Thermoelectric Materials

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Thermoelectric Tin Selenide: The Beauty of Simplicity**

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Solid-state thermoelectric (TE) modules can couple heat flow and electric current. This approach offers a viable route for power generation from different sources of waste heat, such as car exhausts and industrial plants. Compared to competing technologies, such as traditional heat engines, thermoelectric devices that contain no moving parts or fluids are noise- and emission-free. They can be of small size and operate at low powers (milli- or microwatts) as an energy source for remote sensors.[1] TE modules are also used for many cooling applications.

The efficiency of the TE module cannot exceed the Carnot limit, $\eta_{max} = (T_H - T_C)/T_H$, where T_H and T_C are the temperatures of the hot and the cold side of the device, respectively. Because of irreversible heat losses through the Joule heat and heat conduction, real TE devices operate at only a fraction of the Carnot efficiency: $\eta = \eta_{max}[(1+ZT)^{1/2}-1]/[(1+ZT)^{1/2}+T_C/T_H]$. This expression introduces the thermoelectric figure of merit, ZT, which relates the device efficiency to the material properties: $ZT = (S^2\sigma T)/\kappa$, where S is the thermopower, which is also known as the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity. In most materials, S, σ, and κ are interrelated in a way that makes it challenging to achieve ZT values greater than unity, which are needed for commercial deployment beyond a few niche applications.[2] The strategies for improving this value can be roughly divided into two groups. One set of approaches aims at maximizing the power factor $S^2\sigma$ through electronic doping and band engineering.[3] The other methods target κ, which is a sum of the electronic (κ_e) and lattice (κ_L) thermal conductivity. In fact, the most significant progress in ZT enhancement came from a reduction in κ_L by the development of clever strategies for phonon scattering. For example, Biswas et al. reported ZT values of approximately 2.2 at 915 K in Na-doped PbTe containing phonon-scattering endotaxial SrTe nanostructures and grain boundaries.[4] The high ZT value was attributed primarily to a low κ_L value of 0.5 $\mathrm{W\,m^{-1}\,K^{-1}}$. Alternatively, low κ values along with high ZT values have been observed in “phonon glass electron crystal” materials where the low κ value is attributed to complex unit cells, such as in $CeFe_3CoSb_{12}$ skutterudite and $Yb_{14}MnSb_{11}$ Zintl phases.[5] To summarize, the rational engineering of TE materials is based on the use of heavy elements and highly doped semiconductor phases, ideally with complex multi-atomic unit cells. The introduction of nanoscale inclusions and grain boundaries improves phonon scattering to further reduce the κ_L values.[6] Unfortunately, the heavy elements that are used for TE materials are often either toxic (e.g., Pb) or scarce (e.g., Te). Complex unit cells as well as nanostructuring require a tight control over the synthesis process and the associated manufacturing costs.[5]

A surprising and potentially transformative discovery was recently reported by Zhao and co-workers:[7] Single crystals of SnSe gave a ZT value of approximately 2.6 at 923 K along a particular crystallographic direction, the b axis. This finding is a new ZT record for bulk materials. A very high ZT value of about 2.3 was also observed along the c axis, whereas a moderate ZT value of approximately 0.8 was measured along the a axis (Figure 1). Such a TE performance goes against established rules as SnSe is made up of light elements and has a small and simple unit cell. Expectedly, this known semiconductor was ignored by the TE community in the past.

The record ZT value was achieved without optimization of the carrier concentration, and as a result, the power factors of the SnSe crystals were only moderate: Values of 2.1, 10.1, and 7.7 $\mathrm{\mu W\,cm^{-1}\,K^{-2}}$ were obtained at 850 K along the a, b, and c axes, respectively. It is likely that the ZT value of SnSe will be further enhanced through systematic optimization by making use of doping, alloying, band engineering, and other methods developed for PbTe and other established TE materials. For comparison, the power factors of optimized p-type BiSbTe[6c] and PbTe[4] are approximately 40 $\mathrm{\mu W\,cm^{-1}\,K^{-2}}$ and 27 $\mathrm{\mu W\,cm^{-1}\,K^{-2}}$ and thus several times larger than that of SnSe.

SnSe outperformed other materials because of the ultra-low κ value observed for the high-temperature *Cmcm* phase. Above 800 K, the κ_L values along all of the crystal axes were smaller than 0.25 $\mathrm{W\,m^{-1}\,K^{-1}}$, which is significantly lower than the κ_L value of p-type PbTe containing carefully engineered phonon scattering nanostructures and grain boundaries (ca. 0.5 $\mathrm{W\,m^{-1}\,K^{-1}}$).[4] Zhao et al. discussed the underlying physics of the extremely low κ_L value of the SnSe single crystals, and attributed it to the strong anharmonicity of chemical bonds in this layered compound. Density functional theory (DFT) was

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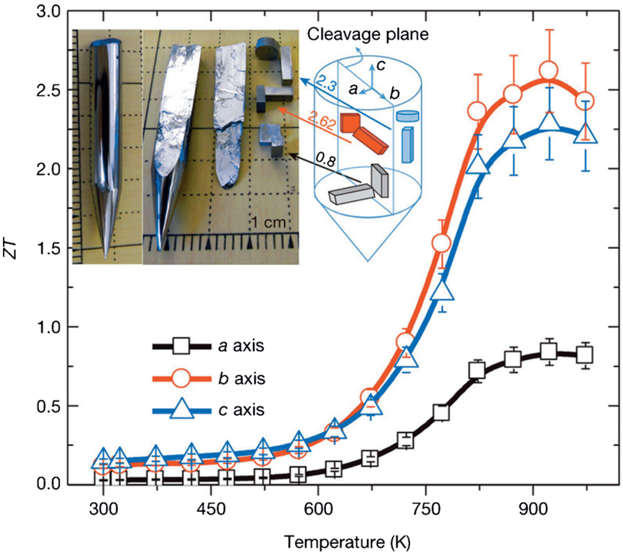

Figure 1. *ZT* values along different axial directions of the SnSe crystal. Inset, left: a typical crystal. Inset, right: a crystal cleaved along the (100) plane, and specimens cut along the *a*, *b*, and *c* axes. The inset diagram shows how crystals were cut for directional measurements. Reproduced from Ref. [7] with permission from the Nature Publishing Group.

used to calculate the Grüneisen parameter (γ), which describes the changes in the phonon frequency on crystal-lattice expansion or contraction. For a crystal with harmonically oscillating bonds, γ should be zero. The lattice vibration in SnSe shows unusually large anharmonicity, with average γ values along the *a*, *b*, and *c* axes of 4.1, 2.1, and 2.3, respectively, with a peak γ value as high as 7.2. For comparison, PbTe has a γ value of about 1.45. In an anharmonically vibrating crystal lattice, the phonons cannot be considered as infinitely long-lived elementary excitations. Instead, they scatter, merge, and decay, which leads to low κ_L and enhanced *ZT* values. Hopefully, it will be possible to obtain experimental γ values in the near future (e.g., by recording Raman spectra at different hydrostatic pressures) to either confirm the DFT predictions or to reveal yet another surprising feature of the SnSe material.

Anharmonicity may become a paradigm for designing efficient TE materials. This finding will stimulate further theoretical and experimental efforts in seeking new compounds with high phonon anharmonicity and, most importantly, high TE efficiency. In fact, SnSe is not the only unanticipated newcomer to the TE family. It has recently been reported that polycrystalline $Cu_{1.97}S$[8] and $Cu_{2-x}Se$[9] also show very low κ_L values, leading to *ZT* values for these materials as high as approximately 1.7 and 1.5, respectively, near a temperature of 1000 K. As with SnSe, $Cu_{1.97}S$ and $Cu_{2-x}Se$ consist of light elements and adopt simple crystal structures. A special feature of these materials is the high degree of disorder of the Cu^I ions, which are highly mobile within the rigid face-centered cubic framework of the sulfur or selenium anions. At high temperatures, it results in a phonon-liquid electron crystal (PLEC) behavior,[9] which leads to reduced κ_L values. Counterintuitively, $Cu_{1.97}S$, which is made of lighter elements, showed lower κ_L ($< 0.35\ W\,m^{-1}\,K^{-1}$) and higher *ZT* values than heavier $Cu_{2-x}Se$. He et al. attributed this effect to the stronger anharmonic character of the copper–sulfide bonds.[8]

Organic semiconductors are yet another emerging class of TE materials that contain only earth-abundant non-toxic elements (C, H, O, N, S, P, etc.). In addition to the many benefits of organic materials, such as flexibility, light weight and low cost, organic semiconductors often show a weak correlation between the σ and κ values (i.e., they do not always follow the Wiedemann–Franz law).[10] By optimizing the doping level in composites of poly(3,4-ethylenedioxythiophene) and poly(styrene sulfonate), a *ZT* value of approximately 0.42 at room temperature was recently achieved.[11]

The recent burst of investments in energy-related research begins to pay off as new materials and concepts are developed that may turn into technological breakthroughs in the near future. Zhao et al. introduced the first material that is made of earth-abundant non-toxic elements with a *ZT* value of > 2, which could have real commercial prospects for waste-heat recovery. Equally importantly, this finding urges us to revisit the material design principles adopted by the TE community and to remember that out-of-the-box thinking may require us to set aside what has been established as "common sense".

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