

Nanostructured Thermoelectrics: Big Efficiency Gains from Small Features

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The field of thermoelectrics has progressed enormously and is now growing steadily because of recently demonstrated advances and strong global demand for cost-effective, pollution-free forms of energy conversion. Rapid growth and exciting innovative breakthroughs in the field over the last 10–15 years have occurred in large part due to a new fundamental focus on nanostructured materials. As a result of the greatly increased research activity in this field, a substantial amount of new data—especially related to materials—have been generated. Although this has led to stronger insight and understanding of thermoelectric principles, it has also resulted in misconceptions and misunderstanding about some fundamental issues. This article sets out to summarize and clarify the current understanding in this field; explain the underpinnings of breakthroughs reported in the past decade; and provide a critical review of various concepts and experimental results related to nanostructured thermoelectrics. We believe recent achievements in the field augur great possibilities for thermoelectric power generation and cooling, and discuss future paths forward that build on these exciting nanostructuring concepts.

over the past 15 years. Nanostructuring of semiconductors in the form of quantum wells and superlattices started in the 1960s and early 1970s for electrical and optical devices, and now plays an important role in commercial products such as compact disc laser diodes, high electron mobility transistors and quantum cascade lasers. These are all examples where electron wave effects and quantum confinement created by nanostructuring are used to significantly enhance device performance. In contrast, as discussed in this review article, the primary benefit to date of nanostructuring for thermoelectric materials has been the impact on thermal properties, rather than electronic.

The performance of thermoelectric materials is quantified by a unitless figure of merit, ZT , which is defined as $\sigma \cdot S^2 T / \kappa$, where σ is the electrical conductivity, S is the thermoelectric power (the product $\sigma \cdot S^2$ is often referred to as the power factor), κ

is the thermal conductivity of the material, and T is the absolute temperature. In the 1950s alloys of Bi_2Te_3 were discovered to have $ZT \sim 1$ near room temperature, and they have played a dominant role in the field of thermoelectrics through today. While each property of ZT — S , σ , and κ —can individually be changed by several orders of magnitude, the interdependence and coupling between these properties have made it extremely difficult to increase $ZT > 1$ despite five decades of active research. The thermoelectrics community is widely targeting $ZT \geq 3$ to make these solid-state systems competitive with traditional mechanical energy conversion systems.

1. Introduction

The phenomenon of thermoelectricity—the direct solid-state conversion between thermal and electrical energy—has been known since discoveries made by Seebeck, Peltier, and Thomson in the early 1800s. Research and development of bulk homogeneous materials for thermoelectric applications began to increase starting in the 1950s, and resulted in commercial solid-state power generation and cooling systems. With the introduction of materials and concepts based on nanostructuring, however, the field has witnessed truly dramatic growth

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DOI: 10.1002/adma.201000839

In 1993, Hicks and Dresselhaus^[1,2] pioneered the concept that quantum confinement of electrons and holes in low-dimensional materials could dramatically increase $ZT > 1$ by independently changing $S^2\sigma$. While this ignited intense research into nanostructured thermoelectric materials, there are still many debates about the exact role that low dimensionality and nanostructures could play in improving thermoelectrics. Enhanced performance ($ZT > 1$) in thermoelectrics with low-dimensional structures was reported by several groups, including Venkatasubramanian *et al.*,^[3] Harman *et al.*,^[4] and Hsu *et al.*^[5] However, these structures have mainly benefited from reduced phonon thermal conductivity, and quantum confinement of electronic carriers has not yet played a role. **Figure 1** plots major milestones achieved for ZT over the past several decades as a function of both year and temperature.^[3–18] It is important to note that some of the ZT values in Figure 1 have not yet been independently verified or reproduced, and corroboration of these key breakthroughs would be helpful to the thermoelectrics community.

In this article we review the basic physics of nanostructured thermoelectric materials (both bulk and thin film), discuss newly emerging insights into how nanostructuring influences thermoelectric properties, and summarize our current understanding in this very active field. We also discuss the challenges of capitalizing on these new insights to realize the benefit from low-dimensional quantum confinement, and evaluate the potential of nanostructures for further significant improvement in ZT . The interested reader is also referred to several other excellent recent reviews covering various aspects of thermoelectrics, including nanoscaled materials^[19–21] and thermoelectric systems.^[22]

2. 2D Nanostructuring: Quantum Wells and Superlattices

The formation of superlattices of alternating materials is perhaps the simplest and most widely investigated method of creating a controlled nanostructure for electrical and optical devices. The impact of the superlattice structure on thermoelectric properties has been studied in numerous material systems, including $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$,^[3] $\text{PbTe}/\text{PbSe}_x\text{Te}_{1-x}$,^[23] $\text{Si}/\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$,^[24–26] $\text{GaAs}/\text{Al}_x\text{Ga}_{1-x}\text{As}$,^[27,28] $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{Al}_y\text{In}_z\text{Ga}_{1-y-z}\text{As}$,^[29] and layered WSe_2 crystals.^[30] The early motivation for these investigations was based on the prediction from Hicks and Dresselhaus^[1] that quantum confinement of in-plane carrier transport could substantially enhance the power factor over that of homogeneous materials, leading to ten-fold increases in ZT . Such enhancement could occur because sharp features in the electronic density of states of quantum-confined structures^[31] (see **Figure 2**) enable a doping-level-tunable increase in the asymmetry between hot and cold electron transport, resulting in a large average transport energy and a large number of carriers moving in the material (i.e., a large Seebeck coefficient and electrical conductivity).

In order to achieve significant enhancement of ZT it was anticipated that superlattice periods of less than 3 nm would be required. A few groups have claimed quantum-well-enhanced in-plane Seebeck coefficients, for material systems including PbTe/Te ,^[32] PbTe/PbSe ,^[33] $\text{PbTe}/\text{Pb}_{0.93}\text{Eu}_{0.07}\text{Te}$,^[8,34,35] and



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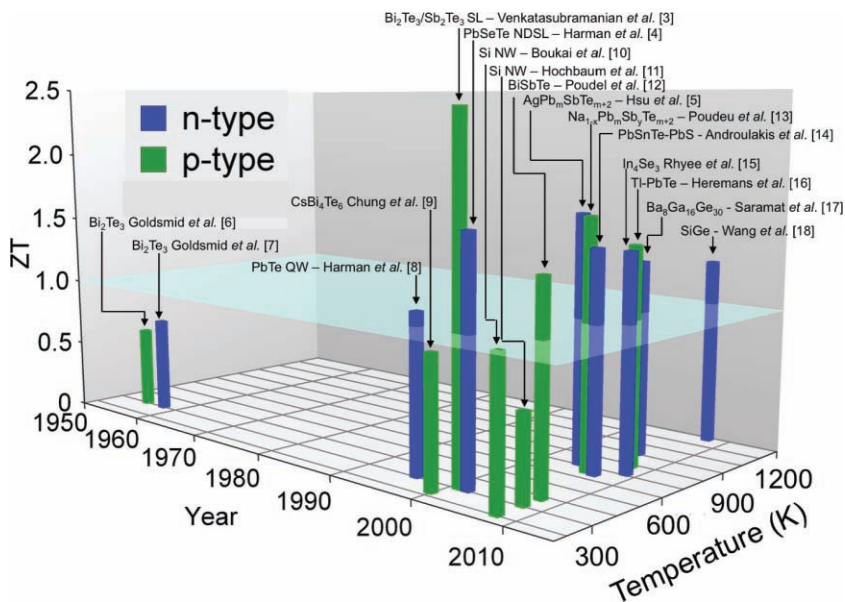


Figure 1. Thermoelectric figure-of-merit ZT as a function of temperature and year illustrating important milestones. Although there have been several demonstrations of $ZT > 1$ in the past decade, no material has yet achieved the target goal of $ZT \geq 3$. The material systems that have achieved $ZT > 1$ have all been based on some form of nanostructuring.

$\text{SrTiO}_3/\text{SrTi}_{0.8}\text{Nb}_{0.2}\text{O}_3$.^[36,37] However, in at least two cases^[32,33] the apparent increase was an error due to inaccurate carrier concentration measurement, and subsequently-corrected measurements confirmed that no Seebeck enhancement was observed (see Appendix B, Vineis *et al.*^[38] for more details). With respect to $\text{SrTiO}_3/\text{SrTi}_{0.8}\text{Nb}_{0.2}\text{O}_3$ superlattices, Ohta *et al.*^[36,37] recently

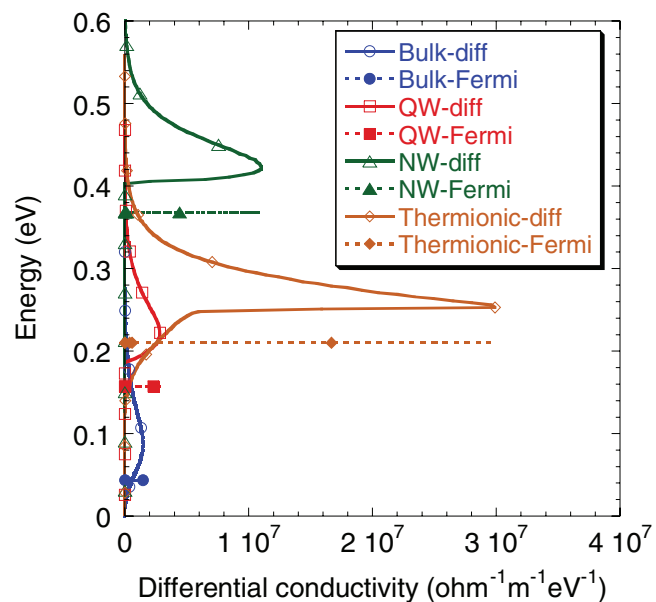


Figure 2. Differential conductivity of bulk, quantum well (QW) and quantum wire (NW) InSb material as well as InSb with hot electron filtering (“Thermionic”). Dashed lines show the respective optimum Fermi level. Increased asymmetry in the differential conductivity gives a higher Seebeck coefficient.

reported a giant Seebeck coefficient and thermoelectric power factor for the confined two-dimensional electron gas. However, the results assume that electrons are strictly confined to the extremely small quantum well region (0.39 nm), an assumption that should be further investigated. Additional measurements, such as optical intersubband absorption or cross-plane photocurrent, and a model for the confinement barriers and electron wavefunction would be helpful to confirm that the wavefunction is not penetrating substantially into the barrier region. Such verification is important for all superlattice systems, where it is typically assumed that all the electronic carriers are confined to the well region but this may not always be true. The extent of the quantum-confined electronic wavefunction is the correct normalization factor to derive the 3D electron density and electrical conductivity from sheet measurements since it determines the minimum separation between quantum wells. In an important recent paper, Kim *et al.*^[39] have revisited the large thermoelectric power factor in extremely small quantum wells or

wires and they point out that the normalization of 2D electrical conductivity to the thickness of the confinement layer is the major source of the diverging large power factors. The actual improvement in the thermoelectric power factor “per conduction channel” is only 12-40%. They also derive a minimum packing density for low dimensional thermoelectric material (even with ideal infinite barrier confinement) to have any improvement compared to the bulk.

That an enhancement of the in-plane power factor has yet to be widely observed for superlattice systems is possibly also explained by the reasons discussed by Broido and Reinecke.^[40] Specifically, their more comprehensive calculations utilizing the full electronic band structure of a superlattice along with multi-sub-band inelastic carrier scattering suggested that the power factor would at best be a relatively weak function of quantum well width due to increased carrier scattering rates for thinner wells. Additionally, for multi-valley semiconductors the lifting of degeneracy in a superlattice structure would likely reduce the power factor compared to a homogeneous material. With respect to ZT , superlattice devices operated in an in-plane fashion would have a further drawback that heat would flow through both the well and barrier materials while electronic carriers would flow through the well only, which can reduce the performance significantly. Attempts to mitigate this latter drawback by thinning the barrier layer are limited, since that inevitably results in tunneling between adjacent quantum wells that broadens the energy levels and reduces any power factor improvement.

Despite a dearth of experimental verification to date of the original Hicks and Dresselhaus predictions and the issue of packing density, this seminal work was important because it stimulated broad interest in the potential of nanostructured materials to enhance thermoelectric performance. Indeed,

several groups have reported improved ZT values, although not for the originally-predicted reason. Rather, a large enhancement in the ZT of superlattice films has been ascribed to a reduction of the lattice thermal conductivity in the cross-plane direction. It is worth noting that thermal conductivity reduction in crystalline or polycrystalline bulk thermoelectric materials was traditionally achieved by making alloys, which introduces atomic scale defects to scatter phonons. However, one reaches the so-called “alloy limit” of thermal conductivity, which has been difficult to surpass. Nonetheless, in several cases for superlattices, the lattice thermal conductivity values have been claimed to be well below the alloy limit, occasionally approaching the value of the amorphous phase. For example, a remarkably low 300-K cross-plane value of $0.22 \text{ W m}^{-1} \text{ K}^{-1}$ was estimated for the $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ system based on 3ω measurements,^[3] a reduction of 2.2x compared to a $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ alloy. We note that a detailed study of extrapolating the lattice contribution to thermal conductivity from total thermal conductivity measurements as a function of carrier concentration would be of value for this and other reports. A record apparent ZT of 2.4 was reported for this superlattice system, although this value has not yet been reproduced to the best of our knowledge. Other examples of significantly reduced lattice thermal conductivity values for superlattice systems include a value of $0.5 \text{ W m}^{-1} \text{ K}^{-1}$ for a $\text{PbTe}/\text{PbTe}_{0.75}\text{Se}_{0.25}$ superlattice, which is approximately half the alloy value;^[23] a value of $3 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K for a dislocation-free 3-nm-period Si/Ge superlattice (40% lower than the thermal conductivity of the comparable $\text{Si}_{0.8}\text{Ge}_{0.2}$ alloy);^[41] and $3.1 \text{ W m}^{-1} \text{ K}^{-1}$ for a short-period (3 monolayers by 3 monolayers) AlAs/GaAs superlattice,^[27] a remarkable 4x reduction compared to an $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ alloy.

The impact of the superlattice structure on lattice thermal conductivity has been attributed to various effects, including modification of the phonon spectrum (e.g., zone folding and bandgap formation) and phonon localization,^[42–45] diffuse or specular scattering of phonons at interfaces due to acoustic mismatch,^[46] and scattering of phonons at defects^[41] (e.g., dislocations from lattice mismatch). It is still unclear to what extent phonon behavior is coherent in these systems, which is a requirement for the first explanation. What is ultimately important, though, is that for ZT to be enhanced in a nanostructured system the reduction in thermal conductivity must be larger than any concomitant reduction in the power factor. To minimize reduction of cross-plane carrier mobility several approaches can be utilized, including selection of pairs of materials with small or no band offsets (e.g., $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ system^[3]), as well as materials with large relative static permittivities (e.g., PbTe with a value of 400 at 300 K) that effectively screen out scattering on crystal defects possibly present at lattice-mismatched material interfaces.

At least two alternative approaches to achieving enhanced thermoelectric performance through two-dimensional nanostructuring have been proposed and investigated recently, which are carrier energy filtering^[47–49] and thermal diodes.^[50,51] Both techniques require cross-plane carrier transport, which is beneficial since this is typically the direction of lowest thermal conductivity. The concept of the former technique is that by introducing tall barriers ($\sim 1\text{--}10$ times $k_{\text{B}}T$) in the conduction band (for n -type materials) or valence band (for p -type materials),

the higher-energy “hot” carriers can be selectively transmitted through the structure by filtering out the lower-energy carriers. This can result in a substantially increased Seebeck coefficient, since its value depends on the thermal energy transported by the carrier. This is illustrated in Figure 2, which shows the contribution of electrons with different energies to the electrical conductivity (i.e., differential conductivity) for bulk, quantum well, and quantum wire structures made of InSb (4 nm film thickness or wire diameter and infinite barriers are assumed). Dashed lines show the respective optimum Fermi level for each structure. The asymmetry of the differential conductivity with respect to the Fermi energy defines the Peltier coefficient, while the integral of the differential conductivity over all energies gives the electrical conductivity of the material. Calculated power factors for bulk, quantum well and quantum wire materials are 0.007, 0.020 and $0.045 \text{ W m}^{-1} \text{ K}^{-2}$, respectively. Figure 2 also shows the differential conductivity of InSb layers with hot electron filtering (barrier thickness of 5 nm and barrier height of 0.25 eV are assumed). In the case of non-conserved lateral momentum, it is anticipated that the power factor could reach a value of $0.058 \text{ W m}^{-1} \text{ K}^{-2}$.

There has been some controversy over the idea of electron filtering or solid-state thermionic emission. Small potential barriers that could increase the power factor were first suggested by Rowe and Min^[52] and by Whitlow and Hirano.^[53] Solid-state thermionic power generation in analogy with vacuum devices was suggested by Moyzhes *et al.*^[54] Shakouri and Bowers presented the first estimations based on ballistic transport theory.^[55] While parasitic thermal resistance at the hot junction—which was not included in the analysis—severely reduces the maximum cooling power density, this paper highlighted the potential of heterostructure barriers for solid-state micro-refrigeration. Subsequent analysis by Mahan and Woods^[56] suggested an improvement by a factor of two in the energy conversion efficiency for multi barrier thermionic devices. However, Vining and Mahan^[57] and Ulrich *et al.*^[58] later concluded that solid-state thermionic devices are always worse than thermoelectric devices. The main shortcoming of these latter analyses is the use of the linearized Richardson equation for electron transport in superlattices. This is not a good approximation when the Fermi energy is near the top of the heterostructure barrier, a condition that is necessary for the highest performance solid-state thermionic energy conversion. Detailed comparison with experimental low temperature current-voltage characteristics of multiquantum-well devices^[59] and the cross-plane Seebeck coefficient in both narrow and wide band superlattices^[60] show that the modified Boltzmann transport equation is more accurate for the modeling of thermoelectric transport in superlattices.

Seebeck enhancement by hot-electron filtering has indeed been experimentally observed^[29] for the $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{Al}_y\text{In}_z\text{Ga}_{1-y-z}\text{As}$ system and predicted for other systems. This enhancement will be offset to some extent by a decrease in the electrical conductivity since fewer carriers participate in conduction, and the extent of this reduction depends critically on whether energy or momentum filtering occurs.^[61] Thus, the overall impact on the power factor from this approach will be dependent on the specific material system under investigation, but it is an exciting area worthy of further investigation especially since it provides a possible avenue to enhanced power factors.

With respect to thermal diodes, an enhancement in the Seebeck coefficient is proposed to occur due to the use of an n - p diode structure that results in a combination of electron injection and blockage of the ohmic return current under a thermal gradient. Enhancement has been reported in the InSb and HgCdTe systems, while simultaneously achieving little or no reduction of electrical conductivity, resulting in substantial increases to the power factor.^[50,51] However, the data presented by Hagelstein and Kucherov^[50] are limited and a detailed experimental investigation of the possible non-linear electro-thermal transport would be useful. In addition, the physics of this device operation are still not well understood, and the preliminary theory based on non-local transport would benefit from further analysis. Specifically, more theoretical development showing the band structure in the material and non-equilibrium electron distribution would provide further insight.

It is also worth noting one additional area of interest for superlattices in thermoelectricity. Kyarad and Lengfellner^[62] have reported transverse Peltier and transverse Seebeck effects in tilted superlattice structures made of Pb/Bi₂Te₃ or Al/Si. Most homogeneous thermoelectric materials of interest do not have a crystal structure that allows such a transverse effect, but the creation of an artificial anisotropy as with a tilted superlattice can break the collinear requirement between the electrical and thermal fluxes. This transverse effect can lead to useful advantages: for example, in a thin-film thermoelectric cooler the importance of the parasitic contact resistance could be decreased if the current flow were along the extended dimension, while the heat pumping capacity could be increased if it occurred along a short dimension. It is also possible that new or different applications may be enabled via this alternative device configuration.

3. 1D Nanostructuring: Nanowires

A natural extension of quantum wells and superlattices is to quantum wires.^[63,64] Theoretical studies predict a large enhancement of ZT inside quantum wires due to additional electron confinement. Detailed analysis of electrical and thermal transport in various III-V and II-VI nanowires suggests that some material systems with small electron effective masses (e.g., InSb) have the potential to achieve high power factor and ZT values at reasonable experimentally-attainable diameters (>5 nm).^[65] Various quantum wire deposition methods have been explored,^[66–68] and interesting quantum confinement effects in electron magnetotransport and semimetal-semiconductor transition in Bi nanowires have been observed. However, there are no experimental results to date indicating any significant enhancement of the thermoelectric power factor due to quantum wires. Recent papers by Boukai *et al.*^[10] and Hochbaum *et al.*^[11] have claimed that rough silicon nanowires can have $ZT \sim 0.6$ at room temperature and ~ 1 at lower temperatures. These are very intriguing reports as the room temperature ZT of bulk silicon is very low, on the order of 0.01. It was proposed that this enormous ZT enhancement is due to a reduction of the thermal conductivity. This reduction is quite significant, and due to the sensitivity of single nanowire thermal conductivity measurements, additional independent characterization

will be extremely helpful. Recent simulations by Martin *et al.* show that boundary scattering, which takes into account phonon frequency dependence, could explain the observed low thermal conductivities in rough nanowires 20–50 nm in diameter.^[69] Boukai *et al.* also reported a large enhancement in ZT at low temperatures (~ 150 K) due to phonon drag effects (heat current affecting electrical transport). This is the first time it has been claimed that phonon-drag can enhance ZT significantly. The argument is that in rough nanowires, the Seebeck coefficient can be increased by the transport of certain phonon modes which have minimal contribution to thermal conductivity. Further analysis of this intriguing concept will be quite useful.

Thermoelectric measurements on individual nanowires have been achieved using a suspended microheater platform.^[70] In many practical energy conversion applications, nanowire arrays are required and the whole structure should be embedded in a matrix. The difficulty of ensuring good electrical contact to all wires in the array, having high packing densities and minimizing matrix heat leakage have prevented measuring any significant enhancement in nanowire composites.

4. 0D Nanostructuring: Nanodots

Nanodots in solid matrices can be formed in a variety of ways, including phase separation of an alloy during bulk crystal growth or via Stranski-Krastanov or Volmer-Weber mechanisms during epitaxial growth. Numerous nanodot systems have been investigated for thermoelectric applications, including PbTe/PbSe nanodot superlattices (NDSLs),^[4] AgPb_mSbTe_{2+m} (LAST- m : lead antimony silver telluride),^[5,71] NaPb_mSbTe_{2+m} (SALT- m),^[13] ErAs:InGaAs,^[72] Pb(Sn)Te-PbS,^[14] PbTe:Sb,^[73] and Si/Ge.^[74]

A common theme among all nanodot material systems to date is that enhanced thermoelectric performance is attributable to a strong decrease in lattice thermal conductivity, rather than an increase in the electrical power factor. Specifically, the lattice thermal conductivity values at room temperature have been reported to be as low as $0.33 \text{ W m}^{-1} \text{ K}^{-1}$ for PbTe/PbSe NDSLs,^[4] which compares to a value of $\sim 2.5 \text{ W m}^{-1} \text{ K}^{-1}$ for PbTe; $0.5\text{--}0.8 \text{ W m}^{-1} \text{ K}^{-1}$ for LAST- m ^[5] and variants such as SALT- m ;^[13] $3 \text{ W m}^{-1} \text{ K}^{-1}$ for ErAs:In_{0.53}Ga_{0.47}As,^[72] which is a factor of two lower than the In_{0.53}Ga_{0.47}As alloy; $0.4 \text{ W m}^{-1} \text{ K}^{-1}$ for (Pb_{0.95}Sn_{0.05}Te)_{0.92}(PbS)_{0.08};^[14] and $8 \text{ W m}^{-1} \text{ K}^{-1}$ for Ge nanodots embedded in Si.^[74] In nearly all cases these lattice thermal conductivity values are below the alloy limit, illustrating the power of nanostructuring to tailor material properties. We point out that the very low value of $0.33 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K reported for PbTe/PbSe NDSLs by Harman *et al.*^[4] was inferred from thermoelectric cooling measurements and not directly measured. Recent direct measurements^[75] of similar samples using time-domain thermoreflectance did not corroborate this value, and indicated that these systems have the same lattice thermal conductivity as homogeneous PbTe/PbSe alloys ($\sim 1 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K).

Looking more closely at the LAST- m system, it is an interesting bulk-grown material that spontaneously nanostructures during cooling from the melt. LAST was originally investigated in the 1950s as a candidate thermoelectric material and

believed to be a solid solution between the NaCl-based isostructural compounds AgSbTe_2 and PbTe .^[76–78] It was found to exhibit a very low thermal conductivity and for this reason selected m values (e.g., LAST-18) can reach high ZT values of ~ 1.7 at 700 K.^[5] High figure of merit and nanoinclusions in the n-type $\text{AgPb}_m\text{SbTe}_{2+m}$ system were subsequently confirmed by additional reports.^[71] These materials are thermally stable up to their melting point at >1200 K, and doping is generally controlled via non-stoichiometry on the Ag, Pb or Sb fractions in the form of $\text{Ag}_{1-x}\text{Pb}_{m+y}\text{Sb}_{1+z}\text{Te}_{2+m}$. The highest power factor in this system, though relatively high, is still lower than that of optimized PbTe itself indicating that electron scattering is somewhat increased. However, the lattice thermal conductivity is estimated to be only about 30% of that of PbTe and lower than what might be expected from a conventional solid solution compound. Thus, the overall impact of the nanoinclusions in LAST-18 is a net enhancement of ZT compared to PbTe . It is important to note that the presence of these nanoinclusions differentiates the LAST system from another well-known thermoelectric material system, $(\text{AgSbTe}_2)(\text{GeTe})_m$. This is the so-called TAGS system (for tellurium, antimony, germanium and silver), which also has a cubic crystal structure but undergoes a phase transition at 520 K to a rhombohedral structure. However, embedded nano-inclusions have not been observed in TAGS which suggests that this material is single phase and does not appear to be nanostructured.^[79,80]

The nanoscale inclusions of minor phases in $\text{AgPb}_m\text{SbTe}_{2+m}$ exhibit coherent or semicoherent interfaces with the matrix, as seen in the cross-sectional transmission electron microscopy (TEM) image in **Figure 3a**. This nanostructuring involves the endotaxial embedding of regions of one composition inside a matrix of another composition. It appears that a reasonable-quality interface is also formed between PbSe nanodots and the PbTe matrix for PbTe/PbSe NDSLs grown by molecular beam epitaxy (see **Figure 3b**),^[4] since this system also exhibits only a modest reduction of ~ 25 – 35% in power factor from pure PbTe —about the same reduction as for a homogeneous alloy of the same composition.^[38] (It is important to emphasize here that some early measurements^[33] of PbTe/PbSe NDSLs erroneously claimed an increased thermoelectric power factor. This was due to inaccurate Hall measurements, as clarified in Appendix B of Vineis et al.^[38]). A similarly coherent interface also holds true for the $\text{ErAs}:\text{InGaAs}$ system shown in **Figure 3c**. In all three systems it is believed that the carrier mobility is only

slightly degraded compared to the pure matrix material due to coherent matrix/nanodot interfaces coupled with small (relative to thermal energy $k_B T$) band offsets.

The sodium-substituted system $\text{NaPb}_m\text{SbTe}_{2+m}$ (SALT- m : sodium antimony lead telluride) is a high-performance ($ZT \sim 1.6$ at 675 K for $m \sim 20$)^[13] p-type variation on the LAST- m system. Again the impressive ZT is attributed to the very low thermal conductivity of the material which is as low as $0.85 \text{ W m}^{-1} \text{ K}^{-1}$, of which $\sim 0.5 \text{ W m}^{-1} \text{ K}^{-1}$ corresponds to the lattice contribution. In this case too, HRTEM images show a broad-based nano-segregated system with features similar to those exhibited by the LAST-18 samples in **Figure 3**. The inclusions are oriented along specific crystallographic axes with respect to the matrix. High resolution imaging shows that the inclusions are coherent with the matrix and produce a coherency strain field that projects outward along an axis normal to the interface. It is the presence of these strain fields that is believed to be responsible for phonon scattering and the observed low lattice thermal conductivity in LAST and the nanostructured materials discussed in this review, in excess of the scattering that can be attributed to mass fluctuation, or solid solution alloying.

Another interesting nanodot system that actually exhibits three scales of inhomogeneity simultaneously is PbTe/PbS . The system $(\text{PbTe})_{1-x}(\text{PbS})_x$ does not form a solid solution but rather phase separates into PbTe -rich and PbS -rich regions to produce coherent nanoscale heterogeneities.^[14] For $x > \sim 0.03$ the materials are ordered on three sub-micron length scales. The coherent nanoinclusions in a close variant, $(\text{Pb}_{0.95}\text{Sn}_{0.05}\text{Te})_{1-x}(\text{PbS})_x$, do not result in excessive electron scattering, and a high electron mobility of $>100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is observed at 700 K. At $x \sim 0.08$ the material achieves a very low room temperature lattice thermal conductivity ($\sim 30\%$ that of PbTe), and a $ZT \sim 1.5$ at 650 K is possible.^[14]

An important question to ask is how much of the observed reduction in thermal conductivity in these systems is explicitly due to the nanodots, since the systems typically have other co-existing defects—including solid-solution behavior—that are known to inhibit heat flow. **Figure 4a** shows a comparison of lattice thermal conductivities for five PbTe -based materials systems plus pure PbTe . It is clear that while solid-solution point defect scattering alone is effective in lowering the κ_{latt} of PbTe by ~ 30 – 40% , nanostructuring contributes additional phonon scattering for an overall 75% reduction. Similar reductions have been observed in PbTe samples containing $<3\%$ nanoparticles

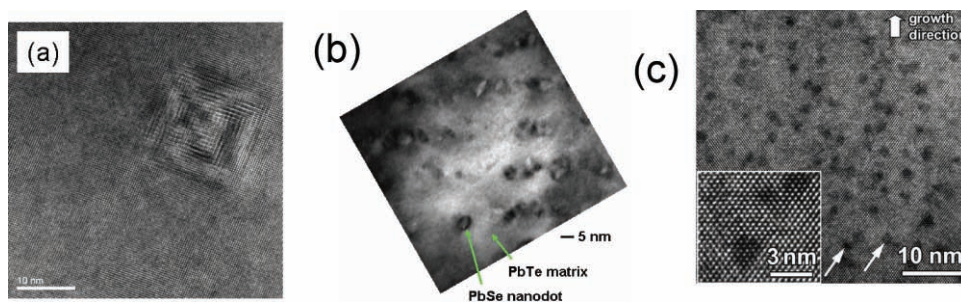


Figure 3. Nanocrystals endotaxially embedded in PbTe - and InGaAs -based materials. Cross-section transmission electron microscopy images of (a) LAST-18 ($\text{Ag}_{0.86}\text{Pb}_{18}\text{SbTe}_{20}$), (b) PbTe/PbSe NDSLs, and (c) 0.3% $\text{ErAs}:\text{InGaAs}$.

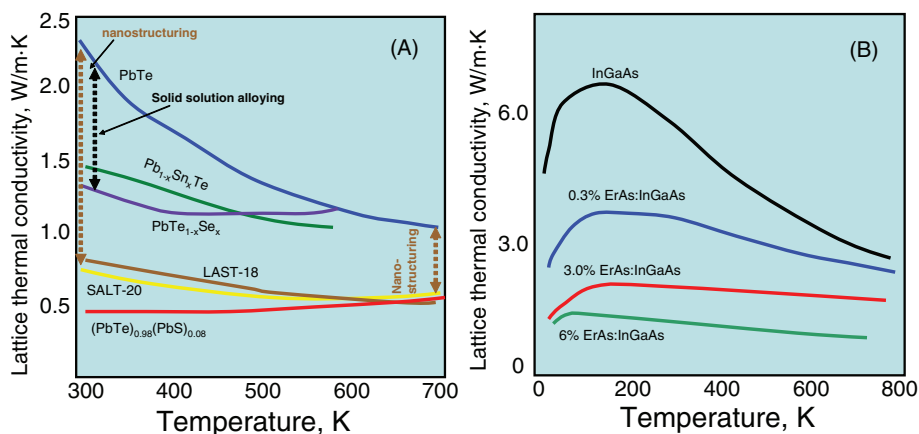


Figure 4. Lattice thermal conductivity as a function of temperature for: (a) various PbTe-based alloys ($x = 0.1$) and nanostructured samples. The value of $x = 0.1$ was chosen because these samples have the same concentration of added component to PbTe as those in LAST-18 and SALT-20. (b) InGaAs with and without embedded ErAs nanodots. It is seen in both cases that the inclusion of nanodots into the microstructure results in a significant reduction to the lattice thermal conductivity. In the PbTe system solid solution alloying is effective around room temperature (see black dotted arrow) but not at high temperature. Nanostructuring is shown to be effective both at room temperature and at high temperatures (see brown dotted arrows).

of Sb.^[73] In contrast, similar fractions of nanoparticles of Bi or Pb (two elements that have the same atomic mass as the Pb ions in the rock salt lattice) were found to have no such effect.^[73,81] ErAs:InGaAs is another interesting example to study along these lines since the size distribution of ErAs nanoparticles in the matrix is not a strong function of the growth parameters and they are typically 2–4 nm in diameter [Figure 3c].^[82] The volume fraction of the embedded nanoparticles can be easily changed from 0.01–6% without introducing defects or dislocations. Thermal conductivity measurements show a reduction by as much as a factor of 3 compared to the bulk alloy [Figure 4b].

The question remains as to why the inclusion of nanodots can reduce the thermal conductivity below the alloy limit. Detailed calculations of phonon transport have been performed for ErAs:InGaAs materials, although the principles developed through these studies are fairly general and apply for other nanodot material systems as well.^[72,82] Atomic scale defects in alloys scatter phonons due to differences in mass or due to generation of strain fields, and the scattering cross-section follows Rayleigh scattering as d^6/λ^4 , where d is the nanodot diameter and λ is the phonon wavelength. Hence, short wavelength phonons are effectively scattered in alloys, but the mid-to-long wavelength phonons can propagate without significant scattering and thereby still contribute to heat conduction. By inclusion of nanoparticles, significant reduction in lattice thermal conductivity can be achieved by the additional scattering of mid- and long-wavelength phonons by the nanoparticles. Calculations show that a wide size distribution of nanoparticles is preferable since it can effectively scatter

different phonon modes and reduce thermal conductivity. A schematic diagram is shown in Figure 5 capturing these various phonon scattering mechanisms, along with the electrical transport within a thermoelectric material.

Thus, in certain cases nanodots clearly play a very significant role in reducing lattice thermal conductivity, probably by effectively scattering phonons that otherwise would have relatively long mean free paths. In many of these cases it has been clearly demonstrated that the reduction in thermal conductivity far exceeds any concomitant reduction in the power factor caused

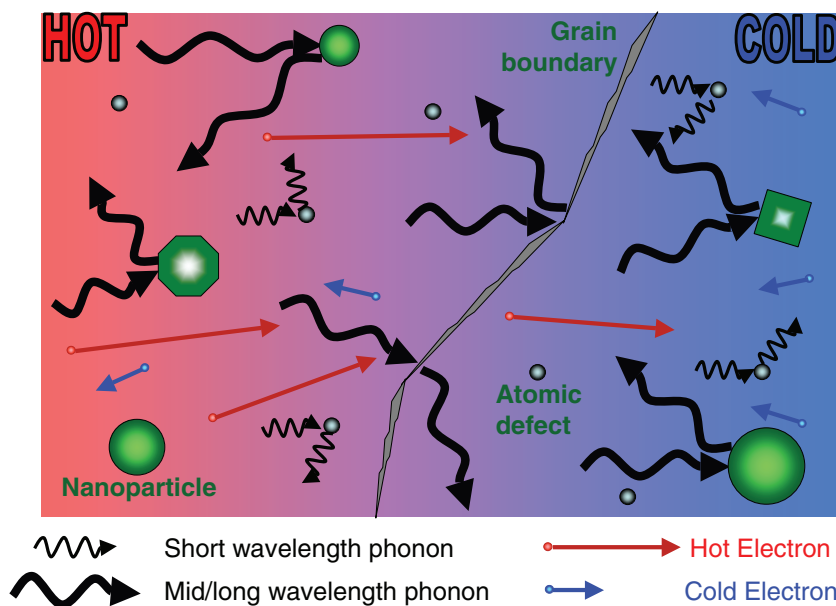


Figure 5. Schematic diagram illustrating various phonon scattering mechanisms within a thermoelectric material, along with electronic transport of hot and cold electrons. Atomic defects are effective at scattering short wavelength phonons, but larger embedded nanoparticles are required to scatter mid- and long-wavelength phonons effectively. Grain boundaries can also play an effective role in scattering these longer-wavelength phonons.

by electronic carrier scattering, thus resulting in enhanced ZT . Nanostructuring of thermoelectric materials for enhanced ZT is thus gaining popularity, and it is a general approach that is broadly applicable to bulk materials as well.^[83,84] For example, recent reports on skutterudites^[85] and half-Heusler alloys seem to confirm that real enhancements in ZT via a thermal conductivity reduction are possible by introducing nano-inclusions.

5. Nanocomposite Materials

Another recent approach to achieve nanostructuring has been through the formation of nanometer-sized (grain size ~ 5 nm– 10 μ m) polycrystalline samples, typically created via hot pressing or spark plasma sintering of fine powders formed by grinding and milling or wet chemistry processing. In this approach, the thermoelectric material is prepared in nanosized particles and these are then hot pressed into monoliths. Instead of the nanoparticles in a matrix model described above, this approach creates extensive interfacing between the compacted nanoparticles which can lower the thermal conductivity. The resulting sample can exhibit certain benefits over techniques that create very large-grain or single crystal material, such as reduced thermal conductivity (due to phonon scattering at grain boundaries as illustrated in Figure 5), increased power factor (due to electron filtering at grain boundaries), better mechanical properties and improved isotropy. Compacting nanocrystalline samples can be a relatively low-cost method to provide the large volume of material necessary for more wide-spread adoption of thermoelectric technology.^[12] However, a major challenge with this approach is obtaining complete removal of any binder or organics used in the grinding, milling or wet chemistry processes, and obtaining as close to 100% of theoretical density during compaction as possible. If this is not achieved, the carrier mobility will be substantially reduced by one or more orders of magnitude for just a few percent decrease in density,^[84] resulting in degraded ZT .

Some very promising nanocomposite results have recently been reported. For example, an enhancement of ZT to 1.2 was reported in bismuth telluride n -type materials prepared from pressed nanoparticles.^[86] Similarly, Poudel *et al.*^[12] obtained a ZT of 1.2 at room temperature and 1.4 at 100 °C from a ball-milled and hot-pressed p -type BiSbTe alloy. These values are about 20 and 40% higher, respectively, than the comparable state-of-the-art ingot BiSbTe alloy results they reported. Interestingly, the electrical conductivity of the nanostructured material was higher than the ingot material over the entire temperature range measured (25–250 °C), while the Seebeck coefficient was higher above ~ 160 °C, yielding a slightly enhanced power factor for the nanostructured material above ~ 75 °C. (It should be noted that it is unclear whether the carrier concentration was identical between the nanostructured and ingot materials.) The large improvement in ZT , though, was primarily due to a greatly reduced thermal conductivity for the nanostructured material, particularly at elevated temperatures.

Nanocomposite boron-doped Si/Ge materials formed by ball milling and hot pressing were also reported^[84] to exhibit significantly reduced thermal conductivities compared to bulk SiGe alloys. In addition, the nanocomposite materials had increased

Seebeck coefficients and only slightly reduced electrical conductivities, resulting in somewhat higher power factors over the temperature range of 300–1000 K. The increased power factor for the nanocomposite is similar to what was observed for the BiSbTe alloy above and predicted based on electron filtering effects at the grain boundaries. Primarily driven again by reduced thermal conductivity, the nanocomposite material exhibited an enhanced peak ZT of ~ 0.72 at 1000 K compared to a value of ~ 0.6 for the bulk SiGe alloy.

Polycrystalline $\text{Ag}_{0.8}\text{Pb}_{18+x}\text{SbTe}_{20}$ formed by mechanical alloying of elemental powders followed by densification through spark plasma sintering produced a material with ~ 20 -nm-sized precipitates. With a compacted density of $\sim 95\%$ of the theoretical value, the ZT of 1.5 measured at 673 K^[87] was only 10% lower than the value reported by Hsu *et al.*^[5] for the related material grown from the melt. The high ZT of the mechanically-alloyed material is believed to result from the same nanoprecipitate-related lattice thermal conductivity reduction as the similar materials prepared from the melt.

For an excellent overview of bulk nanostructured thermoelectric materials, with a particular focus on the impact of grain boundaries on electrical and thermal transport, the reader is referred to the recent review article by Minnich *et al.*^[20]

6. Looking to the Future

What is the lowest thermal conductivity achievable in various thermoelectric material systems through nanostructuring? Although the nanowire and thin film superlattice work has claimed values as low as $0.25 \text{ W m}^{-1} \text{ K}^{-1}$, additional validation is needed to prove such values are in fact reproducibly attainable. Nevertheless, if such values are possible, ZT values of ~ 2 could be reached at 700–800 K without needing any further increase in current power factors. Based on experimental and theoretical results to date, it would appear $\sim 0.25 \text{ W m}^{-1} \text{ K}^{-1}$ is the lowest we might expect to achieve while still retaining a high power factor. Is it possible to reduce the thermal conductivity even further?

The thermal conductivity can be estimated as $\kappa = C \cdot v \cdot l/3$, where C is the specific heat, v is the speed of sound, and l is the average phonon mean free path. The lowest thermal conductivity occurs for an amorphous material, since l is on the order of the lattice constant (~ 0.2 – 0.5 nm). For a material with a low Debye temperature (~ 100 K), $v \sim 2000$ – 4000 m s^{-1} and $C \sim 2 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$ according to the Dulong-Petit limit. Hence, the lowest thermal conductivity can be estimated to be $\kappa \sim 0.25$ – $1 \text{ W m}^{-1} \text{ K}^{-1}$, which is confirmed by more sophisticated theories.^[88,89] Therefore, unless new physics is introduced, it is unlikely that one can lower the thermal conductivity much lower than this value.

Recent reports in superlattices of WSe_2/W layers, however, are quite intriguing as they suggested cross-plane lattice thermal conductivity values as low as $0.02 \text{ W m}^{-1} \text{ K}^{-1}$.^[30] While the mechanism is not fully understood, it is likely that the layering creates large asymmetry in the directional phonon density of states and low coupling between phonons in different directions. It is unclear, though, whether this approach can be exploited while simultaneously achieving a high enough power factor for $ZT \geq 3$.

To reach ZT values of 3 or greater it seems that further reduction in the thermal conductivity—while necessary—will be insufficient; we will also need dramatic enhancements in the power factor. Barring the welcome discovery of some new and unexpected single phase material with a ZT in this target range, what is needed going forward are new physical concepts on how to enhance the power factor by 2–4 fold in the existing leading materials. In addition, such increases must come mainly from enhancements in the thermopower, as opposed to increases in the electrical conductivity. With regards to thermal conductivity, any further reduction below the amorphous limit can only occur if one can actively change the group velocity or reduce the number of phonon modes that propagate. This could result from coherent or correlated scattering effects, but so far this has remained elusive for phonons (although widely known for electrons) and thermal conductivity reduction through such mechanisms has never been conclusively demonstrated. These point to exciting scientific opportunities and create an open challenge to theorists and experimentalists alike to come up with new scattering mechanisms and concepts that will help achieve very large increases in the power factor and simultaneous decreases in thermal conductivity.

The original prediction from Hicks and Dresselhaus^[1,2] that the in-plane power factor could be substantially enhanced over that of homogeneous materials has yet to be realized. However, it is apparent that quantum confinement and nanostructure effects in thermoelectricity are not yet fully understood and they could still play a significant role in enhancing the power factor if the proper conceptual framework could be built. For example, it may be possible to use hot electron filtering in a bulk material with embedded nanoparticles.^[61] If the nanoparticle separation is less than the electron mean free path and with an appropriate potential barrier profile, the power factor could be enhanced without the need for a periodic structure or a uniform nanoparticle size distribution.^[90]

Recently, the concept of reversible diffusive electron transport in nanostructured thermoelectric materials was introduced as a means to improve the thermoelectric figure of merit.^[91] This approach aims to minimize the irreversible effects in thermoelectric materials that limit their efficiency. The proposal includes a fundamental thermodynamic argument for why the optimum density of states in a thermoelectric material is a delta function and how one can achieve energy-specific equilibrium between two reservoirs at different temperatures. This can be achieved via inhomogeneous doping or segmentation along the thermoelectric material. The electronic efficiency for thermoelectric cooling or power generation can approach the Carnot limit if electron transport between the hot and the cold reservoirs occurs in a narrow energy band under a finite temperature gradient and a finite external voltage. This is due to a decrease in electronic thermal conductivity by a significant reduction in the Lorenz number that relates thermal and electrical conductivities.

One should finally note that as nanostructured materials in thermoelectric applications work under high temperatures and temperature gradients, it is important to study and optimize long-term stability, interdiffusion and coarsening of nanostructures. This is still an open area requiring thorough investigation for many of the nanostructured systems discussed in this article.

Two recent reports raise hopes that dramatic increases in the power factor of PbTe may be forthcoming from novel phenomena. Kanatzidis *et al.* have observed that large increases in the thermoelectric power factor at high temperatures are possible when PbTe is co-nanostructured with Pb and Sb.^[92] When Pb and Sb inclusions are present simultaneously throughout the matrix of PbTe the behavior of the mobility becomes novel and results in very high values at high temperatures ~ 700 K. This enhances the power factors by as much as 80–90% over a similarly doped but not nanostructured PbTe sample. Why the mobility at high temperatures is higher in nanostructured PbTe when both Pb and Sb are simultaneously present but not when each of them is present alone, is currently unclear and the mechanism of this behavior requires further scrutiny. In another report Heremans *et al.* confirmed that the incorporation of 2% Tl atoms in the Pb sublattice of PbTe causes a distortion in the valence band density of states via a resonance state^[93,94] which appears to enhance the Seebeck coefficient and the power factor leading to $ZT \sim 1.5$ at 700 K.^[16] This is in agreement with theoretical predictions and also provides an interesting path forward.^[95]

The current decade has witnessed the most significant advances in the field of thermoelectrics since the 1950s. Not only have ZT values well broken the longstanding barrier of ~ 1 , but new materials, new concepts and enhanced understanding have emerged that will help drive the field forward in the years to come. Such progress could not have come at a better time as energy issues such as production, conservation and efficiency are becoming critical to the long term survival of the human standard of living. Indeed, recent advances in ZT already raise the real possibility of thermoelectric power generation and refrigeration for more widespread commercial applications instead of just small niche markets. There have been questions about some of the recently reported experimental results and theoretical concepts. This is expected for a rapidly growing and dynamic field, especially since accurate thermal and thermoelectric characterization techniques for small-sized samples are still being developed at the same time as the materials systems themselves. We have tried to summarize our current understanding and critically review some of the reported results. There may be mistakes or misunderstandings since we have not been directly involved in all of the new research directions. However, we think that it is important to identify the open issues clearly so that we have healthy discussions in the thermoelectric community. We are hopeful and optimistic that progress continued at the pace of the past ten years will lead to additional large leaps in the figure of merit. This will come from cross-disciplinary research among various fields of science and engineering, coupled with sustained investments from government and industry. The basic science of thermoelectric materials contains great opportunities for creative thinking and experimentation.

Acknowledgements

Financial support from ONR and the ONR MURI program (Dr M. Gross Program Manager) and DARPA NMP program (Dr. K. Latt Program Manager) are gratefully acknowledged. We thank Mr. J. Ravichandran

(UC Berkeley) for providing Figure 1, Prof. Z. Bian (UCSC) for the calculations in Figure 2, and Dr. M. Bulsara (MIT) for providing the TEM image of Figure 3b. In addition, we greatly appreciate critical reviews of this manuscript by Dr. M. Gross, Dr. T. Sands, Dr. J. Bowers, and Dr. D. Morelli.

Received: March 8, 2010
Published online: July 27, 2010

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