COMMENTARY

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High thermoelectric performance sheds new light on low-grade waste heat recovery

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Recovering waste heat from fuel energy supply is a haunting challenge for greatly reducing the emissions of greenhouse gas CO_2, and achieving sustainable economy. Importantly, a significant amount of energy is dissipated to environment as low-grade heat (below 250°C), largely produced in transportation and chemical engineering industry. It accounts for ~30% of the total global energy products but is much more difficult to recycle than high-grade heat (Figure 1 A) [1]. So the reuse of low-grade heat is of great importance for the future energy demands and the issue of climate change [2,3]. So far, several technologies have been developed to recover low-grade waste heat, such as organic Rankine cycle, water desalination, piezoelectric, and thermoelectric conversion [4]. Among them thermoelectricity that enables direct and inverse heat-to-electricity conversion is of great interest due to its wide adaptability and long-lasting reliability. However, the low conversion efficiency of thermoelectric power generation limits its potential application in recovering low-grade wasted heat [5,6].

The efficiency of thermoelectric power generation is calculated by the unit-less figure of merit, $zT=\sigma S^2T/\kappa$, where σ, S, κ, and T are the electrical conductivity, Seebeck coefficient, thermal conductivity of the material, and absolute temperature in kelvin, respectively. To improve the performance, one should expect a high power factor (σS^2), a low thermal conductivity, and material stability with temperature. Unfortunately, the above parameters are entangled, so it is very difficult to adjust them independently. Traditional methods to decouple this interplay issue are to introduce nanoscale precipitates and regulate the band structure and the carrier concentration to approach the optimal magnitude at different temperatures but at a limited extent [7,8]. In addition, regular doping strategies rely on accurate design and hardly introduce a new mechanism that can unlock the state-of-the-art thermoelectric materials, such as PbTe.

Now, as published in *Science*, a research team led by Prof. Jiaqing He at Southern University of Science and Technology (SUSTech) in China has significantly improved the thermoelectric performance in p-type PbTe [9]. They proposed a doping strategy by a clever combination of Na, Mg, and Ge to boost the traditional thermoelectric material PbTe. As a result, the record-high zT in PbTe of 2.8, corresponding to ~15.5% efficiency, is reported. In such a strategy, Na and Mg play the role in p-doping and band convergence, respectively, while Ge has a gigantic effect on the thermoelectric performance with a sudden increase in the

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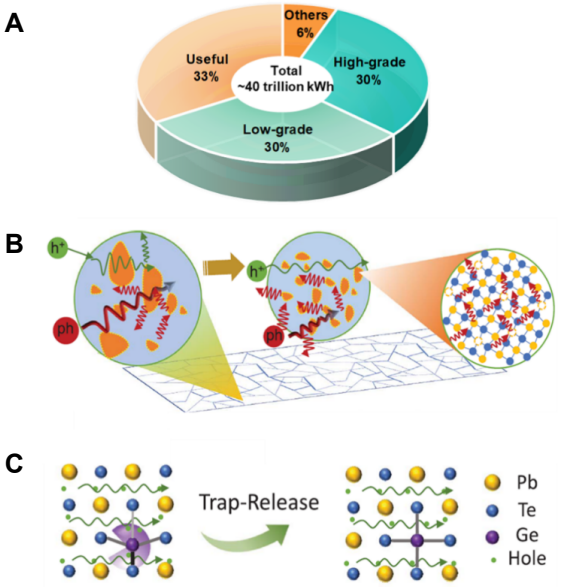

Figure 1 (A) Percentage chart of worldwide energy consumption, in which low-grade waste heat, high-grade waste heat, useful parts, and others account for ~30%, ~30%, ~33% and ~6%, respectively. (B) Schematic illustration of pseudo-nanostructure design in PbTe. (C) Cartoon of structure-dependent hole trap and release. By introducing Na and Ge doping into the PbTe, the size of the pseudo-nanostructure is shrunk, forming a vacancy cluster, which effectively increased the scattering of phonons. Meanwhile, by replacing the Pb with Ge, the carrier is captured at low temperature and released at high temperature, and the carrier concentration can be dynamically controlled. Adapted from Ref. [9]. Reprint with permission from AAAS.

conductivity from 550 to 650 K. Due to the stronger bonding energy between Ge and Te atoms, Ge atoms tend to form a shorter bond length with Te atoms after replacing Pb atoms, which causes Ge atoms to deviate from the center position of the crystal lattice and form an eccentric structure. The eccentric structure tends to redistribute the electron clouds around the Ge, resulting in the formation of many hole trapping centers. Such structural features can trap holes at low temperatures, thereby reducing the carrier concentration. On the other hand, the eccentric Ge returns to the center position at high temperature to release the trapped holes. Consequently, the introduction of lattice distortion can reduce the carrier concentration at low temperature and without affecting the carrier concentration at high temperature. Such that, this strategy enabled the dynamical control of carrier concentration in the whole temperature range (Figure 1 B and C). Since the lattice distortion is also introduced, the regulation of phonon is simultaneously realized. Eventually, He's team achieved the highest peak zT (~2.8 at 850 K) and averaged zT (~1.65 for 300–850 K) among all the present reported p-type PbTe systems. Based on these highest values of zT, they have significantly increased the energy conversion efficiency up to ~15.5%, which has also broken the record in PbTe-based devices [10,11].

To clarify the reason of hole concentration modulation in Na-, Mg-, and Ge-doped PbTe, various characterizations are carried out. Hall measurements show that with increasing the Ge doping the hole concentration initially decreased from 24.2×10^{19} to 5.9×10^{19} cm^{-3}. At low temperatures, the hole concentration exhibits little changes, while at high temperatures, significant increases can be observed, particularly at the temperature range of 550–850 K. A trapped-hole release mechanism based on the off-centered to centered transformation of Ge atoms was thus proposed to explain the significant variation of hole concentration at different temperatures. Electron paramagnetic resonance (EPR) spectroscopy and mid-infrared transient

absorption spectroscopy (MIR-TAS) were conducted to confirm the hole location (trapped holes) at the eccentric Ge. As the temperature increases, the field low-loss electron energy loss spectroscopy (EELS) revealed the transition of the Ge atom from off-centered to centered position, accompanying with the release of holes as verified with density functional theory (DFT) studies.

Ge doping also results in significant reduction in lattice thermal conductivity, consequently reducing the total thermal conductivity by forming pseudo-nano structures. The scanning transmission electron microscopy (STEM) revealed the abundant nanoscale pseudo structures that were coherent with the PbTe matrix with a large number of lattice strains. The pseudo-nano structure effectively scatters phonons. The structural characterization by pair distribution function (PDF) and X-ray absorption fine structure (XAFS) using synchrotron demonstrated the eccentric positioning of Ge and revealed more Pb vacancies generated with Na and Mg doping. The content of Na also has an important effect on the formation of pseudo-nanostructures. The 3 at.% doping of Na results in a more evenly distribution in the PbTe matrix below 1 nm than those with 2 at.% Na. It is also found that Ge doping can reduce the size of Pb vacancy clusters, thereby further reducing the thermal conductivity. These results substantially support for the hole trapping and releasing mechanism, and provide an in-depth explanation of how this mechanism affects the overall thermoelectric properties of PbTe. Furthermore, the authors fabricated a thermoelectric module to prove its applicability. By optimizing the structure of the module design and the choice of materials, they succeeded in achieving a high thermoelectric conversion efficiency of approximately 15.5%, demonstrating good stability.

Prof. He and his team have provided invaluable innovations into the development of high-efficient thermoelectric conversion and made an important step to practical application. The breakthrough that they have achieved depends not only on proposing new doping schemes, manipulating the pseudo-nanostructured precipitates, but on adopting crafted module designs as well. So far, Ge-doping only boosts the p-type PbTe and the current module fabrication has to be paired with n-type Bi_2Te_3. One exciting possibility almost within reach is to focus on unveiling the secret doping methodology for n-type PbTe and tuning the maximum zT at the same temperature range. The research can be guided with deep learning algorithms for better modeling the energy landscape of electrons and phonons, thereby facilitating a more efficient material design. Further breakthroughs are expected to practically pair the n- and p-type PbTe and fully exploit its potential in low-grade waste heat recovery, an important step for lifting the energy issue worldwide.

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Conflict of interest

The authors declare no conflict of interest.

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