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EDITORIAL

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Cascade thermoelectrics: Cooling the cooler

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Solid-state thermoelectric (TE) cooling technology (Figure 1), based on the Peltier effect, has emerged as an important solution for precise temperature control in infrared detectors, microelectronics, and medical equipment, due to the unique advantages of noise-free, miniaturization, and long-serviceability. Bi_2Te_3-based alloys, including the p-type $Bi_{2-x}Sb_xTe_3$ and the n-type $Bi_2Te_{3-x}Se_x$, have long been the dominant commercialized materials utilized for TE cooling applications. The development of new materials demonstrating TE performance comparable to or surpassing that of Bi_2Te_3-based alloys has remained a central research focus in the TE community.

In the past decade, an emerging system, i.e., n-type $Mg_3Sb_{2-x}Bi_x$ alloys, has attracted extensive attention from both academic and industrial fields, due to its great TE potential for both power generation and refrigeration applications.[1] Mg_3Sb_2 and Mg_3Bi_2 are its two parent compounds. The former is a narrow bandgap semiconductor with an indirect gap of about 0.5 eV while the latter is a semimetal. Luckily, these two parent compounds can form solid solutions without an observable miscibility gap. Thus, the bandgap of $Mg_3Sb_{2-x}Bi_x$ can be tuned successively. This is very important for the different TE applications of $Mg_3Sb_{2-x}Bi_x$, i.e., power generation or cooling, because the peak performance of a TE material generally occurs near the temperature where the bipolar conduction becomes obvious. For power generation, Sb-rich $Mg_3Sb_{2-x}Bi_x$, e.g., $x \le 1.0$, are favorable, due to its larger bandgap which can effectively push bipolar conduction occurring at elevated temperatures. In contrast, Bi-rich $Mg_3Sb_{2-x}Bi_x$, e.g., $x \ge 1.0$, are desirable for near-room-temperature cooling applications. One important characteristic of $Mg_3Sb_{2-x}Bi_x$ is that its phonon transport is insensitive to grain boundaries whereas the electronic transport can be significantly degraded by the grain boundary scattering[2], especially near room temperature. Consequently, single-crystalline or coarse-grained $Mg_3Sb_{2-x}Bi_x$ generally exhibits good TE performance near room temperature.[2]

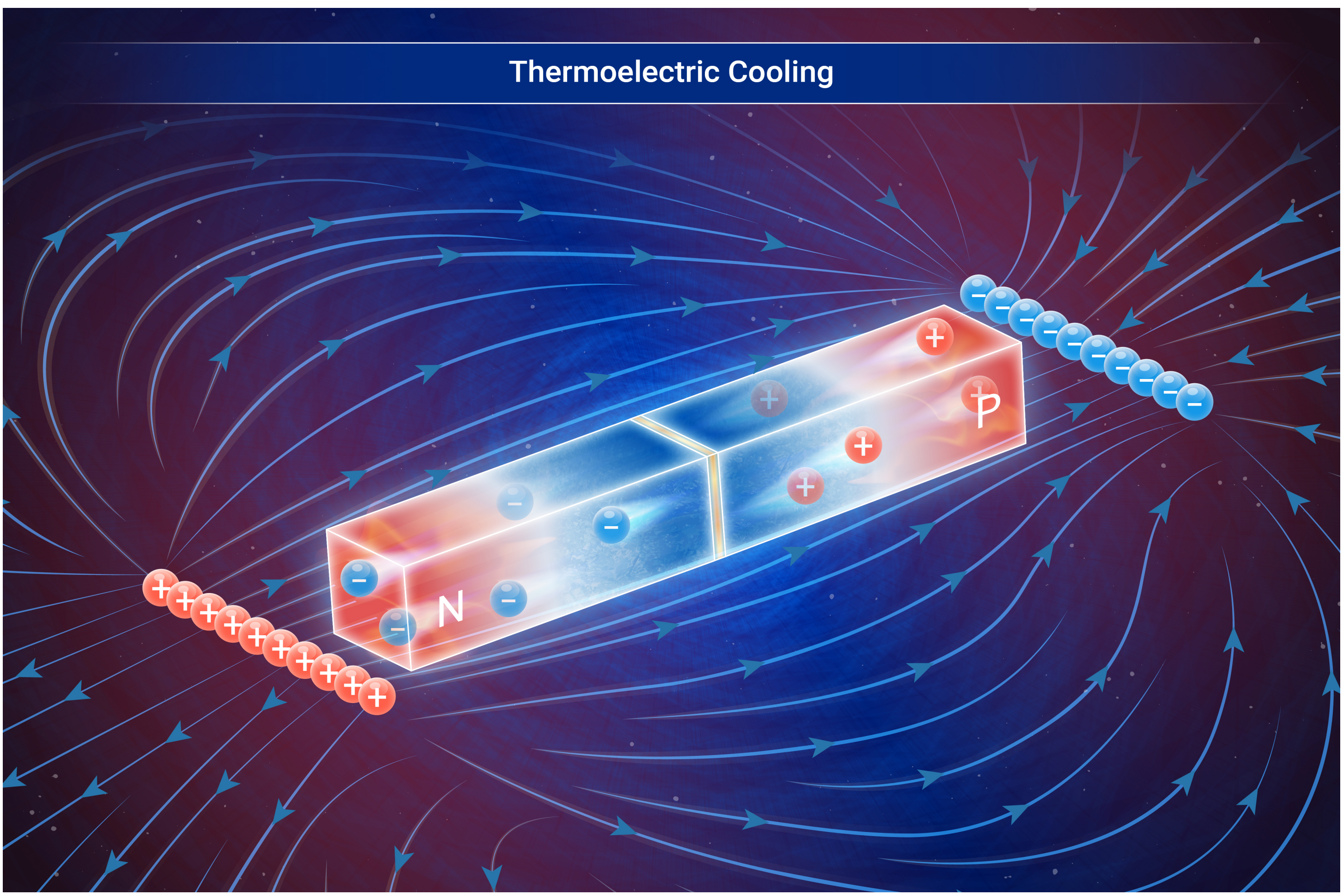

Figure 1. Schematic illustration of the thermoelectric cooling using a pair of n- and p-type semiconductors under the electric field.

Recently, published in volume 6 issue 5 of *The Innovation*, centimeter-sized $Mg_3Bi_{1.497}Sb_{0.5}Te_{0.003}$ single crystals have been synthesized using a slow-cooling method by Ma and colleagues.[3] The elimination of grain boundaries makes the n-type single-crystal $Mg_3Bi_{1.497}Sb_{0.5}Te_{0.003}$ exhibit high electron mobility, contributing to a good TE figure of merit value of ~1.05 at room temperature. This value is comparable to the state-of-the-art n-type $Bi_2Te_{2.7}Se_{0.3}$, making it competitive for near-room-temperature cooling applications. Based on this single crystal and p-type $Bi_{0.5}Sb_{1.5}Te_3$, they assembled a cascade TE module which comprises a hierarchical arrangement of 7 TE pairs in the upper stage and 17 pairs in the lower stage. This double-stage TE module can principally present a more powerful cooling capability since the lower stage can serve as a cold source to make the upper stage cooler. As a result, this cascade TE module shows a maximum cooling temperature difference of ~106.8 K at the hot-side temperature of 350 K. Importantly, the cooling performance does not show an obvious degradation after approximately 2000 cycles. Parallelly, writing in the sister journal of The Innovation, i.e., *The Innovation Materials*, Yang and colleagues demonstrate the assembly of a double-stage TE cooler using polycrystalline n-type $Mg_{3.1}Sb_{0.497}Bi_{1.5}Te_{0.003}$ and p-type $Bi_{0.5}Sb_{1.5}Te_3$, which gives a maximum cooling temperature difference of ~103.2 K at the hot-side temperature of 350 K.[4] Together, these two efforts demonstrate the potential of Bi-rich $Mg_3Sb_{2-x}Bi_x$ as cooling applications in the sub-ambient temperature range.

Previously, single-stage TE modules were commonly assembled to highlight the application potential of $Mg_3Sb_{2-x}Bi_x$ materials[1]. Cascade TE modules can achieve a greater maximum cooling temperature difference, as the lower stage effectively cools the upper stage, enhancing overall performance. However, the fabrication of a high-performance cascade TE module requires optimal structural design, precise assembly processes, and the integration of TE legs with ceramic substrates. For example, the heat flux matching between stages—where the upper stage's thermal output aligns with the lower stage's cooling capacity—is governed by the number of p-n pairs in each stage. Therefore, the numerical simulation using COMSOL Multiphysics was carried out to guide the structural design.[4] Compared to cascade devices, single-stage TE devices feature a more straightforward fabrication process, involving simple assembly of TE legs and ceramic substrates followed by a single reflow soldering for device integration. Cascade TE modules necessitate sequential soldering operations when assembled from individually prepared stages. Although this approach can simplify the assembly procedure, it increases the fabrication complexity due to multiple soldering. Moreover, repetitive reflow soldering induces large thermal stress and the cycled heating during soldering can potentially deteriorate the properties of the TE legs. To resolve this issue, a custom-made fixture for assembling the TE legs and ceramic substrates was developed, enabling a single reflow soldering.[3] This single reflow soldering should be applicable for assembling double-stage TE modules using other TE materials. Moreover, cascade TE modules with multiple stages could also be assembled using single reflow soldering if suitable fixtures are used.

Although the great TE cooling potential of n-type $Mg_3Sb_{2-x}Bi_x$ compounds is demonstrated using both single-stage and cascade TE modules.[1,3,4], the industrial applications of this rising-star TE material still face multiple challenges. In addition to competitive TE performance, an equally compelling advantage lies in the material's cost-efficiency, derived principally from its inexpensive raw constituent elements, particularly Mg. Compared to its competitor, n-type $Bi_2Te_{3-x}Se_x$, in which Te has a much lower abundance in the Earth's crust, the abundance of Mg is several orders of magnitude higher. However, the large-scale applications of this material are hindered by the high reactivity of Mg and the moisture sensitivity of $Mg_3Sb_{2-x}Bi_x$,[5] which could bring a high cost of storage and transportation, as well as security, considering that the fabrication of $Mg_3Sb_{2-x}Bi_x$ ingots generally requires high-temperature melting, mechanical alloying, and vacuum condition. In addition, for Bi_2Te_3-based TE modules, the interfacial barrier layer is generally constructed using the low-cost Ni electroplating technique. Whereas for $Mg_3Sb_{2-x}Bi_x$-based modules, the interfacial barrier layer was fabricated using spark plasma sintering to ensure low electrical resistance and robust mechanical bonding.[3,4] This brings the additional cost of module assembly. How to lower these costs brought by the high reactivity of Mg, chemical instability of $Mg_3Sb_{2-x}Bi_x$, and low-resistance interfacial construction is key for promoting this rising-star material for large-scale industrial application.

Considering that n-type $Mg_3Sb_{2-x}Bi_x$ was discovered less than 10 years ago, while Bi_2Te_3-based alloys have been commercialized for more than 60 years, it cannot be fairer to give more time for this emerging TE system. Additional research efforts on materials and modules can focus on the balance of the "Golden Triangle", i.e., high TE performance, good stability, and low cost.

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DECLARATION OF INTERESTS

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