ACCELERATING THERMOELECTRIC MATERIALS DISCOVERY VIA DOPABILITY PREDICTIONS

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EXECUTIVE SUMMARY

Nowadays, the experimental realization of new thermoelectric materials—which convert wasted heat to useful electricity—is greatly accelerated through computational guidance, with first-principles calculations providing relevant materials properties such as electronic and phonon transport and thermodynamic stability. Semiconductors are called semiconductors because they exhibit intermediate electrical conductivity (better than typical insulators but not as good as metals). For thermoelectrics, researchers need to improve their electrical conductivity by "doping" the semiconductor. Doping refers to the intentional introduction of defects in the material that help to improve the electrical conductivity—typically by several orders of magnitude.

The current bottleneck in the discovery of new thermoelectric materials, however, is that greater than 90% of the materials identified as promising on a computer cannot be doped in the laboratory. To overcome this, the research team uses Blue Waters to carry out dopability assessments through defect calculations on a diverse set of candidate semiconductors including Zintl compounds, sulvanites, and diamondlike semiconductors. The systems simulated on Blue Waters will be incorporated into TEDesignLab, an online open platform for easy, searchable data exchange to enable data-driven approaches to thermoelectrics design and discovery. This work would not be possible without Blue Waters, which to date has allowed the calculation of full defect properties of a class of approximately 30 candidate thermoelectric semiconductors.

RESEARCH CHALLENGE

Of the 101.2 quadrillion BTUs of energy consumed in the United States in 2018, only 32.3% was used to carry out useful work while the other 67.7% was wasted, largely as heat loss to the environment [1]. This wasted energy provides a huge opportunity to reduce carbon emissions and improve carbon efficiency, if only it could be captured and harnessed for further use. A thermoelectric material is one that responds to a temperature gradient by creating electricity; these materials have the potential for large-scale conversion of waste heat to usable energy. So far, however, thermoelectric materials are not yet efficient enough for large-scale deployment and utilization. New materials need

to be discovered that are good at thermoelectric energy conversion, but thermoelectric energy conversion requires a strict and rare set of properties: the materials need to exhibit high electrical conductivity and low thermal conductivity.

Over the last several years, members of the team have used high-throughput first-principles calculations of materials properties (electronic, thermal, and thermodynamic stability) to classify the thermoelectric conversion potential of a wide set of materials (Fig. 1a) [2]. Approximately 50,000 high-throughput calculations were conducted; distilled results of these calculations are available at the TEDesignLab website (www.tedesignlab.org) [3]. This initial effort uncovered a vast array of new candidates but also revealed a new limitation: most of the semiconductors identified (~90%) have proven not to be dopable in the laboratory—thus limiting their electrical conductivity. The current bottleneck to discovering high-performance thermoelectrics, then, is that experimentally, it has been found that only 10% of the candidate materials identified are readily dopable to the desired concentration.

The ability to control the carrier concentration of semiconductors represents both a scientific and a practical challenge. Scientifically, general understanding of the factors controlling the dopability of semiconductors is currently largely phenomenological and qualitative. This knowledge gap leads to wasted experimental efforts on compounds that cannot be optimized for thermoelectric performance. The research challenge then is to use high-performance computing to accurately select the materials that can successfully be doped, opening up rapid routes to thermoelectric materials design and discovery.

METHODS & CODES

To overcome the bottleneck of identifying high electrical conductivity semiconductors as candidate thermoelectrics, the research team used Blue Waters to carry out high-throughput quantum mechanical calculations of semiconductor dopability and predict the best candidate materials before they are even synthesized in the laboratory. The dopability of a semiconductor is a result of its defect chemistry: some semiconductors resist doping via formation of intrinsic defects that counteract the effect of the dopant whereas others do not. Therefore, assessing dop-
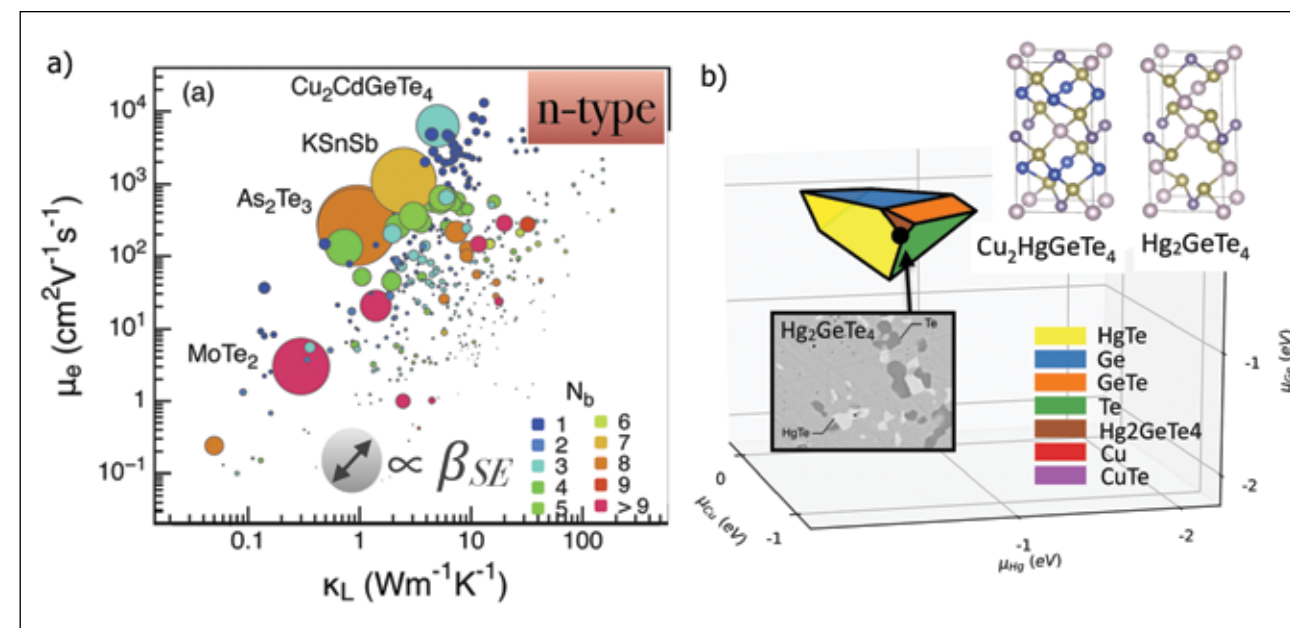

Figure 1: (a) Data set of thermoelectric materials: low thermal conductivity κ_L and high electron mobility μ_e is desired. However, the dopability of these materials is generally not known and experimentally intensive to establish. After [2]. (b) High-throughput screening of materials on Blue Waters enables large-scale dopability predictions to accelerate thermoelectric materials discovery.

ability requires a comprehensive analysis of the possible intrinsic defects that could form in a material in response to any attempts to dope it. Identifying low-energy defects requires solving the quantum mechanical Schrödinger equation to determine the defect formation energy, which governs how readily the defect may form. For this, the team used first-principles quantum mechanical methods based on the framework of density functional theory, which approximates the Schrödinger equation to make it solvable.

As the new candidate materials being considered are structurally complex ternary and quaternary semiconductors, a large number of intrinsic defects are possible, requiring a large set of quantum mechanical simulations to accurately predict dopability and the laboratory growth environments that will maximize it. To streamline the simulation process, the team has developed an automated simulation workflow and protocol on Blue Waters to facilitate the large-scale analysis. This has enabled us to establish a closed feedback loop between simulations and experimental validation, enabling rapid screening of candidate materials in a manner not previously demonstrated.

RESULTS & IMPACT

To date, using Blue Waters the team has carried out systematic investigations of a set of approximately 30 new candidate thermoelectric materials. The group has helped to predict several new ternary and quaternary materials that exhibit the desired degree of dopability, which have subsequently been synthesized in the laboratory or are soon to be synthesized [4–6]. Over the course of this project, the researchers expect this work to create

the largest data set of semiconductor dopability focused on complex ternary and quaternary thermoelectric materials. Selected results highlighting some new materials identified using this approach are shown in Fig. 1b.

WHY BLUE WATERS

Practically, the key hurdle to this computation-driven approach is the need to calculate a large number of intrinsic and extrinsic point defects to directly assess dopability of semiconductors. The large computational costs historically had limited dopability calculations to case-by-case studies in which one material was considered at a time in a serial manner. Harnessing the predictive power of computation to model dopability on a large scale is critical in accelerating the transition from novel semiconductors to functional devices. Only Blue Waters offers the large-scale computational resources that are essential to the research team's integrated simulation/experimental approach to the discovery of new thermoelectric materials.

PUBLICATIONS & DATA SETS

T. Zhu and E. Ertekin, "Mixed phononic and non-phononic transport in hybrid lead halide perovskites: glass-crystal duality, dynamical disorder, and anharmonicity," *Energy Environ. Sci.*, vol. 12, pp. 216–229, Jan. 2019, doi: 10.1039/C8EE02820F.

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