Anderson Localization for Better Thermoelectrics?

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Abstract

Solid-state thermoelectrics are of great interest because they directly convert between thermal and electrical energy. However, wider application of thermoelectrics is dependent upon improving their performance. Anderson localization of charge carriers has been generally perceived as detrimental to thermoelectric performance, but in their paper in this issue of *ACS Nano*, Lee *et al.* propose a concept of using selective charge Anderson localization for synergetic enhancement of thermoelectric performance. To facilitate discussions and research on Anderson localization to improve thermoelectrics, this Perspective shares potential directions to explore the viability of using Anderson localization or related strategies to drive thermoelectric performance.

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Thermoelectrics can directly convert heat into electricity if a temperature gradient is applied, based on the Seebeck effect.[1] When current is passed through a thermoelectric device, it can either heat or cool the junctions *via* the Peltier effect.[1] Thus, thermoelectrics offer a green option for renewable energy generation and solid-state refrigeration or heat pumping. The energy conversion efficiency or coefficient of performance is largely determined by the figure of merit, $ZT = S^2\sigma T/k$, where S is the Seebeck coefficient, σ is electrical conductivity, T is the absolute temperature, k is thermal conductivity, and $S^2\sigma$ is the power factor. Total thermal conductivity is the sum of the lattice contribution and electronic contribution, given by $k = k_l + k_e$. Electronic thermal conductivity comprises the unipolar electronic conductivity of electrons and holes and the bipolar thermal conductivity. An ideal thermoelectric material has a high electrical conductivity, a high Seebeck coefficient, and a low thermal conductivity. However, it is challenging to optimize ZT because the Seebeck coefficient, electrical conductivity, and thermal conductivity are inherently intertwined in conventional materials. Strategies to decouple and to adjust these parameters quasi-independently to boost ZT values are in great demand. In the past two decades, the major advances in thermoelectrics can be attributed to (1) nanoengineering to reduce the lattice thermal conductivity without considerably sacrificing the electronic properties,[2,3] and (2) band engineering to increase the power factor.[4] However, applications of thermoelectrics remain limited to niche markets where reliability and simplicity are of major concern. New physical mechanisms are needed to push thermoelectrics to higher levels of performance to be competitive with other energy-conversion technologies and primed for more widespread use, including in heating and/or cooling devices.

Anderson localization, first observed 1958,[5] describes electron localization in a random potential. Anderson localization originates from the destructive interference from multiple coherent scattering events in strongly disordered media. Sixty years later, the subject has been vigorously evolving. Although electron localization is hard to confirm due to its interactive nature, researchers have made direct experimental observations of Anderson localization with microwaves,[6] ultracold atoms,[7] and ultrasound.[8] However, the study of using Anderson localization for thermoelectrics has been rather limited. Theoretically, thermoelectric transport properties near the Anderson localization transition at the low temperature limit have been reported.[9,10] Computationally, Anderson localization of the majority carriers has been shown to be *detrimental* to the power factor because the increase in Seebeck coefficient cannot compensate for the exponential decay of the electrical conductivity.[11,12] Experimentally, the paper by Lee *et al.* in this issue of *ACS Nano* proposes using selective Anderson localization of minority charge carriers to enhance ZT and demonstrated a ZT value of 2.05 at 800 K.[13] This paper has garnered great interest and also raised questions about whether Anderson localization represents a new strategy to increase ZT.

The idea of using selective charge Anderson localization to decouple the entangled thermoelectric properties and to enhance ZT is intriguing, and this concept resonates with the old "electron–crystal phonon–glass" paradigm[14] for thermoelectrics. More specifically, Lee *et al.* experimentally characterize the thermoelectric properties of *n*-type Bi-doped PbTe/Ag_2Te. By introducing random potentials *via* Ag_2Te nanoparticles, the Seebeck coefficient was enhanced, thermal conductivity was reduced, and high electrical conductivity was preserved. They attribute the synergetic enhancement of thermoelectric performance to selective charge Anderson localization and delocalization. Although the delocalization of majority carriers gives high electrical conductivity, Anderson localization of the minority carriers suppresses bipolar diffusion and results in a high Seebeck coefficient and a low bipolar thermal conductivity. Lattice thermal conductivity is also reduced due to phonon scattering by nanoprecipitation. To demonstrate the change between localization and delocalization, Lee *et al.* intentionally selected Ag_2Te because it undergoes a structural phase transition at 417 K from monoclinic β-Ag_2Te to cubic α-Ag_2Te with increased bandgap to match that of Bi-doped PbTe more closely. Below the phase transition temperature, the large potential barriers of β-Ag_2Te could lead to localization of both minority and majority carriers. Above the phase transition temperature, the decrease of potential barriers could give rise to partial delocalization of the majority carriers while the minority carriers remain localized. The experimental trends of thermoelectric properties indicate possible formation of Anderson localization in the following aspects: (1) Whereas the electrical conductivity of both Bi-doped PbTe and Ag_2Te exhibit metallic behavior, a small addition (5 mol%) of Ag_2Te into Bi-doped PbTe shows insulating behavior, implying carrier localization because grain boundary scattering alone at such dilute concentrations should not have led to such a significant decrease in electrical conductivity. Also, the dilute concentration of Ag_2Te leads random distributions, consistent with the requirement of a randomly distributed potential for Anderson localization. (2) Although β-Ag_2Te has higher electrical conductivity than α-Ag_2Te, the electrical conductivity of the nanocomposites with β-Ag_2Te is smaller, suggesting that the charge carriers were localized below the phase transition. (3) The suppression of bipolar thermal conductivity at high temperatures may come from the minority charge carrier localization.

More decisive evidence of Anderson localization is essential because of the immense challenge to demonstrate Anderson localization of charge carriers in a three-dimensional (3D) structure at high temperature. Anderson localization, a coherent wave interference phenomenon, is more challenging to realize in 3D compared to in one dimension (1D) or two dimensions (2D).[15] Moreover, inelastic scattering processes including both phonon–electron (hole) and electron (hole)–electron (hole) scattering can induce dephasing of charge carriers and significantly affect Anderson localization. As temperature increases and the electron coherence length decreases, it becomes even more difficult to satisfy the Anderson localization criteria where sufficient coherence length is needed to enable destructive interference. In the dilute limit of concentration, questions remain regarding whether it exceeds the threshold to generate disorder at the level required to render Anderson localization. More work is needed to test the existence of Anderson localization and to establish the validity of this concept before pursuing it further in other materials systems. The key question is whether we can computationally or experimentally observe the hallmark of Anderson localization—the exponential decay of the wavefunction or transmission coefficient with respect to device length or its statistical signature, the relative fluctuation of certain transmission quantities. Meanwhile, it is instructive to develop comprehensive theoretical or computational models with careful inclusion of the inelastic processes to assess the feasibility of using Anderson localization to enhance ZT in practical temperature ranges, as most of the previous modeling work only considered noninteracting electrons at low temperature.

The basic premise of the concept is that selective charge localization can be realized. One good starting point to test this conjecture is in low-dimensional thermoelectric materials where it is easier to achieve Anderson localization. For example, in simple systems like *n*-type aperiodic silicon (Si)/germanium (Ge) superlattices, selective localization of holes could potentially be observed because the valence band of Ge is significantly offset from that of Si while the conduction band is essentially at the same energy as that of Si. Low dimensionality also comes with the additional benefits of an enhanced Seebeck coefficient, due to the sharp density of states near the Fermi level, and reduced lattice thermal conductivity, due to classical and quantum size effects.[3] If the effects of Anderson localization on thermoelectric properties can be demonstrated convincingly in 1D and 2D, we could then move on to 3D to tackle the more challenging parts of the problem, since 3D structures are easier for mass fabrication and practical implementation into devices.

If selective charge Anderson localization and its impact on ZT are confirmed, it is exciting to imagine what other breakthroughs may lie in wait in thermoelectrics when this new strategy is deployed for better thermoelectrics. Potential directions that may be worth exploring include the following.

General Guidelines for Selective Charge Localization. It would be practical and impactful to establish the general routes for achieving selective charge localization. Specifically, we suggest the following steps, taking 3D nanocomposites as an example. The first step is to identify potential candidates for matrix and filler materials. In theory, selective Anderson localization can be realized when the band offset is negligibly small for the majority carrier to be itinerant while the band offset is large enough for the minority carrier to be localized. Density functional theory is efficient for calculating electronic band structure, although the selection of exchange-correlation functionals warrants cautions to guarantee accuracy. Machine-learning-based data analytics could be further applied to predict the candidate materials based on their band alignment. The second step is to determine the size and concentration of fillers, which can be tricky. The size effect is critical for achieving Anderson localization. The filler sizes should be smaller or comparable to the coherence length and the system size needs to be larger than the localization length. The concentration should be carefully examined as strong random disorder is required for Anderson localization while the fillers need to be randomly distributed instead of agglomerated. The third step is to choose the proper synthesis method. Phase separation with sharp potential interfaces is needed. As the natural phase separation that occurs during heat treatment does not create a sharp interface, Lee *et al.* used low-temperature sintering below the phase separation temperature and extrinsic phase mixing with separate Bi-doped PbTe and Ag_2Te powders to control a sharp potential difference between the matrix and the nanoparticle phase.

Phonon Localization. Although Anderson localization has been discussed in the context of charge carriers, it is natural to wonder if it is ever possible to combine it with Anderson localization of phonons. Phonon localization is a relatively new area. Phonon localization may offer a new lattice thermal conductivity minimum, even smaller than the theoretical minimum in the phonon particle picture,[16,17] and further enhance ZT. Because of the interacting features of phonons and the broad spectrum of heat-carrying phonons, there are challenges in achieving Anderson localization of phonons. Similar to electrons, localization in reduced dimensions is considerably easier.[18] Experiments on thermal conductivity of superlattices with nanodots have shown evidence of phonon localization below 100 K.[19] Meanwhile, aperiodicity in superlattices might offer a feasible way to tune the mid- to low-frequency phonons without fabricating structurally complex nanoinclusions and maintain the crystalline structure for charge transport.[20,21] With proper band alignment, the minority charge carrier of aperiodic superlattices could also be localized, as discussed above. Then, the combined effects of Anderson localization of phonons and minority carriers on ZT could be manifested. It is also appealing to go beyond superlattices to achieve phonon localization for broader applications. However, it remains elusive as to whether broadband phonon localization could be achieved in 3D nanocomposites. More research on phonon localization, including direct observation of mode-specific localization, is needed. Green's function methods are powerful tools to calculate the transmission coefficient and the inverse participation ratios of eigenstates are useful parameters for identifying phonon localization. If there is a structure that can simultaneously localize *both* minority charge carriers and phonons in practical temperature ranges, this material would have the ultimate advantage in using Anderson localization for thermoelectrics (Figure 1).

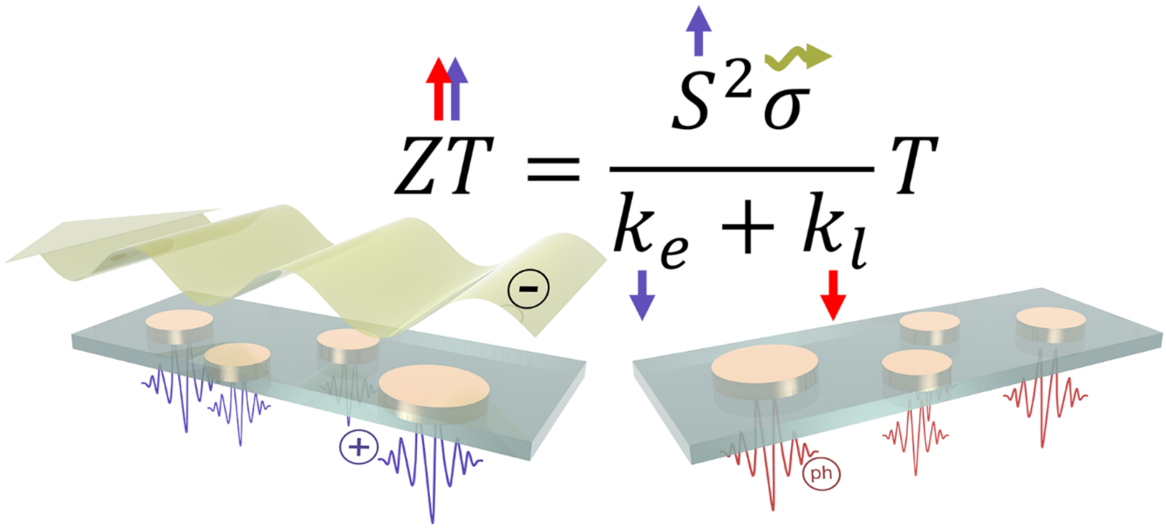

Figure 1. Schematic of simultaneous Anderson localization of minority charge carriers and phonons to enhance ZT. This figure is for *n*-type materials with holes being the minority charge carriers. Similarly, one can have electrons being localized for *p*-type materials.

Extension to Organic and Hybrid Thermoelectric Materials. It would be interesting to evaluate whether selective Anderson localization can be applied to organic and hybrid thermoelectrics. In general, organic and hybrid materials are more disordered than inorganic semiconductors and can drive Anderson localization more easily. Meanwhile, due to the prevalent localization of majority charge carriers, polarons, and/or excitons, the conditions for selective localization of minority charge carriers in organic and hybrid materials become even more stringent. Efforts to delocalize the majority carriers in organic and hybrid materials are thus imperative. For organic semiconductors, including small organic molecules and conducting polymers, we can, in principle, calculate the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) energy levels and align them properly to satisfy the band offset criteria for selective charge localization. The reality is far more complicated because the electronic structures can be heterogeneous due to the coexistence of crystalline and amorphous domains, and molecular doping can concomitantly change the electronic landscape at high dopant concentrations.[22] In addition, energetic and spatial disorder could impact their thermoelectric properties differently. Despite these challenges to aligning molecular orbitals, unique opportunities do exist. For example, incorporating selective Anderson localization into low-dimensional conducting polymers may surpass the state-of-the-art ZT values – the electrical conductivity of conducting polymers increases with reducing dimension due to increased crystallinity and charge mobility, which is distinct from inorganic semiconductors. In other words, the extra control parameter of the morphology in conducting polymers could be harnessed to enhance ZT in conjunction with selective Anderson localization. For hybrid materials, it is vital to characterize and to understand the orbital alignment and charge transfer at the organic–inorganic interfaces. Localized holes and delocalized electrons were observed in photoexcited inorganic perovskites,[23] which indicates that selective charge localization might be possible for hybrid organic–inorganic perovskites that have shown promises for thermoelectrics.

Beyond Anderson Localization. It is inspiring to identify alternative approaches that share the essence of Anderson localization effects on ZT. The selective localization of minority charge carriers essentially restrains minority carrier diffusion. Minority carrier diffusion has two negative impacts on ZT: (1) reducing the Seebeck coefficient and (2) increasing the bipolar thermal conductivity. In other words, we can search for more general strategies that suppress the minority carrier diffusion while preserving the dispersive majority carriers, not necessarily through Anderson localization. For example, selective blocking of minority carriers using high heterostructure barriers was theoretically proposed in 2014.[24] The average inter-barrier spacing was on the order of the electron mean free path and the minority carriers were trapped within the nanoscale region between the barriers, resulting in the suppression of detrimental bipolar diffusion and the enhancement of ZT. We may also want to look into weak localization, such as coherent backscattering, which could possibly play a similar role in suppressing minority carrier diffusion. However, it remains a question as to how one can realize selective weak localization of minority charge carriers while maintaining the mobility of major carriers.

It is certainly not an easy task to achieve the delicate balance among many different mechanisms needed to reach the sweet spot of selective Anderson localization for minority charge carriers. It is even more difficult to localize minority charge carriers and phonons simultaneously. Understanding the combined effects of interactions and disorder also remains challenging. Nevertheless, we hope the paper by Lee *et al.* and this Perspective spark greater interest and activity on Anderson localization for better thermoelectrics. Once we learn how to localize electrons in *p*-type materials and holes in *n*-type materials selectively, we will be able to build the next level of thermoelectric devices based on Anderson localization. It is exciting to envision how the thermoelectric field will unfold as Anderson localization and similar phenomena come into play, and what other doors may be opened by understanding the impact of Anderson localization on thermoelectric properties.

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Suggested Pull Quotes

New physical mechanisms are needed to push thermoelectrics to higher levels of performance to be competitive with other energy-conversion technologies and primed for more widespread use, including in heating and/or cooling devices.

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