Preface*

Organic conductors, polymers, and composites have clearly demonstrated considerable potential as electronic and photonic materials for a variety of applications that previously depended on the use of inorganic compounds. The progress on conducting organic materials and polymers beginning with the discovery of polyacetylene has resulted in a host of devices being demonstrated including organic and polymer-based field effect transistors, organic solar cells, sensors, batteries, and many passive components. A logical progression of this evolution is for these materials to be pursued as thermoelectric materials for conversion of thermal energy into useful electric power predominantly in moderate temperature range. A combination of organic, polymeric, and nanostuctured materials have created a rich array of materials that can be combined to form thermoelectric systems that have begun to display operating characteristics that may lead practical alternatives to current inorganic thermoelectric alloy systems for appropriate applications.

The volume begins with a broad perspective of thermoelectric materials by Poehler and Katz extending from the early work on bulk intermetallic compounds such as the widely investigated compound Bi_2Te_3 and Bi_2Te_3 alloys capable of higher thermoelectric power generation because of reduced thermal conductivity due to greater

*Howard Katz is grateful to the Department of Energy, Office of Basic Energy Sciences, Grant Number DE-FG02-07ER46465, for supporting his contributions.

acoustic phonon scattering in the alloys. A summary of solid-state chemistry approaches to synthesize better thermoelectric materials through structural and chemical methods in ternary and quaternary systems are described. A series of alloys are illustrated including half-Heusler alloys, skutterides, and chalcogenide compounds that have proven to be thermoelectrics with low thermal conductivity and high power factors. New materials are described using a series of structural innovations comprising nanostructures, composites, and polymer materials that succeed in modifying dimensionality, decoupling electrical and thermal conductivity, and extending the field of thermoelectric materials beyond the traditional inorganic compounds. The chapter concludes with the recognition that there is much work to accomplish to fulfill the promise of these new materials and develop an understanding of theory to extend the effectiveness of these new materials.

The second chapter in the volume by Lee and Chen discusses how the introduction of nanostructures in thermoelectric materials has led to significant improvements in the thermoelectric figure of merit by modifying transport properties such as carrier concentration and tailoring band structure yielding a density of states that selectively promotes the transport of energetic carriers as well as carrier scattering. It describes some of the advantages and outcomes in polymer-based thermoelectric materials, as well as in polymer–inorganic nanomaterials that hold promise for enhancement of the electronic properties by introduction of nanostructures to tailor the electron and phonon transport more effectively than prior methods. The advantages of nanostructures are a major focal point of the discussion, but a number of other tactics are also described that have potential for improving the performance of bulk thermoelectric materials as well.

In the next chapter by Schlitz, Glaudell, and Chabinyc the authors concentrate on the thermoelectric performance and transport models employed to comprehend organic polymers and solution processed organic semiconductors. Thermolectric behavior in materials synthesized by vapor deposition techniques has recently been the subject of a study by Walzer *et al.* particularly with respect to injection layers in organic light emitting diodes (OLEDs). *Chem*

Rev. **107**, 1233–1271 (2007). This work provides a comprehensive summary of recent progress in n- and p-type materials together with a thoughtful assessment of barriers to be overcome to enhance organic thermoelectric materials.

In the fourth chapter by Urban and Coates the focal point of the discussion is the design rules for polymer-based thermoelectric nanocomposites. A universal aspect of improvements in thermoelectric materials performance in recent years is the greater complexity used in their production, and the most recent manifestation of this is present in polymer nanocomposite materials. In organic–inorganic nanoscale composites carrier filtering or energy filtering by selection of carriers with high energies, or power factor enhancement through trap states can produce electronic carriers improved thermoelectric performance. The authors have explained the primary rules for creating the optimum thermoelectric transport in polymer composite materials that have the potential to lead to design unique materials of vastly improved performance.

The next chapter by Kim and Pipe reviews the role of dopant atoms or molecules in establishing the optimum thermoelectric parameters so as to maximize the thermoelectric figure of merit ZT. In thermoelectric materials, the opposite dependence of the Seebeck coefficient and the electrical conductivity on carrier concentration implies that there is an optimum concentration that will maximize the power factor $S^2\sigma$. In order to achieve the optimum carrier concentration, the density of impurity or dopant atoms must adjusted, and may affect the electronic carrier mobility. In contrast to inorganic semiconductors, where mobility declines at increasing carrier concentration through higher impurity scattering, in organic semiconductors the mobility increases with carrier concentration until the dopant volume becomes quite large. The authors describe a model that demonstrates the importance of minimizing dopant volume in maximizing ZT, and simultaneously enhancing the values of the three parameters that constitute ZT.

The sixth chapter by Ireland and Katz describes the potential for improved thermoelectric performance from complex polymer–inorganic composites. Polymer–inorganic composites have been

prepared by techniques including physical mixing, solution processing, and *in situ* synthesis of polymers and inorganic materials with improved properties compared to separate components. Integrating conducting organic compounds in conjugated polymers is anticipated to result in the composite material having improved electrical conductivity and a higher Seebeck coefficient with the polymer matrix containing the inorganic compound exhibiting a low thermal conductivity. Highly ordered composites are expected to have enhanced thermoelectric performance as a result of highly engineered semiconductors incorporating better current pathways, morphological confinement, energy filtering, and alignment and interfaces with selective scattering.

The next chapter by Brown and Snyder describes the role that structural entropy can play in strongly enhancing the thermopower of complex thermoelectric materials yielding a new approach to creating systems with high ZT and wide applications for these thermoelectric materials. In particular, the authors have demonstrated that coupling of a continuous phase transition to carrier transport in CuSe results in a striking peak in thermopower, increased scattering of electrons and phonons, and a doubling of ZT. The correlation of improved performance in the material with the nature of the phase transition is indicative of the entropy being associated with ion ordering. This implies that a new mechanism for high thermoelectric performance may be recognized and utilized as an approach to enhancing function.

The chapter by Walker describes some of the predominant techniques for modeling and predicting the transport properties of contemporary thermoelectric materials. From these models, we enhance our ability to comprehend the physical characteristics of materials that influence when a material will function effectively as a thermoelectric material. The modeling involves both the electronic and thermal systems with a concentration on noncontinuum models that include both particle-oriented techniques such as the Boltzmann model, quantum-based techniques, for instance, the nonequilibrium Green's function method, and atomistic simulation. Notwithstanding that the energy-bearing carriers, electrons and phonons, are

clearly joined, the two systems are treated independently inasmuch as the coupling is generally minimal. Methods such as the nonequilibrium Green's function model appear to match experimental data well when predicting thermoelectric parameters like the Seebeck coefficient.