

Advanced Thermoelectrics

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Expanding new avenues for renewable energy and reducing the consumption of fossil fuels in a time of ever-increasing demand for energy is challenging. Harvesting heat, either from the Sun or dissipated from industrial applications, as an alternative energy source has become an important area of research. Thermoelectricity, associated with generating electric power due to an applied temperature gradient or thermal flow due to an applied voltage, offers the potential to utilize some of this “free” energy in all-solid-state conversion devices for power generation. Thermoelectric refrigeration, with several existing applications, is equally enticing with potential applications that can be realized with enhanced material performance.

Thermoelectric devices are reliable, have no moving parts, and do not release harmful gases into the atmosphere. Despite these attractive features, thermoelectricity has remained a niche field due to low conversion efficiency. In terms of materials requirements, the main challenge has been in overcoming the disadvantages from the interrelation between electric and thermal properties of typical materials. Given the lack of a fundamental limit to the thermoelectric figure of merit, a unitless scalar quantity specific to the material properties, and the ever-increasing materials library, the field of thermoelectricity is experiencing a new push for materials with enhanced properties. New developments in the search for useful compounds, as well as advances in theoretical and computational modeling capabilities, have led to a more rapid evaluation of materials as well as the design and discovery of new systems by combining theoretical and experimental efforts. We have organized the “Advanced Thermoelectrics” Special Topic in *Journal of Applied Physics* as a forum, where the recent progress and advances in the field are presented. It is our hope that this Special Topic will provide an overview of the current state in the field of thermoelectric materials research and development. We outline only part of the work presented in this Special Topic below.

Thermoelectricity is, in part, essentially a material driven field. This relation has become even more prominent with the availability of powerful computing resources and new and versatile

first principles simulations capabilities. In the “Advanced Thermoelectrics” Special Topic, recent work on several promising classes of materials is reported. This research aims not only at fundamental investigations of the material transport properties, and using alloying and doping for enhanced performance, but also addresses the effort into earth-abundant compounds as well as the cost of synthesizing materials. The best thermoelectric materials have a low thermal conductivity; thus, the pivotal role of understanding phonon transport is addressed in the Special Topic, particularly in light of vibrational properties computations.^{1–3} Device-related research is also part of this Special Topic^{4–13} and indicates how improvements are necessary beyond material enhancements. Research on devices and modules involves diverse areas of applied physics, including bonding between thermoelectric materials and metals or electrodes, corrosion, durability, mechanical properties, and processing technologies of materials.^{8–10} The specific geometries of p-type and n-type legs in modules can also be optimized; traditional cuboid shapes can be altered to optimize the thermoelectric properties.⁷ Investigation into diffusion barrier materials is also an important topic¹³ and represents an area of research that is essential for thermoelectric module optimization.

Materials containing earth-abundant constituents are especially important and are needed in order to reduce the cost of synthesis and address rising issues about health and safety concerns for large scale device production and usage. In the perspective by Powell,¹⁴ sulfur is recognized as being abundant and widely available in nature. This perspective examines recent progress of several classes of sulfides whose common building block is the CuS₄ tetrahedron. These include chalcopyrite phases, zinc blende derived quaternary chalcogenides, binary copper sulfides, bornites, colusites, and tetrahedrites. These scientific advances have been possible due to fundamental investigations of structure–property relations of materials as well as specific systems. For example, *ab initio* simulations¹⁵ demonstrate that doping Mg₃Sb₂ with Bi can be beneficial in turning p-type to n-type transport while enhancing the electrical properties at low carrier concentrations. Other materials in this category are

Cu_2SnS_3 and CuFeS_2 ,^{16,17} where the interrelation between different transport characteristics in nonstoichiometric derivatives of these materials for enhanced performance is reported. In addition, the new quaternary chalcogenides $\text{CuZn}_2\text{InTe}_4$ and $\text{AgZn}_2\text{InTe}_4$ were synthesized and calculated,¹⁸ and they may also form sulfides.

Copper chalcogenides have also emerged as good thermoelectrics. These are characterized as phonon-liquid electron crystals (PLECs), where the electron transport is enhanced but the heat conduction resembles that of liquids. The PLEC concept, as with other similar approaches in the field, can be regarded as an extension of the now famous phonon-glass electron crystals (PGEs) approach first proposed by Slack.¹⁹ However, the stability of copper chalcogenides remains an issue. Derivatives of the copper chalcogenides, by doping with Ba and Te, were synthesized in order to find ways to increase their stability via doping, synthesis methods, and decreased temperature of operation.^{20,21} Half-Heusler alloys are intermetallics that, unlike some chalcogenides, are structurally and mechanically robust at high temperatures. They have attractive properties for thermoelectricity that can be optimized via doping in individual materials²² as well as via cross atom substitution.²³ Electronic structure and relaxation scattering time calculations on several Co-doped half-Heuslers²⁴ were used to rank the thermoelectric performance of these materials.

Oxygen-containing inverse perovskites also display promising features such as high electrical conductivity due to Dirac cones in the electronic structure, high Seebeck coefficient due to band degeneracy, and low thermal conductivity.²⁵ The thermoelectric phase diagram of doped SrTiO_3 and LaTiO_3 perovskites was studied, addressing important questions of classifications and transport control routes.²⁶ Although tungsten bronze is structurally different from perovskites, this material also contains oxygen, which has the advantage of easier processing with relatively good thermoelectric properties.²⁷ Tetrahedrites have also attracted attention as suitable thermoelectrics. This is a large class of materials with complex crystal structures for which doping is used to enhance the thermoelectric figure of merit.²⁸ In addition, many Zintl phases are attractive due to their good thermoelectric properties.²⁹ Certain pnictides belong to the Zintl family of compounds; the synthesis and characterization of several rare-earth metal substituted variants of $\text{Ca}_{14}\text{CdSb}_{11}$ reveal that these degenerate semiconductors have small gaps and low thermal conductivity.³⁰ Furthermore, doping of magnesium silicides with Sn and the addition of Sc was found to result in an increased figure of merit.³¹ It is also interesting to note that quasi-one-dimensional materials are emerging in the field of thermoelectricity, for example, $\text{Sn}_{1.2-x}\text{Nb}_x\text{Ti}_{0.8}\text{S}_3$ materials.³²

All of this research was driven by the materials side of thermoelectricity, which is further guided by band structure theory from first principles. However, in addition to an expanding materials library, there is currently a search for new fundamental concepts in order to further promote an increase in the figure of merit. Urban *et al.*³³ give compelling evidence that several areas have emerged that hold promise for such new paradigms. These include anisotropic transport, non-Fermi liquid behavior, wave effects in phonon transport, organic systems, and new and more powerful computational approaches. Some of the papers in the “Advanced Thermoelectrics” Special Topic report research precisely in this direction. For example, combining first principles simulations with analytical modeling brings forward

our understanding of how the electronic structure and scattering mechanisms affect the transport properties of SnSe .³⁴ This material is highly anisotropic, and doping plays a major role in modifying its transport. Shiraishi *et al.*³⁵ have shown that perovskites can exhibit a photo-induced electrical conductivity and the Seebeck coefficient at low temperatures, where quantum effects are important. A combined experimental and theoretical study³⁶ shows transport properties of topologically nontrivial Bi_nTeBr , revealing the bulk physical properties of tellurohalides and their potential for thermoelectric applications. This work emphasizes that a focus on understanding the fundamental bulk properties of new topological insulators is of growing interest. To further broaden our fundamental knowledge on transport, theoretical studies on the Seebeck effect in solid dielectrics in the presence of space charge in capacitors were also reported.³⁷ The thermoelectric properties due to magnon drag in Fe-Co alloys were studied experimentally and computationally showing the potential of such systems for cooling applications.³⁸ Promising thermoelectric behavior was found in ozone treated carbon nanotube thin films,¹² while interfacial phenomena and percolation transport were studied in hybrid Bi_2Te_3 -conjugated polymer composites.³⁹

As indicated above, one of the most important aspects of thermoelectricity is that of phonon thermal transport. The pivotal role of computational science toward first principles methods in calculating vibrational properties of materials, together with challenges in understanding the thermal conductivity, was examined in the perspective by Lindsay *et al.*² Perhaps, one of the biggest advances in this regard is the implementation of the *ab initio* Peierls–Boltzmann equation, with which novel physical insights were obtained in superlattices, alloys, and other materials. Such an approach was applied to CrS_2 , a material predicted to have a very low thermal conductivity, making this sulfide material attractive for thermoelectricity.¹ Experimental data and analyses are also important in identifying scattering mechanisms and associate them with trends in the vibrational dynamics.³ In addition to scattering from defects, impurities, and other imperfections in the lattice using the phonon Boltzmann equation,² a number of studies demonstrate the importance of nanostructures as an effective means of thermal transport control. For example, several reports found that, depending on the types of interfaces, inclusions, and chemical composition, the overall thermal transport can be affected significantly in silicon and CrS_2 nanocomposites,^{40,41} SnSe polycrystals,⁴² and nanofilms and nanowires.⁴³ Other studies in the “Advanced Thermoelectrics” Special Topic^{44–46} present descriptions of the electric and thermal properties in materials with reduced dimensions, which may be beneficial for thermoelectric property enhancements.

It is clear that thermoelectric materials research continues to be vibrant and of great interest. We are grateful to the *Journal of Applied Physics* Driving Editor for the “Advanced Thermoelectrics” Special Topic, Professor Simon Phillpot, for his enthusiastic support, as well as the American Institute of Physics publishing staff for all their help and support. Of course, the research and efforts of all the authors that led to the articles included in the Special Topic, as well as the efforts of our reviewers who made numerous helpful comments and suggestions that strengthened all the articles, are also gratefully acknowledged. GSN and LMW acknowledge the support from the US National Science Foundation (NSF) under Grant No. DMR-1748188.

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