Ioffe found that doped semiconductors showed a much larger TE effect than other materials. This led to research of binary semiconductors as TE materials in the 1950s, with Bi_2Te_3 having the greatest TE effect at room temperature. The research led a good understanding of the properties displayed by a good TE material. It was not until the 1990s that interest increased again due to new materials discoveries with the potential for excellent TE properties. Discovery of practical materials with $ZT > 2$ for $\Delta T = 400 \pm 50°\mathrm{C}$ can yield fuel savings of 10% in vehicles. Additional fuel savings are possible using TEs to enable new climate control concepts, e.g. localized on demand cooling. The potential uses of TE materials such as Peltier refrigerators, or for power generation are limitless if the dimensionless figure of merit, ZT can reach a value of 3 or larger. There are currently a few applications in practice that require high reliability, most notably NASA’s use of TE materials to cool deep space probes to temperatures as low as 160 K (Kimmel 1999).

The primary criterion for TE materials is the figure of merit given by $Z = \sigma S^2 \big/ k$, which depends on the Seebeck coefficient, S, thermal conductivity, λ, and electrical

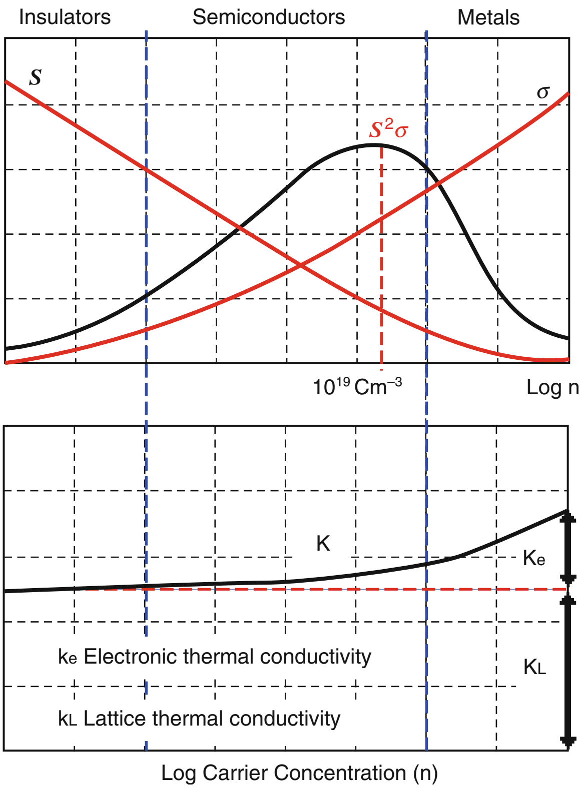

Fig. 11.4 Sketch of the dependence of $S^2\sigma$ and k on the concentration of free carriers. The relatively moderate values of electrical and thermal conductivity make semiconductors the best known thermoelectric materials (Rowe 1994).

conductivity, σ. In this equation, thermal conductivity and electrical conductivity are typically intertwined. Figure 11.4 shows a rough approximation of the dependence of TE properties on carrier concentration. It can be seen in the figure that semiconductors display the largest value of σS^2, and they also have moderate values of k, which making the semiconductors the best known TE materials. The efficiency of modern TE materials still cannot compete with more conventional methods because the electrical conductivity is too low and the thermal conductivity is too high. A ZT value of roughly 3 is needed in order for TEC systems to compete with vapor compression refrigerators (Venkatasubramanian et al. 2001).

In order to optimize the figure of merit, phonons which are responsible for thermal conductivity must experience the material as they would in a glass (experiencing a high degree of phonon scattering-lowering the thermal conductivity) while electrons must experience it as a crystal (experiencing very little scattering-maintaining the electrical conductivity). It is through the adjustment of each these properties independently of the other that the figure of merit can be improved. The selection and design rule for TE materials is likely to have high Seebeck coefficient and high *ZT*. Goal is to use these rules in the selection of materials for further investigation by first principles. First principles calculations are used to obtain electronic structure and vibrational properties. Boltzmann transport theory can be applied to first principles band structures to obtain electrical transport quantities, especially Seebeck coefficient, *S*(*T*). Apply linear response and direct methods for lattice vibrations thermal transport functions and thermal conductivity (Madsen and Singh 2006):

$$\text{Conductivity: } \sigma_x(T) = e^2 \int \mathrm{d}\varepsilon N(\varepsilon){v_x}^2(\varepsilon)\tau(\varepsilon, T)(-f'(\varepsilon)), \tag{11.17}$$

$$\text{Thermopower: } S(T) = (e/T\sigma(T)) \int \mathrm{d}\varepsilon N(\varepsilon){v_x}^2(\varepsilon)\tau(\varepsilon, T)\varepsilon(-f'(\varepsilon)), \tag{11.18}$$

$$\text{At low } T\text{: } S(T) = (\pi^2 k^2 T/3e\sigma)(\mathrm{d}\sigma/\mathrm{d}\varepsilon)|E_\mathrm{F}. \tag{11.19}$$

There, high *S* implies high log derivative of σ, i.e. strong energy dependence of electrical transport: band structure and scattering. More practical materials can be found by (1) Metallic conduction can be realized through mixed valence transition element such as Co, and very strong metal–oxygen hybridization. (2) High Seebeck coefficient at high carrier density can be reached with very narrow bands: A consequence of bonding topology (near right angle M–O–M bonds in edge sharing octahedra), and electron count is near crystal field gap. The dimensionless figure of merit *ZT* can be expressed by (Nolas et al. 2001a, b):

$$ZT = \left(\frac{e\alpha}{k_\mathrm{B}}\right)^2 \frac{1}{\dfrac{\sigma_0}{\sigma\beta} + \left(\dfrac{e}{k_\mathrm{B}}\right)^2 L} = \frac{e^2\alpha^2}{\dfrac{\sigma_0 k_\mathrm{B}^2}{\sigma\beta} + e^2 L} = \frac{\alpha^2}{\dfrac{\sigma_0}{\sigma\beta}\left(\dfrac{k_\mathrm{B}}{e}\right)^2 + L}, \tag{11.20}$$

where the dimensionless materials parameter $\beta = \sigma_0 T/\lambda_\mathrm{L}(k_\mathrm{B}/e)^2$.

Although large Seebeck coefficient values are important to good TE materials, other factors are also important. Because charge carriers must move through the material to transport heat, the material should conduct electricity well; otherwise, the deleterious effect of resistive heating will be enhanced. In addition, the material should act as a thermal insulator; the purpose of the device (when operated as a heat pump) is to produce a hot and cold region, therefore, a good thermal conductor will rapidly dissipate the temperature difference established. The best TE materials involve a trade-off among the three factors, combining a high Seebeck coefficient and electrical conductivity with low thermal conductivity. All three parameters are affected by the carrier concentration, *n*, of a solid. Carrier concentrations range from about 10^{14} to 10^{21} carriers/cm^3 in a semiconductor, and are about 10^{22}/cm^3 in a metal. Electrical conductivity, σ, increases with *n*. The thermal conductivity, *k*, has two components, a lattice thermal conductivity k_L and an electronic thermal conductivity k_e, such that $k = k_\mathrm{L} + k_\mathrm{e}$. The lattice component does not vary significantly with *n*; the electronic component increases with *n*. The Seebeck coefficient, S, generally decreases with increasing carrier concentration. The greatest Z value is obtained with a carrier concentration between 10^{18} and $10^{21}/\text{cm}^3$. This implies that the best TE materials will be semiconductors with a relatively high carrier concentration. The choice of carrier type is also important. The direction of both the Seebeck and Peltier effects is reversed depending on whether the carriers are electrons or holes. If both carrier types are present in a material, their effects will work against each other. Semiconductors always contain both carrier types, but often the semiconductor is intentionally laced with impurities ("doped") so that one carrier type is greatly predominant. In this case, the semiconductor is said to be extrinsic. Intrinsic semiconductors, on the other hand, have roughly equal numbers of each type of carrier, causing their performance as TE materials to suffer. Extrinsic semiconductors, then, are the better choice for TE devices. Strategies to further improve the figure of merit of semiconductors generally involve decreasing the lattice thermal conductivity through a number of techniques that affect the microstructure of the material. These include solid-solution alloying of different semiconductors and dispersing inert particles in the semiconductor. Both treatments disrupt the regular ordering of the crystalline grains and decrease the ability of the material to carry heat through lattice vibrations. In another word, the mean free path of phonons (quantized lattice vibrations) in the material decreases. Narrow band-gap semiconductors are generally used for cooling and for power generation applications. Most Peltier coolers are made with alloys of bismuth telluride (Bi_2Te_3), antimony telluride (Sb_2Te_3), and/or bismuth selenide (Bi_2Se_3), the best materials to date for near-room-temperature operation. At higher temperatures, lead telluride (PbTe) is used. For power generation systems, which typically operate at still higher temperatures, silicon–germanium (Si–Ge) alloys are often used.

More specifically, the best TE materials will have a small electronic contribution to the thermal conductivity, k_e, thus maximizing the electronic conductivity while minimizing the thermal conductivity. The Weidmann–Franz law states that (Kimmel 1999):

$$k_e/\sigma T = L_0 = 2.44 \times 10^8 V^2/K^2. \tag{11.21}$$

Therefore, the electronic contribution of the thermal conductivity is a constant (Lorenz number $= L_0$) at a given temperature. The total thermal conductivity, is the sum of the electronic and lattice contributions $k = k_e + k_L$. Finding materials that minimize the lattice contribution to the thermal conductivity will maximize the dimensionless figure of merit (Kimmel 1999). Metals are poor TE materials because they have a low Seebeck coefficient, and large electronic contribution to thermal conductivity, so S and k will cancel each other out. Insulators have a high Seebeck coefficient, and a small electronic contribution to thermal conductivity, however their charge density and therefore electrical conductivity are low leading to a low TE effect. The best TE materials are between metals and insulators; i.e., semiconductors with an electronic density of $10^{19}/\text{cm}^3$. The next step is finding semiconductors with a low lattice contribution to the thermal conductivity, thus maximizing the dimensionless figure of merit. The materials with the lowest k_L

have a large number of atoms in the unit call, a large average atomic mass, and a large average coordination number per atom thus lowering the mean free path. Another method of reducing k_L is finding a unit cell with cages, or voids, with loosely bound atoms that can "rattle" and thus scatter phonons. Based on these principles, four groups of materials have been explored: normal broadband semiconductors, semiconductors with rattling atoms or molecules, "correlated" metals or superconductors, and superlattices, also called multiple quantum well materials. Semiconductors with "rattling" atoms and multiple quantum wells have the greatest potential for improving the *ZT* value, and improved values of *ZT* have already been shown experimentally (Kimmel 1999).

There has been a substantial effort in finding p-type or n-type binary semiconductors with high dimensionless figures of merit. The current state of the art materials include Bi_2Te_3, $ZT = 0.9$ at room temperature; PbTe, $ZT = 1.2$ at 700°K; and SiGe, $ZT = 0.6$ at 1,000°K. Large values of electronic conductivity are necessary for good TE materials; thus large values of electron or hole mobility are needed. It can be shown that maximizing *ZT* is equivalent to maximizing U/k_L, where U is the weighted mobility for electrons and holes $U = Nvm^{3/2}$, N is the number of equivalent parabolic bands, ν is the electron or hole mobility, and m is the effective mass. Covalently bonded semiconductors will have the highest effective mobility. To maximize *ZT*, superconductors are needed with $U > 0.02\ m^2/V\ s$, and $k_L < 3$ W/m K. These quantities are a good starting point to determine the TE efficiency of semiconductor materials. Ternary materials are one of research directions to maximize *ZT* (Kimmel 1999). The main approach to reducing the lattice contribution of the thermal conductivity has been to lower the mean free path by using heavy atoms within large unit cells. However, the lowest thermal conductivity is seen in amorphous structures. The idea is to find a material that group of the periodic table. To form the loosely bound void, the R atom radius has to be smaller than the void radius of the unit cell. By adding La – 1.79 Å, Nd – 1.70 Å, and Sm – 1.69 Å to the $IrSb_3$ binary (not filled) skutterudite unit cell with a void radius of 2.04 Å, an order of magnitude decrease in the k_L was exhibited. The best dimensionless figure of merit at room temperature is only $ZT = 0.25$, but these structures show great promise at higher temperatures (Kimmel 1999).

Correlated metals and semiconductors, or Kondo insulators are described by rare earth intermetallic compounds usually containing Ce. Metals are not good TE materials due to a low Seebeck coefficient; however, this is not true for rare earth intermetallic compound where the 4f level is close to the fermi energy. These compounds have a high density of states near the Fermi energy, thus scattering conduction electrons. A simple power law no longer describes the scattering time, but exhibits resonant scattering. The Kondo effect, which relates to the scattering of conduction electrons, shows compounds with large Seebeck coefficients at low temperatures. Compounds such as $CePd_3$ exhibits the dimensionless figure of merit, $ZT = 1$ (Kimmel 1999).

Superlattices or multiple quantum well (MQW) structures are materials that will only conduct electrons in two dimensions, thus increasing the density of states with decreasing well widths. The increase in density of states will increase a materials figure of merit, assuming no change in the thermal conductivity. Lowering the well thickness and using MQW structures shows a large increase in Z. For instance, 20% improvement in the *ZT* of MQW structures has achieved versus bulk material. At quantum wells <10 Å, phonons will be scattered by the interfaces between quantum wells, thus lowering the thermal conductivity, and further enhancing the *ZT* value (Kimmel 1999).

Consequently, nanostructured materials such as superlattices, quantum dots, nanowires, and nanocomposites have shown promising TE properties. By exploiting nanoscale effects, these materials are able to obtain enhancements in TE properties which cannot be achieved in traditional bulk materials, resulting in large increases in the TE figure of merit. Although a high *ZT* has been reported, many of these materials are not practical for large-scale commercial use because they are fabricated by atomic layer deposition processes such as molecular beam epitaxy, making them slow and expensive to fabricate and restricting the amount of material that can be produced. Another type of nanostructured material, known as a bulk nanostructured material, is a material which is fabricated using a bulk process rather than a nanofabrication process, and has the important advantage of being able to be produced in large quantities and in a form that is compatible with commercially available devices. Thus far, of all the nanostructured materials only bulk nanostructured materials have been produced in enough quantity to be used in this manner; superlattice or quantum dot structures are currently only able to be produced as thin films. This practicality is a key reason why there is significant interest in bulk nanostructured materials and optimism that they can be used in a commercial setting. Indeed, efforts to commercialize the first generation of these materials are ongoing (Minnich et al. 2009).

On the other hand, for bulk TE materials, oxides and chalcogenides promise potentially low cost. For low-dimensional materials, highly textured or single crystal material may be required, and therefore increase costs. Anisotropies are often accompanied by poor mechanical properties. TE nanomaterials may combine the advantages of both bulk and low D materials. In addition, entire doping range with theory can be explored to reduce the need for extensive synthesis characterization to find optimal composition.

Bulk Thermoelectric Materials

There has been substantial renewed research interest in the investigation of new and/or significantly more efficient TE materials for applications in solid-state refrigeration or power generation. Over the past 30 years, bulk TE materials based on the Bi_2Te_3 and Si–Ge systems have been extensively studied and optimized to perform a variety of solid-state TE refrigeration and power generation applications. There appears little room for improvement of the figure-of-merit from these materials. Therefore, entirely new classes of compounds need to be investigated if substantial material improvements are to be made. Some of the new materials that have been investigated include skutterudites, oxides, quantum well materials, superlattice structures, and low-dimensional and disordered systems. The enhanced interest in new TE materials has been driven by the need for higher performance and extended temperature regimes for TE devices in many civilian and military applications. As one of bulk TE materials, the skutterudite material system has drawn the most attention for TE applications (Nolas et al. 1999).

Due to the natural superlattice formed by the layered structure in homologous compounds (such as those of the form $(\mathrm{SrTiO3})_n(\mathrm{SrO})_m$ – the Ruddleson-Popper phase), oxides are also being considered for high-temperature TE devices. These materials exhibit low thermal conductivity perpendicular to these layers while maintaining electrical conductivity within the layers. The figure of merit in oxides is yet relatively low (~0.34 at 1,000 K), but the enhanced thermal stability, as compared with conventional high-*ZT* bismuth compounds, makes the oxides superior in high-temperature applications (Senthilkumar and Vijayaraghavan 2009).

Established Materials: Bismuth Chalcogenides

These materials involve Bi_2Te_3 and Bi_2Se_3 and comprise some of the best performing TEs at room temperature with a temperature-independent figure of merit, *ZT*, between 0.8 and 1.0. Nanostructuring of these materials to produce a layered superlattice structure of alternating Bi_2Te_3 and Bi_2Se_3 layers produces a device within which there is good electrical conductivity but perpendicular to which thermal conductivity is poor. The enhanced *ZT* can reach approximately 2.4 at room temperature for p-type. Bismuth telluride, antimony telluride, and bismuth selenide have a nine-layer structure. They are composed of close-packed anions (Te or Se) with cations (Bi or Sb) occupying two-thirds of the octahedral holes. Let *A*, *B*, and *C* represent different relative orientations of the anion close-packed layers; and *a*, *b*, and *c* represent different relative orientations of the cations in the octahedral holes that lie midway between the close-packed layers. The structure can then be written as *AcBAcBaCBaCbACbA*. One of the most important features of Bi_2Te_3 is that high rate thermal diffusion of Cu, Ag, and Au can take place in its crystal lattice at relatively low temperature. These elements can act as donor impurities to move into or out of the lattice of Bi_2Te_3 in a TE device. For instance, during the manufacturing of TE modules, it is possible for Cu that dissolved in molten solder to pass through the nickel plated contacts into the thermoelements in several minutes. On the other hand, the copper can move out the lattice at ordinary temperature by emerging the thermoelements in a suitable aqueous sink. Because of weak bonding, and relatively large spacing between Te layers, the copper ions can also easily move from one site to another (Nolas et al. 1999).

With the same crystal structure as Bi_2Te_3, antimony telluride (Sb_2Te_3) and bismuth selenide (Bi_2Se_3) are particularly good TE materials, and furthermore, the addition of one or both to Bi_2Te_3 will improve its *ZT* by reducing the thermal conductivity. There is complete solid solubility among the three compounds Bi_2Te_3, Sb_2Te_3, and Bi_2Se_3. Within the Bi_2Te_3–Sb_2Te_3–Bi_2Se_3 pseudoternary system, the optimal compositions for TEC are normally $Bi_2Te_{2.7}Se_{0.3}$ and $Bi_{0.5}Sb_{1.5}Te_3$ for the n-type and p-type, respectively (Cui 2009).

Conventionally, many methods have been utilized for fabrication of TE materials, such as (1) a crystal ingot fabrication method in which starting materials are alloyed by melting, converted into an ingot and then sliced; (2) a powder sintering method in which a starting material powder or starting materials which have been alloyed by melting and then powdered, are molded and sintered, and sliced, if necessary; (3) a polycrystallization-zone melting method; (4) an amorphous fabrication method; and (5) a thin or thick film fabrication method. These methods have been used in some limited fields due to intrinsic drawbacks, for example, a long-term treatment of alloying by melting at high temperatures is needed, which resulted a low productivity and high energy consumption. In methods including a slicing step, super-small sized elements are difficult to produce, and in the polycrystallization-zone melting method, undesirable electrical or mechanical anisotropy result from crystallization. Additionally, the conventional molding methods have limitations to get various desirable molded shapes.

An improved method have been developed to provide a TE material obtained by sintering a molding of a mixture prepared by copulverizing a material containing at least bismuth and a material containing at least tellurium without alloying by melting. The process for producing a TE material comprises copulverizing and intermixing a material containing at least bismuth and a material containing at least tellurium, directly, without alloying by melting, and then molding and sintering. Raw materials (starting materials) for the above TE material are those containing at least bismuth and those containing at least tellurium. In addition to bismuth and tellurium, antimony, selenium, an alloy of tellurium and antimony, can be used. These raw materials are preferably in powder form. The particle diameters of the materials are 100–150 mesh pass. In the case of powders having a large particle diameter, it is preferred to control the particle diameter to be within the above range by such techniques such as grinding. In connection with the type of the raw material and the mixing ratio, various embodiments are considered. Examples are Bi:Te = 2:3 (molar ratio), Bi:Sb:Te = 2:8:15 (molar ratio), or (BiSb):(TeSe) = 2:3 (molar ratio). Particularly, by compounding bismuth (Bi) or bismuth antimony (BiSb) and tellurium (Te) or tellurium selenium (TeSe) in a ratio of about 2:3, a TE material, exhibiting excellent performance at temperatures of 600 K or less can be obtained. As the raw material, metal elements which is not alloyed by melting, or an alloy or a compound which is obtained in the course of scouring can be used as long as it contains the above component. The above raw material preferably contains a suitable amount of dopants. Dopants used conventionally can be added to the raw material by the usual methods. For example, in production of an n-type (negative type) TE material, SbI_3, CuTe, Cu_2 S, CuI, CuBr, AgBr, etc. can be used. In production of a p-type (positive type) TE material, Te, Cd, Sb, Pb, As, Bi, etc. can be used. Particularly in the case that bismuth and tellurium are added in a ratio of about 2:3, from viewpoints of solubility and stability, SbI_3 is preferably used in the n-type, and Te is preferably used in the p-type. The amount of the dopant added is determined appropriately depending on the type and mixing ratio of the raw material, and the type of a substance as the dopant. It is usually 0.01–10 mol% and preferably 0.05–5 mol%. To the raw material or starting material powder which has been copulverized and intermixed, a substance having low thermal conductivity (thermal conductivity reducing agent) can be added. The figure of merit can be improved by adding such thermal conductivity reducing agents. Examples of such thermal conductivity reducing agents are SiO_2, TiO_2, ZrO_2, B_2O_3, BN, and Si_3N_4. The added amount of the thermal conductivity reducing agent is determined depending on the purpose of use, particularly upon temperatures to which an apparatus is required to cool. It is usually 0.1–50% by weight and preferably 0.5–30% by weight. By adding a thermal conductivity reducing agent, even if the figure of merit of a TE material is the same, the thermal conductivity drops and thus cooling to a lower temperature can be achieved (Ohta et al. 1992).

In the process, the raw materials thus compounded are sufficiently mixed by copulverization and intermixing. In this case, it is desirable that pulverization and intermixing are carried out at the same time to further reduce the particle diameter of the raw materials. The pulverization and intermixing can be carried out simultaneously by various techniques such as a ball mill, an impact fine pulverization machine, a jet pulverization apparatus, and a tower-type friction machine. In the case that a ball mill is used as the pulverization and mixing method, it is preferred that a planetary-type ball mill or similar is used instead of the conventional dropping-type ball mill. Copulverization and intermixing can be carried out either in dry or wet conditions. For example, in the case of a wet condition, alcohols such as ethanol or butanol and various solvents can be used as mixing aids. In connection with the mixing power or mixing time in the above copulverization and intermixing, they are desirably controlled so that the average particle diameter of the starting material powder after copulverization and intermixing is 0.05–10 μm. The starting material powder after copulverization and intermixing is compression molded into a desired form by means of applying pressure such as press molding without the processing of alloying by melting employed conventionally. This compression molding can be carried out by adding a binder component (such as polyvinyl alcohol) if necessary. The pressure at the time of compression molding is usually 0.2–20 ton/cm^2 although it varies with the type and particle diameter of the starting material powder. As molding methods, in addition to the above compression molding, any desired molding methods such as hot press, extrusion molding, injection molding, coating, and a screen printing method can be employed. It is necessary to apply sintering after molding. A sintered product obtained exhibits high performance as a TE material. This sintering is applied to a molding obtained by the above mentioned molding, under reduced pressure or atmospheric pressure, or under pressure, specifically in the range of 10^{-3} to 10^6 Torr in an inert gas such as argon or nitrogen. The sintering temperature is chosen appropriately depending on the type and mixing ratio of the starting material, and it is usually 300–600°C. The heating-up rate, particularly at a temperature exceeding 200°C, and especially 400°C is preferably controlled to not more than 10 K/h. If the temperature is raised at a higher rate, the TE material obtained sometimes has reduced performance. If the heating-up rate is too slow, a long time period is needed to reach a predetermined temperature. For example, it is suitable to control the speed to about 3–10 K/h. The time of heating-up varies with the atmosphere under pressure and the composition, and is not necessarily limited to the above range. When the predetermined sintering temperature is reached at the above heating-up rate, the green molding is maintained at the temperature for the time needed to thereby sinter it, whereupon the desired TE material is obtained. This sintering time is usually 0.5–30 h. The figure of merit can be further increased by carrying out the above sintering treatment in a sealed condition, i.e., the green molding is not exposed to the atmosphere during sintering. The sealed condition can be produced by sealing the green molding in an ampule. At the time of sintering, the surrounding gas may comprise only one generated from the molding. The surrounding gas comprises another one, preferably inert gas, and more preferably reducing gas or a mixed gas of reducing gas and inert gas. As the inert gas, Ar (argon), is preferably used, and H_2, and CO are preferably used as the reducing gas. In sintering under a pressure of more than atmospheric pressure, it suffices that sintering with gas pressure in a nonoxidizing atmosphere is carried out. When sintering is carried out under a pressure of not more than atmospheric pressure, it suffices that a green molding is placed in a sealed container such as an ampule and after setting it at a predetermined pressure corresponding to a pressure increase generated by raising the sintering temperature, sintering is carried out at a raised temperature. In the case of reduced pressure (i.e., under a pressure of not more than atmospheric pressure), it is preferred for the sintering to be carried out in the presence of reducing gas. The reason why reducing gas is used as a preferred atmosphere is that the copulverized and intermixed starting material powder is relatively small in particle diameter and, as a result, is readily subject to oxidation and, therefore, the reducing gas is used to reduce the material. It is preferred that sintering is carried out under a pressure of not more than atmospheric pressure, thus a TE material obtained by sintering is decreased in density and is reduced in thermal conductivity. The TE material thus sintered is preferably annealed at a temperature of 50–200°C below the sintering temperature for a period of 0.5–30 h, if necessary. This annealing can be carried out in a reducing atmosphere and preferably in a sealed condition. In carrying out the reduction treatment in sintering or annealing, no special additional steps are necessary, and it suffices that the sintering or annealing is carried out in a reducing atmosphere. The figure of merit can be increased by carrying out the reduction treatment in at least any copulverizing and intermixing, sintering and annealing in the course of production of the above mentioned TE material. The reduction treatment usually proceeds by heating in a reducing gas such as H_2 or CO atmosphere. In this reduction treatment, a mixed gas of the reducing gas and inert gas such as Ar can be used. The reduction treatment is not critical for operation and can be carried out in various manners. Pressure conditions in the reduction treatment are also not critical. When the reduction treatment is carried out at the time of sintering or annealing, it is preferable that it be carried out in a sealed condition (Ohta et al. 1992).

The TE material can be easily obtained by copulverizing and intermixing metal elements as starting materials (particularly by the use of a planetary-type ball mill), molding, and then sintering. Particularly, because a powder element is used as a starting material, starting materials can be easily prepared. Furthermore, the TE material can be easily produced without a complicated procedure or a special apparatus, and thus the production cost of the TE material can be reduced. Additionally, the figure of merit can be improved by choosing specified sintering conditions. The thermal conductivity κ of the TE element produced by the process is not more than 1.4 W/m K and particularly 0.7–1.3 W/m K. Thus the TE element has the feature that it has lower thermal conductivity than that of the conventional TE element. The reason for this is that grain growth is less likely to occur at the time of sintering and a fine grain structure is obtained. Thus, a TE material is obtained having an increased figure of merit. Undesirable anisotropic properties and production loss do not arise. Moreover, because a material in any desired form can be directly produced, miniaturization is realized and one-body molding of a module is possible. Thus, the TE material can be used in a wide variety of fields such as TE power generation and TE cooling, a temperature sensor, space development, marine development, and electric power generation in the remote areas (Ohta et al. 1992).

Skutterudite Thermoelectrics

Skutterudite materials have structures in the form of (Co, Ni, Fe)(P, Sb, As)$_3$ and are cubic with space group Im^3. Unfilled, these materials contain voids into which low-coordination ions (usually rare earth elements) can be inserted in order to alter thermal conductivity by producing sources for lattice phonon scattering and decrease thermal conductivity due to the lattice without reducing electrical conductivity. Such qualities make these materials behave with phonon-glass electron-single-crystal behavior.

The skutterudite material system possesses the basic conditions for high *ZT* values: a large unit cell, heavy constituent atom masses, low electronegativity differences between the constituent atoms, and large carrier mobilities. In addition, skutterudites form covalent structures with low coordination numbers for the constituent atoms and can thereby incorporate atoms in the relatively large voids formed. Therefore, compounds can be formed with atoms filling the voids of the skutterudite structure. Placing atoms in the interstitial voids of this crystal system would substantially reduce thermal conductivity by introducing phonon-scattering centers. Thus these atomic void-fillers would rattle around in their oversized cages, thereby providing an approach to drastically reduce thermal conductivity, in the highly conductive binary compounds and thereby maximize *ZT*. Another advantage of this cubic material system is that single crystals are not necessary to investigate the electrical and thermal transport properties of the skutterudites, which makes their promise for TE applications more feasible if the appropriate materials parameters are achieved. In addition, these materials are hard and have a relatively low coefficient of thermal expansion (Nolas et al. 2001a, b). These factors make the skutterudites attractive as TE materials.

The basic family of binary semiconducting compounds forming the skutterudite structure consists generally of CoP_3, $CoAs_3$, $CoSb_3$, RhP_3, $RhAs_3$, $RhSb_3$, IrP_3, $IrAs_3$ and $IrSb_3$. The skutterudite structure, indicated by MX_3 where M represents a metal atom and X a pnictide atom, belongs to the body-centeredcubic space group Im^3.

The crystallographic unit cell consists of eight MX^3 units, with the eight M atoms occupying the *c* sites and the 24 X atoms situated on the *g* sites. The structure can be uniquely specified from the lattice constant and the two positional parameters *y* and *z* specifying the *g* site. The skutterudite structure can be considered a distortion of the more symmetric cubic perovskite ReO_3 structure (Nolas et al. 1999).

The filled skutterudites crystallize in the cubic space group Im^3 with two formula units (RM_4X_{12}) per unit cell. There are three unique atomic positions in the normalized unit cell. The rare earth position is (0, 0, 0), the transition metal position is (0.25, 0.25, 0.25), and the pnicogen (P, As, Sb) position (0, *y*, *z*) is variable with $y \approx 0.35$, $z \approx 0.16$. The positions of the remaining 31 atoms in the unit cell are determined by the symmetry operations associated with the Im^3 space group (Sales 2003). By alloying with Fe on the Co site or Sn on the pnictide site, compounds with lanthanide-filling fractions between zero and one have been obtained. However, it is also possible to fractionally fill the binary skutterudites without any metal atom substitution. For example, with this approach, $La_{0.2}Co_4P_{12}$ and Ce0.25Co4P12, as well as $Ce_{0.1}Co_4Sb_{12}$ and $La_{0.23}Co_4Sb_{12}$ have been formed. The relationship between the metal atom charge state, the lanthanide valence, and structural and electronic stability of these compounds is subtle and important. A novel approach to skutterudite compound synthesis has resulted in the preparation of many compounds that could not have been successfully formed employing traditional synthesis techniques. The formation of metastable skutterudite compounds in thin-film form was achieved through controlled crystallization of amorphous reaction intermediates formed by low-temperature interdiffusion of modulated elemental reactants. In this approach the elements are deposited sequentially in layers thin enough that the layers interdiffuse before nucleation occurs. The formation of the desired metastable compound, for example $FeSb_3$, is achieved at low-temperatures from the amorphous intermediates that have the same composition. In this way the formation of more thermodynamically stable compounds, such as $FeSb_2$, can be avoided. By employing this technique, in addition to the binary skutterudite $FeSb_3$, filled skutterudites with the general formula TFe_4Sb_{12} were formed, with T being all the lanthanide group elements as well as hafnium. This technique was also used in the synthesis of filled skutterudite with void fillers even smaller than the large mass lanthanides. These included Sn, Al, Ga, In, and Zn (Nolas et al. 1999).

Therefore, a large number of filled skutterudites have been developed and investigated. For instance, $CeFe_4Sb_{12}$ and $YbFe_4Sb_{12}$ are moderately heavy fermion metals. $CeRu_4Sb_{12}$ exhibits nonfermi liquid behavior and may be near a ferromagnetic quantum critical point. $PrOs_4Sb_{12}$ is the first example of a Pr compound that exhibits both superconductivity and heavy fermion behavior. $PrRu_4P_{12}$ and $SmRu_4P_{12}$ each undergo a metal-to-insulator transition and antiferromagnetic order. $PrFe_4P_{12}$ is an extremely unusual material in which quadrupolar order and heavy fermion ground states are extremely close in energy. At low temperatures a magnetic field ($\approx$ 4 T) can drive $PrFe_4P_{12}$ between the two ground states. The density of states in $PrFe_4P_{12}$ is remarkably sharp in energy as evidenced by a two order of magnitude change in the Hall coefficient below 5 K and a huge value for *S* at 5 K of -130 μV/K. Most of the La-filled skutterudites and two of the

Pr-filled skutterudites are superconductors with a maximum T_c of 10.3 K for $LaRu_4As_{12}$. Several of the Ce-filled skutterudites are narrow gap semiconductors (also called Kondo insulators) where the gap is created by a strong hybridization between the Ce 4f level and the transition metal and pnicogen states near the Fermi energy. The Nd, Eu, Gd and Tb filled skutterudites order magnetically at temperatures ranging from 2 K for $NdFe_4P_{12}$ to 100 K for $EuFe_4P_{12}$. The coupling between the lanthanide magnetic moments and the conduction electrons is large in these compounds. This large coupling results in unusual peaks in electrical transport data near the onset of magnetic ordering, and in some cases multiple magnetic transitions. Finally, the TE figures of merit for the La, Ce and Yb filled skutterudites are among the highest values reported for any material at elevated temperatures (600–1,000 K). By varying the extrinsic carrier concentration in the filled skutterudites, the yielded maximum value for *ZT* of 1.4 at 1,000 K, and a maximum *ZT* value of 0.3 at 300 K. The *ZT* values of the filled skutterudites are too small for room temperature applications. The relatively large band gap of these compounds ($\approx$0.6 eV) makes it unlikely that further research will result in a skutterudite-based TE material with properties better than the Bi_2Te_3-based materials currently in use near room temperature. Only at temperatures in the 600–900 K temperature range are the TE properties of the filled skutterudite antimonides of interest for use in power generation applications (Sales 2003).

The synthesis process of the skutterudites is rather complicated. The skutterudites do not melt congruently and involve pnicogens (P, As, Sb) that generally have high vapor pressures at the formation temperatures of the compounds. The high melting temperatures of Fe, Ru and Os coupled with the reactivity of the lanthanide metals with convenient crucible materials (e.g., SiO_2) makes the synthesis of many of these compounds difficult. Small single crystals of most of the lanthanide phosphides can be grown in a molten tin flux. For example, $LaFe_4P_{12}$ crystals were grown using La filings, Fe powder, red phosphorus, and Sn in the atomic ratio 1:4:20:50. The mixture was sealed in an evacuated silica tube, annealed for one week at 1,050 K, and slow cooled (2 K/h) to about 773 K, followed by rapid cooling to room temperature. A 1:1 mixture of HCl and water was then used to dissolve the Sn flux. Single crystals with typical dimensions from 0.1 to 2 mm can be grown by this method. Polycrystalline skutterudite phosphides have also been synthesized directly from the elements using a high pressure (4 GPa) and high temperature (800–1,200°C) wedge-type cubic-anvil apparatus (Shirotani et al. 1996, 1997; Sekine et al. 1997; Uchiumi et al. 1999). This technique avoids contamination from residual Sn flux. Lanthanide arsenides with the filled skutterudite structure were prepared: Lanthanide arsenides (RAs), were first prepared by reacting lanthanide filings with As in a silica tube at 900 K for 2 days. The RAs material was then ground together with the transition metal and excess As (R:T:As = 1:4:20) and sealed again in evacuated silica tubes, rapidly heated to 1,150 K and kept at temperature for 3 h. The samples were then annealed at 1,000 K for 4–7 days. The excess As was removed through sublimation. In spite of this elaborate synthesis procedure, the overall products were only 70–90% single phase. However, small single crystals of the skutterudite phase suitable for X-ray structure refinement could often be isolated from the reaction product. A dense single-phase sample of $CeFe_4As_{12}$ was prepared by a similar procedure followed by the densification of the powder with a hot-press (Watcharapasorn et al. 2002). Single-phase arsenides with a variety of compositions have also been prepared via direct high-pressure high-temperature synthesis from the elements (Shirotani et al. 1997). Synthesis of the lanthanide antimonides with the filled skutterudite structure have been synthesized using a procedure similar to that described above for the synthesis of the arsenides. The phase purity of the antimonides prepared in this manner was only about 80%. A better synthesis procedure was used (Sales et al. 1996, 1997): a thin layer of carbon was deposited on the inside of a round-bottomed silica tube by the pyrolysis of acetone. Stochiometric amounts of high purity lanthanide metal pieces (99.99% electropolished bar), Fe rod (99.9985%), and Sb shot (99.999%) were loaded into the precarbonized tube. The tube was sealed under vacuum at a pressure of 10^{-3} Pa and transferred into a programmable furnace. The silica ampoule was heated to 600°C at 2°C/min, left at 600°C for 3 h, and then slowly (0.5°C/min) heated to 1,050°C and left for about 20–40 h. It is important to slowly heat the tube because of the highly exothermic reaction between the lanthanide elements (particularly Ce) and antimony. The silica ampoule containing the homogeneous molten liquid was removed from the furnace and quenched into a water bath. The same ampoule (containing the prereacted elements) was then placed in a furnace and annealed at 700°C for 30 h to form the correct crystallographic phase. The completely reacted solid was removed from the silica tube and cleaned with a wire brush to remove small amounts of carbon from the surface. To form a completely dense polycrystalline solid, the reacted material was ball milled into a fine powder in an argon atmosphere, loaded into a graphite die, and hot-pressed (5,000 psi) in a helium atmosphere at 700°C for 40 min. This procedure results in single-phase and dense polycrystalline samples. Single crystals of the antimonides can also be grown using excess antimony as a flux (Chakoumakos et al. 1999). High purity elements in the ratio R:T:Sb = 1:4:20 are loaded into an evacuated carbon coated quartz tube. The tubes are heated to 900°C for 24 h and then cooled slowly (1–3°C/h) to 600°C, followed by a quench to room temperature. The excess Sb flux can be removed by etching in acid ($HCl:HNO_3 = 1:1$). Small quantities of new compounds with the skutterudite structure can also be synthesized using a clever nonequilibrium thin film method pioneered by D.C. Johnson and colleagues at the University of Oregon (Hornbostel et al. 1997). The new compounds are formed by the low-temperature interdiffusion of multilayer elemental reactants (Sales 2003).

Oxides

Oxide TE materials have been rapidly developed since high TE performance of layered cobalt oxide $NaCo_2O_4$ reported in 1997. These p-type oxides in single crystal form have been proved to show $ZT \approx 1$. However, performance of n-type oxides had remained at a relatively low level $ZT \approx 0.3$ for Al-doped ZnO in 1996. The efforts have been made to overcome disadvantages of oxides such as low carrier mobility and high lattice thermal conductivity: electron correlation, quantum wells, and bulk nanocomposites, and promising results on n-type ZnO-based bulk nanocomposites showing $ZT \approx 0.65$ (Ohtaki 2002).

Metal oxides have attracted much attention as TE power generation materials at high temperatures on the basis of their potential advantages over heavy metallic alloys in chemical and thermal robustness. To clarify the intrinsic TE properties of oxides, high-quality epitaxial films of several TE oxides, including Na_xCoO_2, Li_xCoO_2, Sr_xCoO_2, Ca_xCoO_2, $Ca_3Co_4O_9$, $SrTiO_3$:Nb, TiO_2:Nb, and $SrO(SrTiO_3)$:Nb have been investigated. Two representative oxides, p-type $Ca_3Co_4O_9$ and n-type $SrTiO_3$:Nb, exhibit the best ZT among these oxide TE materials.

Generally, a vapor-phase epitaxy (VPE) method, such as pulsed-laser deposition (PLD), is appropriate for high-quality epitaxial film growth of oxide materials. However, fabrication of a Na_xCoO_2 epitaxial film is very difficult by a conventional VPE method (growth temperature, $T_g \sim 700°C$) because revaporization of Na due to its extremely a large vapor pressure of $\sim 10^4$ Pa at 700°C occurs during film growth. A method of reactive solid-phase epitaxy, is a powerful means to fabricate single-crystalline films of layered oxides, and subsequent topotactic ion exchange. First, a high-quality epitaxial film of CoO was deposited on the (0001) face of an α-Al_2O_3 substrate at 700°C by PLD using a Co_3O_4 sintered disk as a target. Then the PLD-deposited CoO film was heated together with a $NaHCO_3$ powder at 700°C in air to give a c-axis-oriented Na_xCoO_2 ($x \sim 0.8$) epitaxial film. The Na_xCoO_2 film can be converted into Li_xCoO_2, Sr_xCoO_2, Ca_xCoO_2, and $Ca_3Co_4O_9$ epitaxial films by the appropriate ion-exchange treatment.

Although very high ZT values ~ 1 have been reported for p-type $Ca_3Co_4O_9$ and n-type $SrTiO_3$:Nb, reliable ZT values of both materials were clarified to be ~ 0.05 at 300 K and ~ 0.3 at 1,000 K. Thus, nanostructural control such as an artificial superlattice or 2DEG may be necessary to obtain a high ZT TE oxide. For example, utilizing a 2DEG in $SrTiO_3$ provide a new route to realizing practical TE materials without employing toxic heavy elements. A two-dimensional electron gas (2DEG) in $SrTiO_3$ demonstrates a Seebeck coefficient S that is enhanced by a factor of ~ 5 compared with the bulk and an optimized ZT that reaches 2.4, twice that of conventional TE materials (Tervo et al. 2009).

Other oxide materials such as Na_2CoO_4, $CaMnO_3$, $(ZnO)(In_2O_3)$, ZnO and $CuAlO_2$ appear promising because they are chemically stable at high temperatures and they have high oxidation resistance. They are also nontoxic. Na_2CoO_4 has especially been reported to show unusually high Seebeck coefficient at room temperature, i.e., 100 μV/K. General problems with oxide TEs, however, were reported to be weak mechanical strength, high contact resistance at interfaces of oxides and electrodes (Tervo et al. 2009).

Flexible Graphite

Flexible graphite is quite unusual in its combination of compliance and strong TE behavior. Therefore, it can be used as a compliant TE material to reduce thermal stress between a TE cell and the wall of a heat exchanger of a TE energy conversion system, improving the thermal coupling as well as the system's durability. Flexible graphite is much more conductive thermally in the in-plane direction than in the out-of plane direction. The high in-plane thermal conductivity, together with the resilience in the out-of plane direction, helps the attaining of a good thermal contact between flexible graphite and a hot/cold surface. On the other hand, the low out-of-plane thermal conductivity is favorable for the Seebeck effect in the out-of-plane direction. The Seebeck effect in the through-thickness direction of flexible graphite can be used for the generation of electrical energy, as a Seebeck voltage is generated between the two opposite in-plane surfaces of a flexible-graphite sheet when the sheet is placed on a hot object or a cold object. The flexibility of the sheet facilitates the placement on a surface that is not flat. A related application is the sensing of the temperature of the hot or cold object (Luo et al. 2002). Further research would be need for feasible applications.

Low-Dimensional Thermoelectric Materials

Low-dimensional materials, such as quantum wells, superlattices, quantum wires, and quantum dots offer new ways to manipulate the electron and phonon properties of a given material. In the regime where quantum effects are dominant, the energy spectra of electrons and phonons can be controlled through altering the size of the structures, leading to new ways to increase *ZT*. In this regime, the low-dimensional structures can be considered to be new materials, despite the fact that they are made of the same atomic structures as their parent materials. Each set of size parameters provides a novel low-dimensional material that can be examined, to a certain extent, both theoretically and experimentally, in terms of its TE properties. Thus, searching for high *ZT* systems in low-dimensional structures can be regarded as the equivalent of synthesizing many different bulk materials and measuring their TE properties. Because the constituent parent materials of low-dimensional structures are typically simple materials with well-known properties, the low-dimensional structures are amenable to a certain degree of analysis, prediction and optimization. When quantum size effects are not dominant, it is still possible to utilize classical size effects to alter the transport processes, as for example the exploitation of interfaces and boundaries to scatter phonons more effectively than electrons. Investigations on low-dimensional structures have exploited both quantum and classical size effects for electrons and phonons (Yang and Chen 2005).

The field of low-dimensional thermoelectricity started with the introduction of two strategies (Dresselhaus et al. 2007): the use of quantum-confinement phenomena to enhance S and to control S and k somewhat independently, and the use of numerous interfaces to scatter phonons more effectively than electrons and to scatter preferentially those phonons that contribute most strongly to the thermal conductivity. Three additional concepts, including carrier-pocket engineering, energy filtering, and the semimetal–semiconductor transition have further advanced the potential for using low-dimensional materials to enhance TE performance. This was first demonstrated through a two-dimensional (2-D) superlattice consisting of PbTe quantum wells and $Pb_{1-x}Eu_xTe$ barriers. Experiments on cross-plane transport in Bi_2Te_3/Sb_2Te_3 superlattices demonstrated that the scattering of phonons by the interfaces reduced the thermal conductivity more than the electrical conductivity, thereby establishing proof-of-principle of this second concept, which has since been shown in practice to yield a great enhancement to *ZT*. Following the experimental demonstration of enhanced TE performance in 2-D superlattices, research moved forward in two different directions. In one direction, advances in superlattice design and growth were pursued, while in the second research direction ordered structures of lower dimensionality, such as 1-D quantum wires and 0-D quantum dots were investigated.

Superlattices have been found to be structures that improve *ZT*. The alternating layers of materials can be manufactured from good TE materials. Superlattice consists of several alternating nanosized layers, each less than 5 nm thick. These layers block the travel of atomic vibrations that produce heat flow but still let the electrons to flow as current. Adding interfacial phonon scattering sites, the thermal conductivity can be reduced. Fabrication methods include lithography and electroplating, which are widely used in semiconductor industry (Tervo et al. 2009). Figure 11.5 shows the example of fabricated micro TEC device with Bi_2Te_3 and Sb_2Te_3 deposited on Cr/Au/Ti/Pt hot (bottom) or cold connectors (Da Silva et al. 2003).

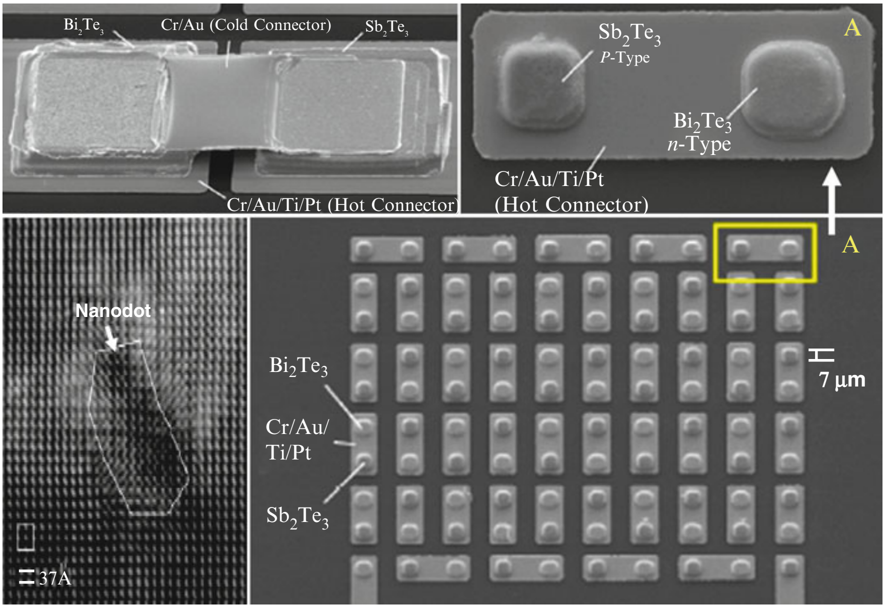

Fig. 11.5 Example of fabricated micro thermoelectric cooler device with Bi_2Te_3 and Sb_2Te_3 deposited on Cr/Au/Ti/Pt hot (*bottom*) or cold connectors

In superlattices, the periodicity has three major effects on the phonon spectra: (1) phonon branches are folded due to the new periodicity in the growth direction, (2) mini band-gaps form, and (3) the acoustic phonons in the layer with a frequency higher than that in the other layer become flat, or confined due to the mismatch in the spectrum. The major impact of these changes is the phonon group velocity reduction in the cross-plane direction, which has been proposed as an explanation for the lowered thermal conductivity. For example, superlattices of such sandwich structures over thousands of periods were grown to produce a quantum-dot superlattice (QDSL) of composition $PbTe/PbSe_{0.98}$ $Te_{0.02}$ on top of a BaF_2 substrate followed by a relatively thin PbTe buffer layer. Using Bi as n-type dopant for this QDSL, values of $ZT \sim 1.6$ and 3.5 were achieved at 300 K and 570 K, respectively. Encouraging results were also reported for a p-type QDSL-based on using Na as the dopant. The very large *ZT* values obtained by using this approach show that it is possible to both increase the power factor $S^2\sigma$ and to decrease the thermal conductivity at the same time in QDSLs, and therefore enhancing *ZT*. The superlattice structures appear to be more than twice as efficient as previous bulk TE materials. However, serious difficulties will be faced due to phenomena taking place in nanoscale. The biggest problem is reported to arise with electrical conductivity as a result of contact resistance and difficulties in predicting thermal conductivity. The problem requires mastering of electron-hole-phonon transport in nanoscale (Bulusu and Walker 2008). Thin-film TEC devices based on improved model system may someday be utilized for high-performance characteristics. In addition, the behavior of bulk thin films of SiGe and superlattice thin films of Si/SiGe was compared as microrefrigerators (Ezzahri et al. 2008). Although superlattice has enhanced electrical properties (larger TE power factor), the maximum cooling of thin film refrigerators based on SiGe alloys are comparable with that of superlattices. This is considered to be due to larger thermal conductivity of superlattices as compared to bulk SiGe thin films. Bulk thin films are also easier to grow by using methods such as chemical vapor deposition. Si-based microrefrigerators as well as other devices are attractive for their potential monolithic integration with Si microelectronics (Tervo et al. 2009).

Following the second research direction of going to lower dimensions, the study of quantum wires for TE applications was pursued (Dresselhaus et al. 2007). One material with very high potential for TE applications has for many years been Bi and Bi-related materials, because of the high S of the Bi. But unfortunately, Bi is a semimetal with both electron and hole carriers, and electrons and holes therefore contribute with opposite signs to its total S. To take advantage of the excellent electronic properties of the electron carriers in Bi materials, they would have to be prepared as an n-type semiconductor. The development of Bi-based quantum-well superlattices was, however, impeded by the difficulty in finding a suitable barrier material for Bi quantum wells in preparing 2-D quantum-well superlattices. Therefore, the development of Bi and $Bi_{1-x}Sb_x$ alloys as low-dimensional materials took the form of preparing ordered arrays of 1-D quantum wires inside the pores of anodic Al templates: Al is a well-behaved barrier material. The mechanism by which Bi can be converted into a semiconductor is the size-dependent semimetal–semiconductor transition. When the size of a semimetal nanowire decreases so that there are relatively few quantum states for the direction normal to the axis of the nanowire, then the energy bands split into discrete sub-bands. In this quantum regime, as the wire diameter decreases, the lowest conduction sub-band edge moves up in energy while the highest valence subband edge moves down in energy until these energy levels cross as the material makes a transition from a semimetal (with overlapping energy states for the lowest conduction band and the highest valence band) to a semiconductor with a band gap between the valence and conduction bands. In the semiconducting phase, the material can be doped to have one strongly dominant carrier type. As alloying Bi with Sb changes the electronic structure of the bulk alloy, the semimetal–semiconductor transition for a Bi–Sb nanowire, is dependent on both wire diameter and Sb concentration. By changing both the wire diameter and Sb composition, two variables can be provided for controlling and optimizing nanomaterials for enhanced TE performance (Dresselhaus et al. 2007).

Nanowires can be used for blocking free movement of phonons. As shown in Figure 11.6a, the electrochemically synthesized large-area, wafer-scale arrays of rough Si nanowires are 20–300 nm in diameter (Hochbaum et al. 2008). These nanowires have Seebeck coefficient and electrical resistivity values that are the same as those of doped bulk Si, but those with diameters of about 50 nm exhibit 100-fold reduction in thermal conductivity, yielding $ZT = 0.6$ at room temperature. For such nanowires, the lattice contribution to thermal conductivity approaches the limit for amorphous Si. Bulk Si is a poor TE material. However, by greatly reducing thermal conductivity without affecting much the Seebeck coefficient and electrical resistivity, Si nanowire arrays show promise as high-performance, scalable TE material. The similar result is as shown in Figure 11.6b, efficient TE performance was achieved from the single-component system of silicon nanowires for cross-sectional areas of 10 nm by 320 nm (Boukai et al. 2008). By varying the nanowire

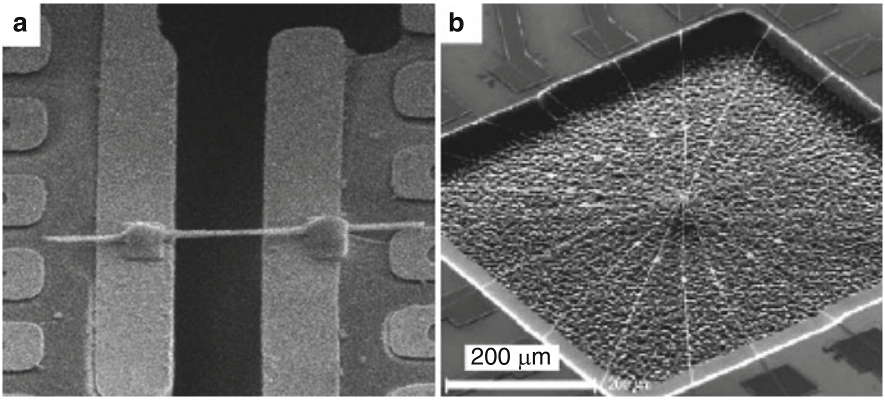

Fig. 11.6 Examples of Si nanowire thermoelectric materials (Tervo et al. 2009): (**a**) Pt-nanowire; (**b**) overview of the suspension arrangement of Si nanowires

size and impurity doping levels, ZT values representing an approximately 100-fold improvement over bulk Si were achieved over a broad temperature range, including $ZT < 1$ at 200 K. Moreover, arrays of quantum dots were synthesized with each only a few nanometers in diameter (Harman et al. 2002). The materials were PbSeTe-based quantum dot superlattice structures grown by molecular beam epitaxy. Improved cooling values relative to the conventional bulk $(Bi,Sb)_2(Se,Te)_3$ TE materials were obtained using an n-type film in a one-leg TE device, which cooled the cold junction 43.7 K below the hot junction temperature of 299.7 K. The typical device consists of a substrate-free, bulk-like (typically 0.1 mm in thickness, 10 mm in width, and 5 mm in length) slab of nanostructured PbSeTe/PbTe as the n-type leg and a metal wire as the p-type leg (Tervo et al. 2009).

Thermoelectric Nanocomposites

Figure 11.7 shows the historic progress of high efficiency TE materials. The maximum ZT has stayed stagnant at around 1 for all temperature ranges over 50 years since the important advancements using alloying approach. In the 1990s, two parallel approaches were proposed for the enhancement of the ZT of TE materials. The first of these approaches is based on new categories of advanced bulk materials,

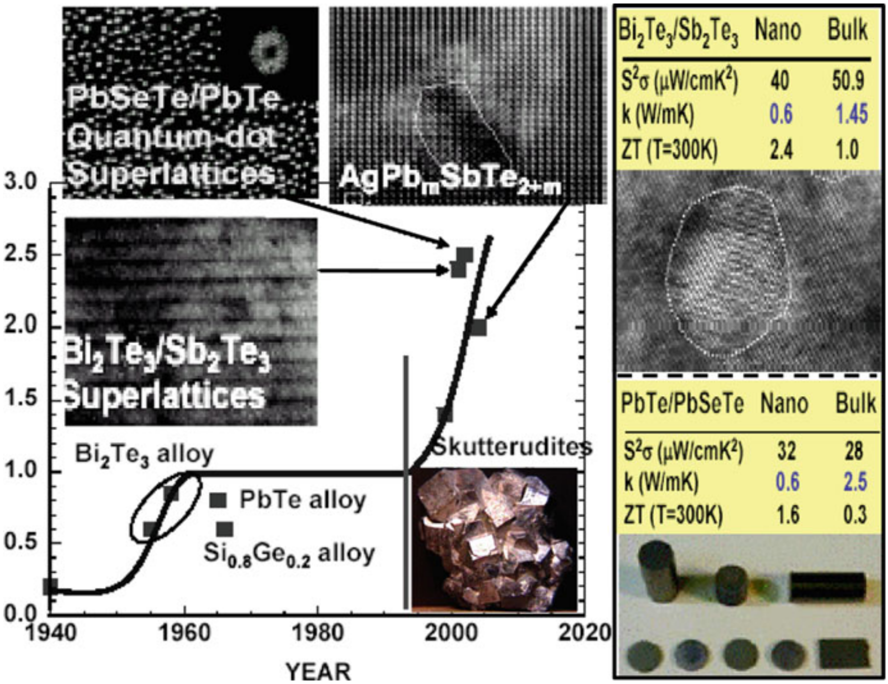

Fig. 11.7 Advances in thermoelectric materials (Dresselhaus 2009)

with crystal structures that contain weakly bound atoms or molecules with large vibrational amplitudes (called ratters) at partially filled structural sites acting as effective phonon scatterers. Material systems, such as skutterudites (e.g., $CoSb_3$), clathrates (e.g., $Ba_8Ga_{16}Ge_{30}$) and Zintl phases belong to this category. The second approach is using low-dimensional materials (such as quantum well superlattices, quantum wires, and quantum dots) that would result in an enhancement of the *ZT* by two mechanisms (Thiagarajan et al. 2009): (1) nanoscale features that introduce quantum confinement effects in the material lead to an enhancement of the power factor $S^2\sigma$, and (2) the use of the numerous interfaces in the nanostructures that scatter phonons more than the electrons, based on the difference in their respective scattering lengths, and thus reducing the thermal conductivity without adversely affecting the electrical conductivity as much.

However, the low-dimensional materials fabricated by atomic layer deposition techniques are not easily incorporated into commercial devices because they are slow and expensive to fabricate, and they cannot be fabricated in sufficient quantities. Modeling of phonon transport in superlattices indicated that the primary benefit from nanostructures, a reduced lattice thermal conductivity, does not require an atomically perfect interface or an exact geometry. All that is required is a material with a high density of interfaces, which can be present in any geometry. This discovery led to the idea of a nanocomposite, which retains the high density of interfaces but does not have a special geometry or structure, significantly simplifying the fabrication process and allowing the material to be produced in large quantities (Minnich et al. 2009).

A TE nanocomposite is a composite constructed by incorporating TE nanostructures in a matrix of a bulk TE material or compacting various TE nanostructures into bulk form. Several methods for the preparation of TE nanocomposites have been exercised. These methods to obtaining bulk samples with nanoscale features can be broadly classified into two categories (Thiagarajan et al. 2009): (1) compaction of nanoscale constituents (nanoparticles, nanowires, etc.) into bulk samples. The essence of all compaction techniques is to apply high pressure for densification, and often a rather high temperature to soften the material so that plastic deformation allows better filling and material flow by diffusion to remove the remaining porosity. The challenge is in achieving high density (and low porosity) without losing the nanoscale microstructure and keeping the material chemically pure. (2) In situ precipitation of nanoscale constituents by means of phase separation. The phase separation method of synthesizing nanostructures in situ in a bulk sample is inspired by precipitation process of a supersaturated solid solution, like hardening of aluminum. In this process, the TE materials will generally be heated up to the liquid-phase state, and then quenched to obtain a supersaturated solid solution or amorphous structure. The as-obtained metastable solid solution or amorphous structure will decompose into different dispersed phases after a nucleation and growth process by annealing at certain duration, and thus forms the nanoscale embedded precipitates in bulk matrix. The size of the precipitates increases as the duration and the temperature of the annealing process increase. Such spontaneous formation of nanoscale features is desirable because it minimizes the possibility of oxidation and the introduction of other forms of impurities, which would lead to degradation of electrical performance.

Therefore, either nanoparticles embedded in a host or a heterostructure geometry with nanoparticles of different materials adjacent to each other can be obtained. For the heterostructure geometry, when the two materials are the same the nanocomposite is essentially a material with nanometer-sized grains. Because these nanostructures have a size smaller than the phonon mean free path but greater than the electron or hole mean free path, phonons are more strongly scattered by the interfaces than are electrons or holes, resulting in a net increase in *ZT*. As nanocomposites are not formed by atomic layer deposition methods, they are significantly quicker and cheaper to fabricate than superlattices or other nanostructures, yet retain the same enhancements in TE properties. When the nanocomposite concept was still being developed, however, nanostructured materials which exhibited enhanced TE properties had only been created using atomic layer deposition techniques, and it was unclear whether any bulk process could create a thermodynamically stable, nanostructured material with an improved figure of merit. A still unresolved question is why certain nanostructured materials exhibit improved properties while others do not. Some fabrication methods, while capable of creating a nanostructured material, cannot produce a material with an improved *ZT* no matter how the fabrication conditions are adjusted (Minnich et al. 2009).

Despite these difficulties, several bulk processes have been developed which have successfully created stable nanocomposites with improved properties over those of their bulk counterparts. One method uses ball milling and hot pressing to create nanograined materials. In this technique, raw component elements, such as Bi and Te or Si and Ge, are ground into a nanoparticle dust using a ball milling machine. The resulting mixture is then hot pressed at an appropriate temperature and pressure. If the pressing temperature and duration are adjusted correctly, the nanoparticles will fuse together but leave the interface between each particle intact, creating a fully dense solid material with nanosize grains. This technique has been successfully implemented on n-type $Si_{80}Ge_{20}$, p-type $Si_{80}Ge_{20}$, and different types of $Bi_xSb_{2-x}Te_3$. The advantages of this method are that it is simple and inexpensive to fabricate the materials, and the technique can be applied to any material system. Another method to create a bulk nanocomposite is to use thermal processing techniques to induce the formation of nanoscale precipitates, an approach which has been successfully used in several material systems. By choosing the appropriate compounds and subjecting the material to a thermal processing procedure, a metastable solid solution of different elements can be made to undergo spinodal decomposition or nucleation and growth mechanisms to create nanoscale features. A related technique, known as matrix encapsulation, uses the fact that some materials are soluble in others in the liquid state but not in the solid state. By rapidly cooling the liquid mixture, the insoluble minority phase will precipitate, forming nanoparticles embedded in the host phase. These techniques have been applied with considerable success to several different solid solutions. High *ZT*s have been reported in n-type $AgPbTe_2/PbTe$, n-type $Pb_{1-x}Sn_xTe/PbS$, and p-type $Na_{1-x}Pb_mSb_yTe_{m+2}$ (Minnich et al. 2009).

Nanocomposites have been successful in increasing *ZT* by reducing the thermal conductivity below that of the bulk material while allowing for large scale, quick,

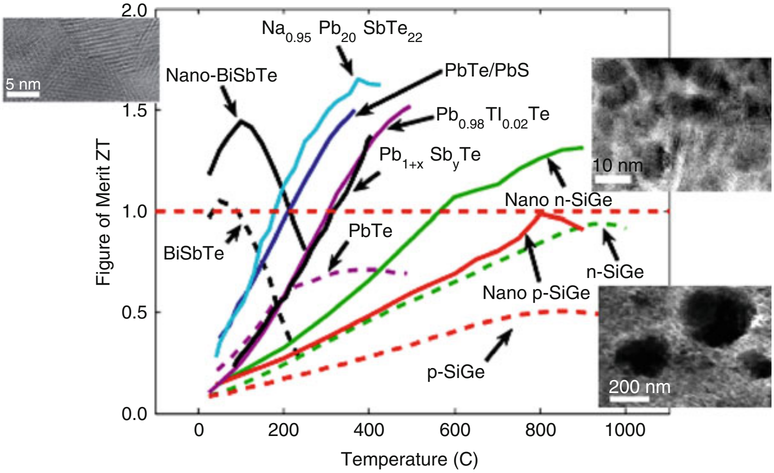

Fig. 11.8 Figure of merit *ZT* of current state of the art thermoelectric materials *versus* temperature. The *dashed lines* show the maximum *ZT* values for bulk state of the art materials, and the *solid lines* show *ZT* values of nanocomposites (Minnich et al. 2009)

and inexpensive fabrication. Figure 11.8 summarizes the figure of merit *ZT* of the current state of the art TE materials versus temperature. The dashed lines show the maximum *ZT* values for bulk state of the art materials, and the solid lines show *ZT* values of some nanocomposites appropriated for different temperature ranges (Minnich et al. 2009). The first generation of nanocomposites has been developed, and efforts to use the materials in commercial devices are currently under way. However, developing the second generation of nanocomposites will require a more controlled design process where the TE properties of different nanostructures can be predicted and the desired structure created using a bulk procedure. The current design process of trial and error will not be sufficient. This goal can only be achieved with a fundamental understanding of transport in these complex materials and how their nanoscale structure affects bulk properties (Minnich et al. 2009).

While there is much to be understood about phonon and electronic transport in nanocomposites, this also means that there is still much room for innovation and improvement. Since the lattice thermal conductivity in nanocomposites has already been reduced, further improved materials will most likely feature some type of improvement in electrical properties combined with a reduction in lattice thermal conductivity. The flowing strategies to improve electrical properties might be used in the next generation of nanocomposite TE materials (Dresselhaus et al. 2007; Minnich et al. 2009).

Increasing the Mobility

Nanostructured PbTe with encapsulated nanodots made of both Pb and Sb has an increased mobility over that of the bulk PbTe, resulting in a *ZT* a factor of two larger than that of bulk PbTe. This increase in mobility only occurs when both Pb and Sb are present together in the nanoparticle. A similar effect is possible in other material systems.

Energy Filtering

In nanocomposites, the obvious scattering mechanism is electron grain boundary scattering, which does reduce the mobility but also preferentially scatters electrons with energy filtering. InGaAs/InGaAlAs superlattice exhibited an increase in power factor $S^2\sigma$ due to energy filtering effects. Increases in the Seebeck coefficient due to energy filtering in bulk nanostructured PbTe-based materials have also been reported, although the mobility was adversely affected. If a bulk fabrication process can be found which minimizes the degredation of the mobility while enhancing the Seebeck coefficient, the resulting material would have a net increase in power factor. This method is a good example of how nanostructuring can be used to improve electrical properties while still maintaining a low thermal conductivity.

Resonant Levels to Enhance the Density of States

In most semiconductors, the addition of impurity atoms introduces states with energies in the band gap. If these states are very close to the conduction or valence band edges, as is the case for P or B in Si, the electrons (or holes) will be thermally activated into the conduction (or valence) bands and will be able to conduct. In some exceptional cases, however, the energy level created by the impurity can actually lie in the conduction or valence bands, creating a resonant level and a local maximum in the electronic density of states. For instance, it should be possible to create a material that uses both the resonant level and the nanocomposite concepts: one simply needs to add Tl to PbTe and generate the nanocomposite in the usual manner. The resulting material should have a lower thermal conductivity than the bulk value but significantly improved electrical properties due to the Tl doping. While Tl-doped PbTe did show a remarkable increase in *ZT*, Tl itself is highly toxic, making the commercial use of this material undesirable. Although resonant levels are not common, it is reasonable to believe that there are at least a few other materials in which impurities can introduce resonant levels near the band edges. These might be able to be identified using density functional theory or spectroscopic techniques to determine the impurity energy levels. These techniques together will hopefully help clarify the origin of the resonant level and allow researchers to fully realize the potential of this approach towards both enhancing the power factor and reducing the thermal conductivity.

Reducing the Bipolar Effect

The major theme of nanocomposites has been a reduction of the lattice thermal conductivity. However, nanocomposites now have such a low lattice thermal conductivity that the other contributions to the thermal conductivity, the electronic thermal conductivity and the bipolar thermal conductivity, can be comparable in magnitude. The bipolar effect is a result of the fact that there are two types of carriers, electrons and holes. At high temperature many electrons are thermally excited from the valence band to the conduction band, leaving behind an equal number of holes. The presence of these two types of carriers allows heat conduction to take place even if the net electrical current is zero. Furthermore, because electrons and holes have opposite charges, the Seebeck coefficient is significantly suppressed if both electrons and holes are present. Thus, reducing the bipolar effect can improve the figure of merit in two ways. While many TE materials are usually so highly doped that this effect is not strong, for some materials at elevated temperature the bipolar thermal conductivity can be a significant component of the total thermal conductivity and the Seebeck coefficient can be markedly reduced.

Reducing the Electronic Thermal Conductivity

The final strategy to enhance *ZT* is reducing the electronic thermal conductivity. At first, it might seem impossible to reduce the thermal conductivity from electrons or holes: after all, charge carriers must travel through the TE material, and when they do so they will inevitably carry heat. To implement this strategy it is necessary to search for materials with very strongly peaked density of states near the Fermi level. Another approach is to use quantum dots, as these 0-D structures inherently only have states at certain specific energies, giving a delta function density of states. The challenge here is to create quantum dots with the correct energy levels and in bulk quantities. Another way one could implement this strategy is to use the resonant level concept discussed earlier. The mechanism by which the Seebeck coefficient is enhanced is by a local maximum in the density of states contributed by the resonant level. If this effect could be enhanced, a simultaneous increase in Seebeck coefficient and reduction in electronic thermal conductivity can be obtained, leading to a dramatic increase in *ZT*.

Consequently, bulk nanocomposites have experimentally demonstrated a higher *ZT* than that of their bulk counterparts by reducing the thermal conductivity to values lower than were previously thought possible. More importantly for practical use, the materials can be fabricated inexpensively, quickly, and in a form that is compatible with existing TE device configurations. The first generation of bulk nanostructured materials is currently being commercialized, and it is promising that TE devices which use these materials will soon find more widespread applications. However, creating the second generation will require a fundamental understanding of carrier transport in these complex materials which is presently lacking. Continuous research in understanding carrier transport might lead to the next generation of bulk nanocomposites. Further research in this field will allow TEs to play a positive role in any future thermal management solution.

Summary

TEC is a popular but inefficient way to remove heat from high-power-dissipating electrical components. The advantages of TEC are silent, compact, reliable, and durable. In addition, the cooling power can be modulated to maintain a fixed temperature. TEC uses Peltier effect to form a solid state heat pump, and works in conjunction with a heat sink or liquid cooling device to dissipate heat from an electronic packing system. A modern TEC is a semiconductor-based electronic component that functions as a small heat pump. By applying a low voltage DC power source to a TE module, heat will be moved through the module from one side to the other. One module face, therefore, will be cooled while the opposite face is heated simultaneously. A TE module may be used for both heating and cooling thereby making it highly suitable for precise temperature control applications.

The TE effect is the direct conversion of temperature differences to electric voltage and vice versa at the junctions of two different conductors. Traditionally, the TE effect encompasses three separately identified effects, the Seebeck effect, the Peltier effect, and the Thomson effect. These three effects, together with several other phenomena, form the basis of functional TE modules. A typical TEC component is an n- or p-type semiconductor (bismuth telluride) sandwiched between two conductors. The semiconductor is used because they can be optimized for pumping heat and because the type of charge carriers within them can be chosen. When an electronic field is applied to two ends of the n-type (doped with electrons) semiconductor, the electrons move towards the positive end to release heat, while the negative end absorbs heat. Therefore, the heat is transported in the direction of current flow. When a p-type semiconductor (doped with holes) is used instead, the holes move in a direction opposite the current flow. The heat is also transported in a direction opposite the current flow and in the direction of the holes. When the electrons fill a hole, they drop down to a lower energy level and release heat in the process. The most efficient configuration is where a p and n TE component is put electrically in series but thermally in parallel. When assembling it into an electronic package, one side is attached to a heat source and the other a heat sink that convects the heat away. In electronic packaging, TECs would be used to cool computer components to keep temperatures within design limits without the noise of a fan, or to maintain stable functioning when overclocking. A Peltier cooler with a heat sink or liquid cooling device can cool a chip to well below ambient temperature.

Peltier TEC performance is a function of ambient temperature, hot and cold side heat exchanger (heat sink) performance, thermal load, Peltier module (thermopile) geometry, and Peltier electrical parameters. TEC modules are considered to be highly reliable components due to their solid-state construction. For most applications they will provide long, trouble-free service. There have been many instances where TE modules have been used continuously for 20 or more years and the life of a module often exceeds the life of the associated equipment.

However, TECs in use today have a COP of only about 0.5. This is quite a low value compared with COPs of larger scale machines, such as air conditioners and refrigerators at levels of 3.0–5.0. For electronic component cooling, advanced emerging TE materials provide probability for improved efficiency of TECS. Two different approaches were taken for developing the next generation of new TE materials: one using new families of advanced bulk TE materials based on crystal structures that contain weakly bound atoms or molecules with large vibrational amplitudes at partially filled structural sites acting as effective phonon scatterers, such as skutterudites, clathrates and oxides; and the other using low-dimensional materials systems, such as quantum well superlattices, quantum wires, quantum dots, thin film, or band engineering structures. Low-dimensional materials systems are now being assembled as nanocomposites containing a coupled assembly of nanoclusters showing short-range low dimensionality embedded in a host material, thereby producing a bulk material with nanostructures and many interfaces that scatter phonons more effectively than electrons.

Bulk nanocomposites have experimentally demonstrated a higher *ZT* than that of their bulk counterparts by reducing the thermal conductivity to values lower than were previously thought possible. More importantly for practical use, the materials can be fabricated inexpensively, quickly, and in a form that is compatible with existing TE device configurations. The first generation of bulk nanostructured materials is currently being commercialized, and it is promising that TE devices which use these materials will soon find more widespread applications. However, creating the second generation will require a fundamental understanding of carrier transport in these complex materials which is presently lacking. Further research in this field will allow TEC to play a significant role in any future thermal management solution.

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