



Thermoelectrics

Design and Materials



HoSung Lee

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THERMOELECTRICS

DESIGN AND MATERIALS

HoSung Lee

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THERMOELECTRICS

For Young-Ae and Yujin

Preface

This book is written as a senior undergraduate or first-year graduate textbook. Thermoelectrics is a study of the energy conversion between thermal energy and electrical energy in solid state matters. Thermoelectrics is an emerging field with comprehensive applications such as exhaust waste heat recovery, solar energy conversion, automotive air conditioner, deep-space exploration, electronic control and cooling, and medical instrumentation. Thermoelectrics involves multiple interdisciplinary fields: physics, chemistry, electronics, material sciences, nanotechnology, and mechanical engineering. Much of the theories and materials are still under development, mostly on the materials but minimally on the design. The author has taught the thermoelectrics courses in the past years with a mind that a textbook is necessary to put a spur on the development. However, the author experienced considerable difficulties, partly because of the need to make a selection from the existing material and partly because the customary exposition of many topics to be included does not possess the necessary physical clarity. It is realized that the author's own treatment still has many defects, which are desirable to correct in future editions. The author has an open mind and appreciation for any comments and defects that may be found in the book. Typically, design and materials are separate fields, but in thermoelectrics, the two fields are interrelated particularly when the size is small and the variation of temperature is large. Hence, this book includes the design and materials for future vigorous engagement.

This book consists of two parts: design (Chapters 1 through 8) and materials (Chapters 9 through 16). The design covers the theoretical formulation, optimal design, experimental verification, modeling, and applications. The materials cover the physics of thermoelectrics for electrons and phonons, experimental verification, modeling, nanostructures, and thermoelectric materials. Each part can be suggestably used for a semester period (usually an introductory session for the subtle phenomena of thermoelectrics is given in the beginning of class) or two parts in a semester period by skimming some topics when students or readers are familiar with the topics. The author put significant effort into managing the contents in Part I with a fundamental heat transfer course as prerequisite and the contents in Part II with an introductory material science course. The author also attempted to provide detailed derivation of formulas so students or readers can have a conviction on studying thermoelectrics, as well as to provide detailed calculations, so that they can even build their own mathematical programs. Hence, many exercise problems at the end of chapter ask students or readers to provide Mathcad programs for the problem solutions.

I would like to acknowledge the suggestions and help provided by undergraduate and graduate students through classes and research projects. Special thanks are given to Dr. Alaa Attar, who is now professor at King AbdulAziz University, Saudi Arabia, for his help in measurements and computations. I am also indebted to Professor Emeritus Herman Merte Jr. for his lifetime inspiration on the preparation of the book. I am very grateful to Professor Emeritus Stanley L. Rajnak, who read the manuscript and made many useful comments.

HO SUNG LEE
KALAMAZOO, MICHIGAN

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Introduction

1.1 Introduction

Thermoelectrics is literally associated with thermal and electrical phenomena. Thermoelectric processes can directly convert thermal energy into electrical energy or vice versa. A *thermocouple* uses the electrical potential (electromotive force) generated between two dissimilar wires to measure temperature. Basically, there are two devices: thermoelectric generators and thermoelectric coolers. These devices have no moving parts and require no maintenance. Thermoelectric generators have great potential for waste heat recovery from power plants and automotive vehicles. Such devices can also provide reliable power in remote areas such as in deep space and mountaintop telecommunication sites. Thermoelectric coolers provide refrigeration and temperature control in electronic packages and medical instruments. The science of thermoelectrics has become increasingly important with numerous applications. Since thermoelectricity was discovered in the early nineteenth century, there has not been much improvement in efficiency or materials until the recent development of *nanotechnology*, which has led to a remarkable improvement in performance. It is, thus, very important to understand the fundamentals of thermoelectrics for the development and the thermal design. We start with a brief history of thermoelectricity.

In 1821, *Thomas J. Seebeck* discovered that an electromotive force or a potential difference could be produced by a circuit made from two dissimilar wires when one of the junctions was heated. This is called the *Seebeck effect*.

Thirteen years later, in 1834, *Jean Peltier* discovered the reverse process—that the passage of an electric current through a thermocouple produces heating or cooling depending on its direction. This is called the *Peltier effect*. Although these two effects were demonstrated to exist, it was very difficult to measure each effect as a property of the material because the Seebeck effect is always associated with two dissimilar wires and the Peltier effect is always followed by the additional Joule heating that is heat generation due to the electrical resistance to the passage of a current. Joule heating was discovered in 1841 by James P. Joule.

In 1854, *William Thomson* (later *Lord Kelvin*) discovered that if a temperature difference exists between any two points of a current-carrying conductor, heat is either liberated or absorbed depending on the direction of current and material, which is in addition to the *Peltier heating*. This is called the *Thomson effect*. He also studied the relationships between these three effects thermodynamically, showing that the electrical Seebeck effect results from a combination of the thermal Peltier and Thomson effects. Although the Thomson effect itself is small compared with the other two, it leads to a very important and useful relationship, which is called the *Kelvin relationship*.

The mechanisms of thermoelectricity were not understood well until the discovery of electrons at the end of the nineteenth century. Now it is known that solar energy, an electric field, or thermal energy can liberate some electrons from their atomic binding, even at room temperature, moving them (from the valence band to the conduction band of a conductor) where the electrons are free to move. This is the reason why we have electrostatics everywhere. However, when a temperature difference across a conductor is applied as shown in Figure 1.1, the hot region of the conductor produces more free electrons, and diffusion of these electrons (charge carriers including holes) naturally

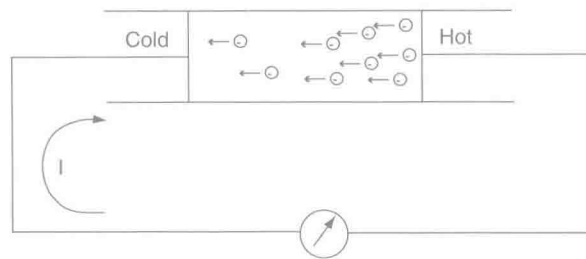


Figure 1.1 Electron concentrations in a thermoelectric material

occurs from the hot region to the cold region. On the other hand, the electron distribution provokes an electric field, which also causes the electrons to move from the hot region to the cold region via the Coulomb forces. Hence, an electromotive force (*emf*) is generated in a way that an electric current flows against the temperature gradient. As mentioned, the reverse is also true. If a current is applied to the conductor, electrons move and interestingly carry thermal energy. Therefore, a heat flow occurs in the opposite direction of the current, which is also shown in Figure 1.1.

In many applications, a number of thermocouples, each of which consists of p-type and n-type semiconductor elements, are connected electrically in series and thermally in parallel by sandwiching them between two high-thermal conductivity but low-electrical conductivity ceramic plates to form a module, which is shown in Figure 1.2.

Consider two wires made from different metals joined at both ends, as shown in Figure 1.3, forming a close circuit. Ordinarily, nothing will happen. However, when one of the junctions is heated, something interesting happens. Current flows continuously in the circuit. this is the *Seebeck effect*. The circuit that incorporates both thermal and

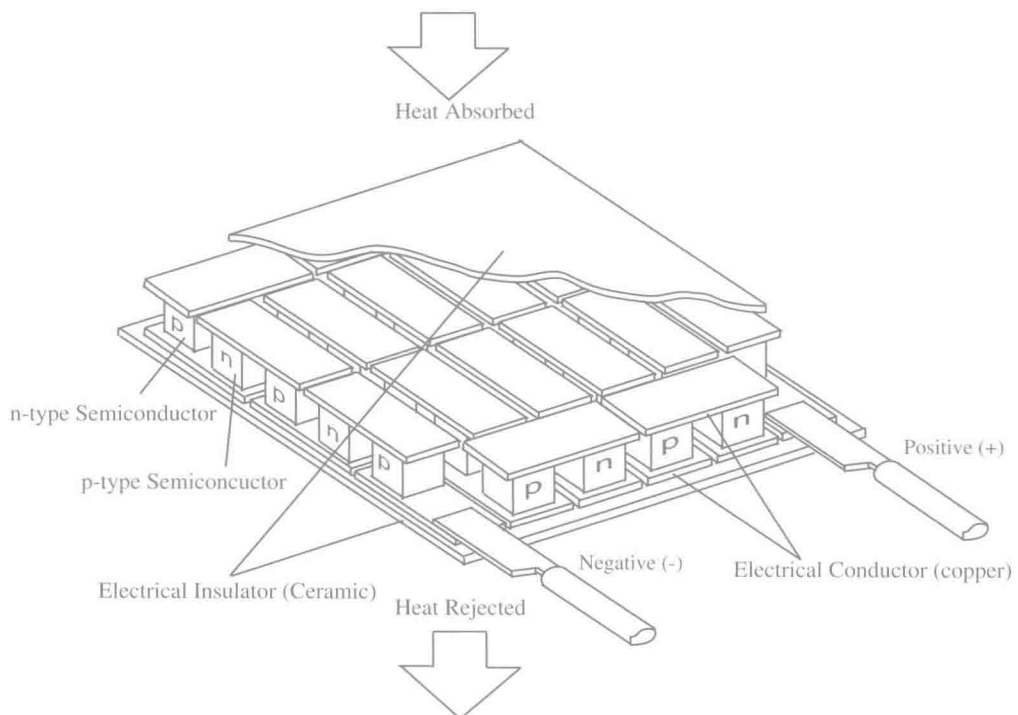


Figure 1.2 Cutaway of a typical thermoelectric module

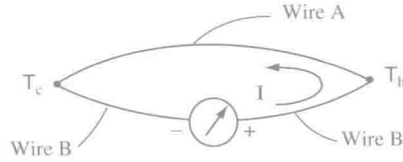


Figure 1.3 Thermocouple

electrical effects is called a *thermoelectric circuit*. A thermocouple uses the Seebeck effect to measure temperature, and the effect forms the basis of a thermoelectric generator.

In 1834, Jean Peltier discovered the reverse of the Seebeck effect by demonstrating that cooling can take place by applying a current across the junction. The heat pumping is possible without a refrigerator or compressor. The thermal energy can convert to electrical energy without turbine or engines.

There are some advantages of thermoelectric devices despite their low thermal efficiency. There are no moving parts in the device; therefore, there is less potential for failure in operation. Controllability of heating and cooling is very attractive in many applications such as lasers, optical detectors, medical instruments, and microelectronics.

1.2 Thermoelectric Effect

The thermoelectric effect consists of three effects: the Seebeck effect, the Peltier effect, and the Thomson effect.

1.2.1 Seebeck Effect

The *Seebeck effect* is the conversion of a temperature difference into an electric current. As shown in Figure 1.3, wire A is joined at both ends to wire B and a voltmeter is inserted in wire B. Suppose that a temperature difference is imposed between two junctions; then, it will generally be found that a potential difference or voltage V will appear on the voltmeter. The potential difference is proportional to the temperature difference. The potential difference V is

$$V = \alpha_{AB} \Delta T \quad (1.1)$$

where $\Delta T = T_h - T_c$ and $\alpha_{AB} = \alpha_A - \alpha_B$; α_{AB} is called the *Seebeck coefficient* (also called the *thermopower*), which is usually measured in $\mu\text{V/K}$. The sign of α is positive if the emf tends to drive an electric current through wire A from the hot junction to the cold junction, as shown in Figure 1.3. In practice, one rarely measures the absolute Seebeck coefficient because the voltage meter always reads the relative Seebeck coefficient between wires A and B. The absolute Seebeck coefficient can be calculated from the Thomson coefficient.

1.2.2 Peltier Effect

When current flows across a junction between two different wires, it is found that heat must be continuously added or subtracted at the junction in order to keep its temperature constant, which is illustrated in Figure 1.4. The heat is

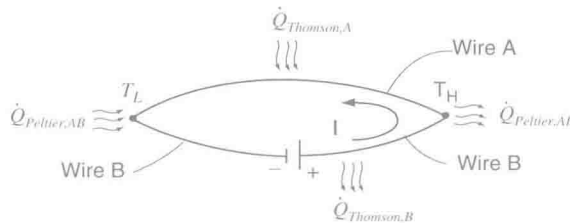


Figure 1.4 Schematic for the Peltier effect and the Thomson effect

proportional to the current flow and changes sign when the current is reversed. Thus, the Peltier heat absorbed or liberated is

$$\dot{Q}_{\text{Peltier}} = \pi_{AB} I \quad (1.2)$$

where π_{AB} is the *Peltier coefficient* and the sign of π_{AB} is positive if the junction at which the current enters wire A is heated and the junction at which the current leaves wire A is cooled. The Peltier heating or cooling is *reversible* between heat and electricity. This means that heating (or cooling) will produce electricity and electricity will produce heating (or cooling) without a loss of energy.

1.2.3 Thomson Effect

When current flows as shown in Figure 1.4, heat is absorbed in wire A due to the negative temperature gradient and liberated in wire B due to the positive temperature gradient, which is experimental observation [1], depending on the material. The Thomson heat is proportional to both the electric current and the temperature gradient, which is schematically shown in Figure 1.4. Thus, the Thomson heat absorbed or liberated across a wire is

$$\dot{Q}_{\text{Thomson}} = -\tau_{AB} I \nabla T \quad (1.3)$$

where τ is the *Thomson coefficient*. The Thomson coefficient is unique among the three thermoelectric coefficients because it is the only thermoelectric coefficient directly measurable for individual materials. There is other form of heat, called *Joule heating* ($I^2 R$), which is irreversible and is always generated as current flows in a wire. The Thomson heat is *reversible* between heat and electricity.

1.2.4 Thomson (or Kelvin) Relationships

The interrelationships between the three thermoelectric effects are important in order to understand the basic phenomena. In 1854, Thomson [2] studied the relationships thermodynamically and provided two relationships as shown in Equations (1.4) and (1.5) by applying the *first* and *second laws of thermodynamics* with the assumption that the reversible and irreversible processes in thermoelectricity are separable. The necessity for the assumption remained an objection to the theory until the advent of the new thermodynamics. The Thomson effect is relatively small compared with the Peltier effect, but it plays an important role in deducing the Thomson relationships. These relationships were later completely confirmed by experiments (See Chapter 5 for details).

$$\pi_{AB} = \alpha_{AB} T \quad (1.4)$$

$$\tau_{AB} = T \frac{d\alpha_{AB}}{dT} \quad (1.5)$$

Equation (1.4) leads to the very useful Peltier cooling in Equation (1.2) as

$$\dot{Q}_{\text{Peltier}} = \alpha_{AB} T I \quad (1.6)$$

where T is the temperature at a junction between two different materials and the dot above the heat Q indicates the amount of heat transported per unit time.

1.3 The Figure of Merit

The performance of thermoelectric devices is measured by the *figure of merit* (Z), with units 1/K:

$$Z = \frac{\alpha^2}{\rho k} = \frac{\alpha^2 \sigma}{k} \quad (1.7)$$

where

α = Seebeck coefficient, $\mu\text{V/K}$

ρ = electrical resistivity, Ωcm

$\sigma = 1/\rho = \text{electrical conductivity } (\Omega\text{cm})^{-1}$
 $k = \text{thermal conductivity, W/mK}$

The *dimensionless figure of merit* is defined by ZT , where T is the absolute temperature. There is no fundamental limit on ZT , but for decades it was limited to values around $ZT \approx 1$ in existing devices. The larger the value of ZT , the greater is the energy conversion efficiency of the material. The quantity of $\alpha^2\sigma$ is defined as the *power factor*. Therefore, both the Seebeck coefficient α and electrical conductivity σ must be large, while the thermal conductivity k must be minimized. This well-known interdependence among the physical properties makes it challenging to develop strategies for improving a material's ZT .

1.3.1 New-Generation Thermoelectrics

Although Seebeck observed thermoelectric phenomena in 1821 and Altenkirch defined Equation (1.7) in 1911, it took several decades to develop the first functioning devices in the 1950s and 1960s. They are now called the first-generation thermoelectrics with an average of $Z \sim 1.0$. Devices made of them can operate at $\sim 5\%$ conversion efficiency. After several more decades of stagnancy, new theoretical ideas relating to size effects on thermoelectric properties in the 1990s stimulated new experimental research that eventually led to significant advances in the following decade. Although the theoretical ideas were originally about prediction on raising the power factor, the experimental breakthroughs were achieved by significantly decreasing the lattice thermal conductivity. Among a wide variety of research approaches, one has emerged, which has led to a near doubling of ZT at high temperatures and defines the second generation of bulk thermoelectric materials with ZT in the range of 1.3–1.7. This approach uses nanoscale precipitates and composition inhomogeneities to dramatically suppress the lattice thermal conductivity. These second-generation materials are expected to eventually produce power-generation devices with conversion efficiencies of 11–15% [3].

Third-generation bulk thermoelectrics have been under development recently, which integrate many cutting-edge ZT -enhancing approaches simultaneously, namely, enhancement of Seebeck coefficients through valence band convergence, retention of the carrier mobility through band energy offset minimization between matrix and precipitates, and reduction of the lattice thermal conductivity through all length-scale lattice disorder and nanoscale *endotaxial* precipitates to mesoscale grain boundaries and interfaces. This third generation of bulk thermoelectrics exhibits high ZT , ranging from 1.8 to 2.2, depending on the temperature difference, and a consequent predicted device conversion efficiency increase to $\sim 15\text{--}20\%$ [3].

Table 1.1 shows the thermoelectric properties of bulk nanocomposite semiconductors. Figure 1.5 shows the dimensionless figures of merit for the materials in Table 1.1.

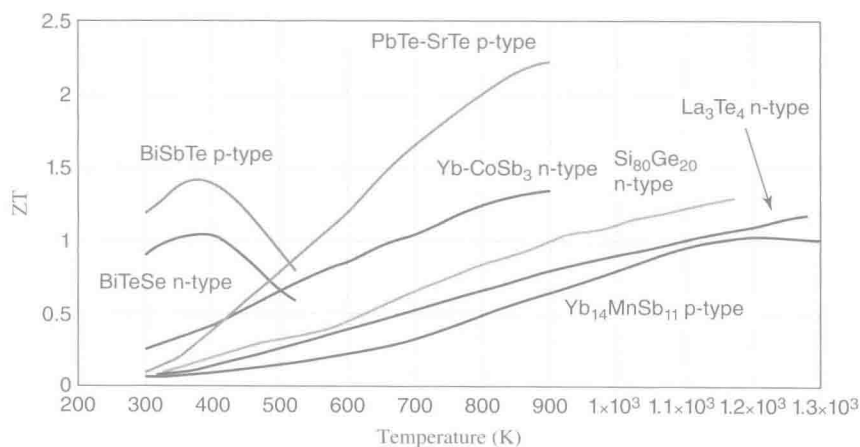


Figure 1.5 Dimensionless figures of merit for various nanocomposite thermoelectric materials