Chapter

Optimization of Thermoelectric Properties Based on Rashba Spin Splitting

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Abstract

In recent years, the application of thermoelectricity has become more and more widespread. Thermoelectric materials provide a simple and environmentally friendly solution for the direct conversion of heat to electricity. The development of higher performance thermoelectric materials and their performance optimization have become more important. Generally, to improve the ZT value, electrical conductivity, Seebeck coefficient and thermal conductivity must be globally optimized as a whole object. However, due to the strong coupling among ZT parameters in many cases, it is very challenging to break the bottleneck of ZT optimization currently. Beyond the traditional optimization methods (such as inducing defects, varying temperature), the Rashba effect is expected to effectively increase the $S^2\sigma$ and decrease the κ, thus enhancing thermoelectric performance, which provides a new strategy to develop new-generation thermoelectric materials. Although the Rashba effect has great potential in enhancing thermoelectric performance, the underlying mechanism of Rashba-type thermoelectric materials needs further research. In addition, how to introduce Rashba spin splitting into current thermoelectric materials is also of great significance to the optimization of thermoelectricity.

Keywords: Thermoelectric materials, Rashba spin splitting, spin-orbit coupling, Seebeck coefficient

1. Introduction

Thermoelectric materials can use the Seebeck and Peltier effects to directly convert heat and electricity into each other [1–3], providing a simple and environmentally friendly solution for the direct conversion of heat to electricity, and is expected to play an important role in meeting future energy challenges effect. Thermoelectric equipment can not only directly convert the heat from the sun, radioisotopes, automobiles, industrial sectors and even the human body into electrical energy, but can also implement solid-state heat pumps based on electric drive for distributed refrigeration. In recent years, the application of thermoelectricity has become more and more widespread. The equipment based on thermoelectric materials has the advantages of miniaturization, quiet operation and no emission of greenhouse gases. The development of higher performance thermoelectric materials and their performance optimization have become more important.

The dimensionless thermoelectric figure of merit (*ZT* value) can be used as a key indicator to quantify thermoelectric performance, which is defined as, where *T* is the absolute temperature, *S* is the Seebeck coefficient, σ is the electrical conductivity, and are the electronic and lattice thermal conductivity, respectively. Improving the *ZT* value has always been the main goal of thermoelectric research. Generally, to improve the *ZT* value, electrical conductivity, Seebeck coefficient and thermal conductivity must be globally optimized as a whole object. In order to obtain a higher *ZT*, a high Seebeck coefficient *S*, a high electrical conductivity σ and a low thermal conductivity κ are required. However, these parameters have very strong coupling in many cases, and it is very challenging to increase the *ZT* value of typical thermoelectric materials. At the micro level, the high thermoelectricity of the material comes from the subtle coordination between bond covalent and ionicity, band polymerization and splitting, localization and divergence of electronic states, and the trade-off between carrier mobility and effective mass. Therefore, how to find a balance point, or even dig out a new *ZT* value optimization mechanism from a different perspective, is an important innovation basis for thermoelectric materials.

2. Common *ZT* optimization strategy

As the basic science of thermoelectric matures, the research of thermoelectric materials has also begun to develop rapidly. Among the materials reported with high thermoelectric properties, the *ZT* value of Bi_2Te_3 compound and its alloy form is about 1 at room temperature, which has been regarded as the highest standard of advanced thermoelectric materials in the thermoelectric field [4]. Until 1990, Hicks and Dresselhaus proposed that better thermoelectric performance could be designed through the "size effect", that is, to reduce the size [5, 6]. They found that Bi_2Te_3 with a quantum well (two-dimensional) or nanowire (one-dimensional)

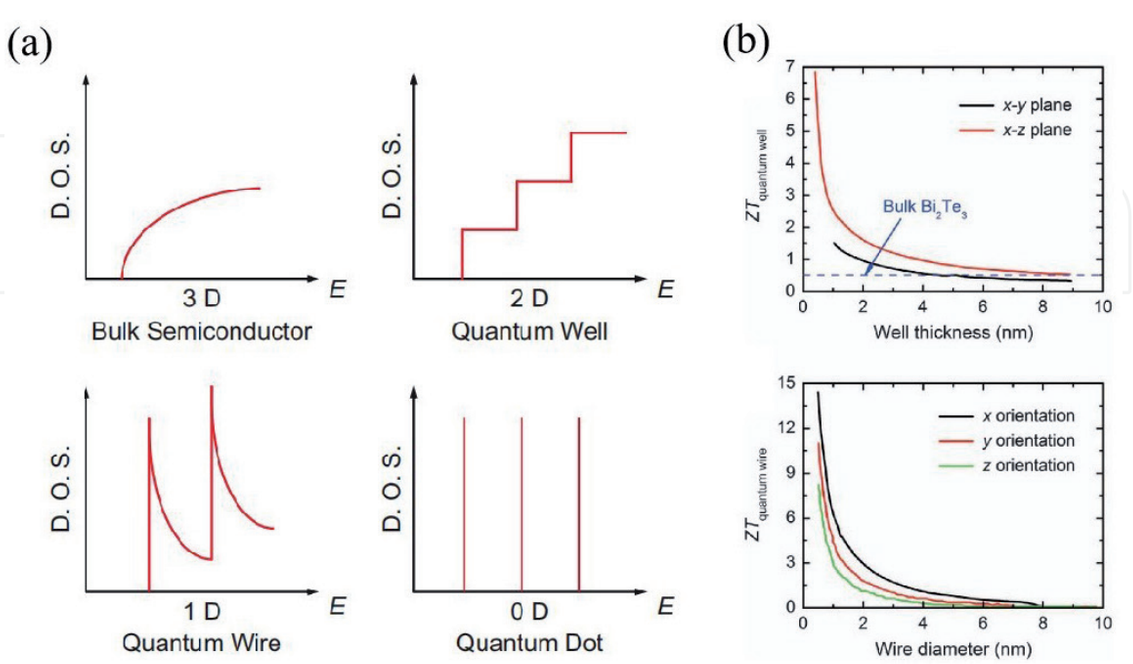

Figure 1.
(a) Schematic diagram of electronic density of states of three-dimensional bulk, two-dimensional quantum scale, one-dimensional nanoribbons, and zero-dimensional quantum dots; (b) the relationship between quantum-scale ZT *and layer thickness; the relationship between* ZT *and diameter of nanowires. The figure is taken from the literature [5–7].*

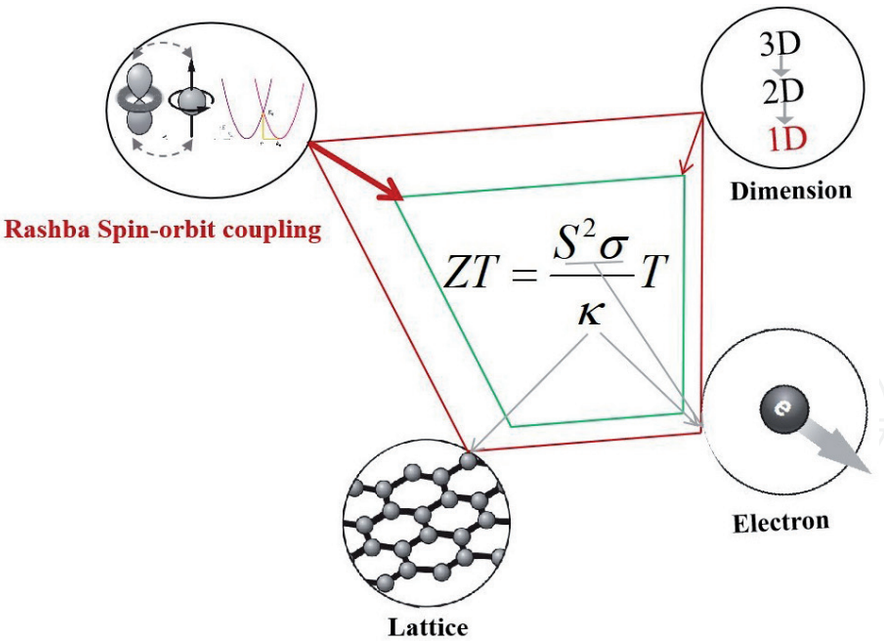

Figure 2.
Thermoelectric parameters can be affected by a combination of dimensions, charge, lattice, and spin-orbit coupling. Among them, the synergy among Seebeck coefficient S*, electrical conductivity* σ*, and thermal conductivity* κ *usually makes them as a whole to increase the* ZT *value, thereby realizing high-efficiency thermoelectric materials. In addition to reducing the size and dimensions, Rashba spin-orbit coupling may be a key direction for the development of next-generation thermoelectric materials.*

structure may have the potential to further increase the *ZT* value, and inferred that the root cause of the improvement in its thermoelectric performance is mainly due to the increased electronic density of states due to the decrease in dimensionality (**Figure 1a**), resulting in an increase in Seebeck coefficient. As shown in **Figure 1b**, the *ZT* value monotonously increases with the decrease of the thickness of the quantum well or the diameter of the quantum wire. Therefore, the use of size effect provides a new strategy for increasing the *ZT* value, because it not only increases the density of electronic states near the Fermi level E_F to increase the Seebeck coefficient, but also increases the phonon at the barrier-well interface. Boundary scattering reduces thermal conductivity.

The synergistic interaction between charge, lattice, and spin-orbit coupling is a necessary factor to further optimize thermoelectric performance (**Figure 2**). In the past three decades, people have discovered a variety of possible mechanisms that may affect transport performance: resonance energy levels, modulation doping, band convergence, classical and quantum size effects, anharmonicity, and spin-related effect, such as Rashba effect, spin Seebeck effect and topological state, etc., have been verified in various materials such as V_2-VI_3 compounds, V-VI group compounds, semi-Heusler alloys, diamond-like structure compounds and silicides. Among them, Rashba spin-orbit coupling and controllable anharmonicity may be the key to the development of next-generation thermoelectric materials.

3. *ZT* optimization based on Rashba spin splitting

3.1 The improved $S^2\sigma$ and reduced κ

Note that in the quantum size effect caused by the reduction of dimensionality, a key idea for optimizing the power factor $S^2\sigma$ is to increase the density of states (Density of States, DOS) near the Fermi level E_F. In the low-dimensional

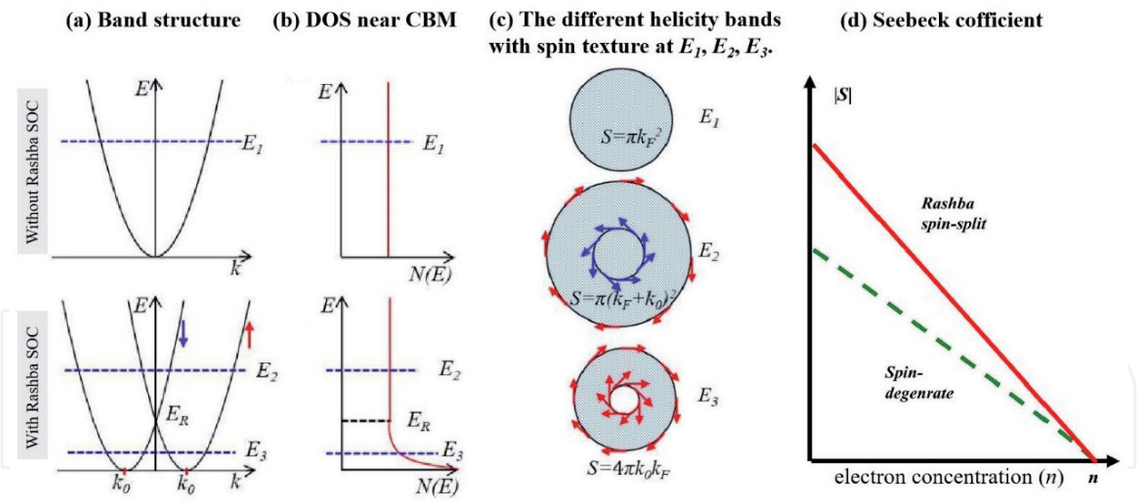

Figure 3.
(a) Rashba SOC leads to the spin splitting of the band structure; (b) the density of states diagram corresponding to figure (a) (near the bottom of the conduction band); (c) the energy levels E_1, E_2, E_3 reflect different spiral bands with spin texture on the Fermi surface. The red arrow represents spin up and the blue arrow represents spin down; (d) the Seebeck coefficient of Rashba spin split system and spin degenerate system varies with electron concentration n. the figure is taken from the literature [8].

Rashba material, DOS produces primitive sharp features near E_F due to spin splitting, which is very beneficial to the electron transport performance [7]. Due to the Rashba effect, the energy bands with different spin directions are split (as shown in **Figure 3a**), the density of states diagram will also show interesting characteristics, that is: when its DOS is located in the low energy region ($E_F < E_R$), it has a sharp peak (**Figure 3b**). The peak value of the low-energy DOS region is closely related to the band splitting amplitude k_0, that is, the larger the k_0, the sharper the DOS peak value. The increase in the density of states will lead to the dominance of ideal spin carriers, that is, a longer carrier lifetime can be maintained at room temperature. Rashba spin splitting can also cause spiral ribbons with different spin textures on the Fermi surface at different energy levels (**Figure 3c**). After considering the spin-orbit coupling (SOC) of Rashba, its power factor $S^2\sigma$ is almost twice that of spin degeneration. This huge enhancement effect is directly related to the special DOS contribution and the longer carrier lifetime caused by Rashba spin splitting. Therefore, when the Rashba SOC is included, the carriers near the band gap have a significant impact on the transmission performance, which plays a key role on obtaining higher $S^2\sigma$ and further optimization of the ZT value.

In addition, the giant Rashba spin splitting in a two-dimensional BiSb monolayer can increase the ZT value by a factor of two at room temperature compared to spin degenerate states [8]. Furthermore, it is confirmed that the Seebeck coefficient in Rashba spin-splitting BiTeX is higher than that in traditional spin-degenerate materials [9, 10], as shown in **Figure 3d**. Xiao et al. also predicted from the theoretical level that the Rashba system will exhibit abnormally enhanced thermoelectric behavior [11]. This is due to the Rashba SOC-induced scission of the density of states and extended carrier lifetime, and due to the relatively high DOS near the Fermi level. A large slope will result in a higher Seebeck coefficient, thereby increasing $S^2\sigma$. The idea that Rashba spin-orbit coupling can increase carrier lifetime has greatly stimulated more attempts in the Rashba system in photovoltaics and thermoelectrics [12]. At the level of phonon transport, Rashba SOC also affects the acoustic and optical branches of lattice vibration. For example, the long-wave optical LO mode will be strongly suppressed by the Rashba splitting energy band, resulting in a longer relaxation time [8, 12]. The

intrinsic electric field in the Rashba system can also introduce non-intermittent phonons, so its lower thermal conductivity is also one of the main reasons for the high thermoelectric performance.

3.2 The link between Rashba and thermoelectric

Actually, the Rashba effect has attracted considerable attention in the fields of spintronics, ferroelectrics, and superconducting electronics [13, 14], Rashba spin-split generally originated from the SOC and inversion asymmetry, the SOC gives rise to a perturbing operator equal to $\lambda L \cdot S$ for electrons, where L and S are the total orbital and spin angular momenta, and λ the coupling constant [15]. The spin-orbital Hamiltonian has a Bychkov-Rashba form $H_{SOC} = \alpha_R(\sigma \times k) \cdot z$, where α_R is the Rashba parameter and represents the strength of the Rashba effect ($\alpha_R \propto \lambda E_z$), σ is the Pauli spin matrices, k is momentum, and z is the electric field direction along high-symmetry axis [16]. The bulk BiTeI with a giant Rashba effect has been confirmed by the angle-resolved photoemission spectroscopy and first-principles calculations [17, 18]. Interestingly, it is found that the heat-electricity converting thermoelectric effects are strongly influenced by the band structures near the Fermi level in BiTeI; thus the Rashba effect may also offer unusual opportunities for thermoelectrics [9].

As we known, thermoelectric materials are commonly composed of heavy elements with strong SOC [19]. In view of this, the spin-enabled mechanisms including the Rashba effect [20] and the spin Seebeck effect [21] offer new channels to manipulate and further optimize thermoelectric properties [22]. However, the spin Seebeck effect is currently limited at cryogenic temperatures. By contrast, the Rashba effect is promising to facilitate performance enhancement in broad thermoelectric materials. It was reported that Rashba spin splitting yielded a unique constant DOS near the E_F, which resulted in high S. On the other hand, the internal electric field induced by Rashba effect reinforced anharmonicity and introduced soft bonds reduced the κ_l [23]. Actually, the Rashba effect is likely to enlarge the band degeneracy for fulfilling a high-quality factor. In the non-centro symmetric materials, the strong SOC induces the Rashba effect where the original single band edge splits into two band extrema with energy shift and momentum offset [24]. Such spin splitting band provides a new way to engineer the band structure and enlarge the band degeneracy for enhancing thermoelectric performance. Thermoelectric materials with a phase transition may exhibit the Rashba effect due to the broken inversion symmetry. For instance, GeTe undergoes a phase transition from rhombohedral to cubic structures near 700 K and shows the giant Rashba effect [25, 26]. Therefore, the cubic-to-rhombohedral phase transition of GeTe provides a unique method to produce the Rashba effect in thermoelectric materials.

Recent classical strategies of quantum confinement effect [27], resonant level [28], band convergence [29], liquid-like ions [30], entropy engineering [31], anharmonicity [32], and modulation doping [33] have enhanced ZT in many thermoelectric material systems. Albeit the advances in thermoelectric theories, there's no doubt that the ZT enhancement have already reached a bottleneck. The Rashba effect, spin-dependent band splitting, has been proved to be a new path to enhance thermoelectric performance [34]. In detail, Hong et al. demonstrated a strong Rashba spin splitting in Sn-doped GeTe and results in the band convergence experimentally, so that $S^2\sigma$ is significantly enhanced. Additionally, the co-existence of stacking faults with other multiscale nanostructures yields an ultra-low thermal conductivity, thus achieved a high ZT over 2.2 [34]. A link between the Rashba effect and the enhancement of

thermoelectric is well established. The demonstrated new strategy of exploring the Rashba effect to increase the band degeneracy for enhancing thermoelectric performance can provide guidelines to develop new-generation thermoelectric materials.

4. Conclusion

Although the Rashba effect has great potential in enhancing thermoelectric performance, the influence of Rashba spin-orbit coupling on various thermoelectric parameters, thermoelectric optimization rule and the exact mechanism are still to be explored to a large extent. In particular, the thermoelectric performance and the underlying mechanism of Rashba-type thermoelectric materials need further research, or how to introduce Rashba spin splitting into current excellent thermoelectric materials is also of great significance to the optimization of thermoelectricity.

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References

[1] DiSalvo, F. J. Thermoelectric Cooling and Power Generation. Science **1999**, *285* (5428), 703-706. https://doi.org/10.1126/science.285.5428.703.

[2] Bell, L. E. Cooling, Heating, Generating Power, and Recovering Waste Heat with Thermoelectric Systems. Science **2008**, *321* (5895), 1457-1461. https://doi.org/10.1126/science.1158899.

[3] Snyder, G. J.; Toberer, E. S. Complex Thermoelectric Materials. In *Materials for Sustainable Energy*; Co-Published with Macmillan Publishers Ltd, UK, 2010; pp 101-110. https://doi.org/10.1142/9789814317665_0016.

[4] D. M. Rowe. *CRC Handbook of Thermoelectrics*; CRC press.

[5] Hicks, L. D.; Dresselhaus, M. S. Thermoelectric Figure of Merit of a One-Dimensional Conductor. Phys. Rev. B **1993**, *47* (24), 16631-16634. https://doi.org/10.1103/PhysRevB.47.16631.

[6] Hicks, L. D.; Dresselhaus, M. S. Effect of Quantum-Well Structures on the Thermoelectric Figure of Merit. Phys. Rev. B **1993**, *47* (19), 12727-12731. https://doi.org/10.1103/PhysRevB.47.12727.

[7] Dresselhaus, M. S.; Chen, G.; Tang, M. Y.; Yang, R. G.; Lee, H.; Wang, D. Z.; Ren, Z. F.; Fleurial, J.-P.; Gogna, P. New Directions for Low-Dimensional Thermoelectric Materials. Adv. Mater. **2007**, *19* (8), 1043-1053. https://doi.org/10.1002/adma.200600527.

[8] Yuan, J.; Cai, Y.; Shen, L.; Xiao, Y.; Ren, J.-C.; Wang, A.; Feng, Y. P.; Yan, X. One-Dimensional Thermoelectrics Induced by Rashba Spin-Orbit Coupling in Two-Dimensional BiSb Monolayer. Nano Energy **2018**, *52*, 163-170. https://doi.org/10.1016/j.nanoen.2018.07.041.

[9] Wu, L.; Yang, J.; Wang, S.; Wei, P.; Yang, J.; Zhang, W.; Chen, L. Two-Dimensional Thermoelectrics with Rashba Spin-Split Bands in Bulk BiTeI. Phys. Rev. B **2014**, *90* (19), 195210. https://doi.org/10.1103/PhysRevB.90.195210.

[10] Wu, L.; Yang, J.; Chi, M.; Wang, S.; Wei, P.; Zhang, W.; Chen, L.; Yang, J. Enhanced Thermoelectric Performance in Cu-Intercalated BiTeI by Compensation Weakening Induced Mobility Improvement. Sci. Rep. **2015**, *5* (1), 14319. https://doi.org/10.1038/srep14319.

[11] Xiao, C.; Li, D.; Ma, Z. Unconventional Thermoelectric Behaviors and Enhancement of Figure of Merit in Rashba Spintronic Systems. Phys. Rev. B **2016**, *93* (7), 075150. https://doi.org/10.1103/PhysRevB.93.075150.

[12] Zheng, F.; Tan, L. Z.; Liu, S.; Rappe, A. M. Rashba Spin–Orbit Coupling Enhanced Carrier Lifetime in CH3NH3PbI3. Nano Lett. **2015**, *15* (12), 7794-7800. https://doi.org/10.1021/acs.nanolett.5b01854.

[13] Mathias, S.; Ruffing, A.; Deicke, F.; Wiesenmayer, M.; Sakar, I.; Bihlmayer, G.; Chulkov, E. V.; Koroteev, Yu. M.; Echenique, P. M.; Bauer, M.; Aeschlimann, M. Quantum-Well-Induced Giant Spin-Orbit Splitting. Phys. Rev. Lett. **2010**, *104* (6), 066802. https://doi.org/10.1103/PhysRevLett.104.066802.

[14] Cappelluti, E.; Grimaldi, C.; Marsiglio, F. Topological Change of the Fermi Surface in Low-Density Rashba Gases: Application to Superconductivity. Phys. Rev. Lett. **2007**, *98* (16), 167002. https://doi.org/10.1103/PhysRevLett.98.167002.

[15] Ziman, J. M. *Principle of the Theory of Solid*; Cambridge University Press: London, 1972.

[16] Bychkov, Yu. A.; Rashba, É. I. Properties of a 2D Electron Gas with Lifted Spectral Degeneracy. *Sov.* J. Exp. Theor. Phys. Lett. **1984**, *39*, 78.

[17] Ishizaka, K.; Bahramy, M. S.; Murakawa, H.; Sakano, M.; Shimojima, T.; Sonobe, T.; Koizumi, K.; Shin, S.; Miyahara, H.; Kimura, A.; Miyamoto, K.; Okuda, T.; Namatame, H.; Taniguchi, M.; Arita, R.; Nagaosa, N.; Kobayashi, K.; Murakami, Y.; Kumai, R.; Kaneko, Y.; Onose, Y.; Tokura, Y. Giant Rashba-Type Spin Splitting in Bulk BiTeI. Nat. Mater. **2011**, *10* (7), 521-526. https://doi.org/10.1038/nmat3051.

[18] Bahramy, M. S.; Arita, R.; Nagaosa, N. Origin of Giant Bulk Rashba Splitting: Application to BiTeI. Phys. Rev. B **2011**, *84* (4), 041202. https://doi.org/10.1103/PhysRevB.84.041202.

[19] Müchler, L.; Casper, F.; Yan, B.; Chadov, S.; Felser, C. Topological Insulators and Thermoelectric Materials. *Phys. Status Solidi RRL – Rapid* Res. Lett. **2013**, *7* (1-2), 91-100. https://doi.org/10.1002/pssr.201206411.

[20] Zhang, X.; Liu, Q.; Luo, J.-W.; Freeman, A. J.; Zunger, A. Hidden Spin Polarization in Inversion-Symmetric Bulk Crystals. Nat. Phys. **2014**, *10* (5), 387-393. https://doi.org/10.1038/nphys2933.

[21] Uchida, K.; Takahashi, S.; Harii, K.; Ieda, J.; Koshibae, W.; Ando, K.; Maekawa, S.; Saitoh, E. Observation of the Spin Seebeck Effect. Nature **2008**, *455* (7214), 778-781. https://doi.org/10.1038/nature07321.

[22] He, J.; Tritt, T. M. Advances in Thermoelectric Materials Research: Looking Back and Moving Forward. Science **2017**, *357* (6358). https://doi.org/10.1126/science.aak9997.

[23] Wu, L.; Yang, J.; Wang, S.; Wei, P.; Yang, J.; Zhang, W.; Chen, L. Two-Dimensional Thermoelectrics with Rashba Spin-Split Bands in Bulk BiTeI. Phys. Rev. B **2014**, *90* (19), 195210. https://doi.org/10.1103/PhysRevB.90.195210.

[24] Manchon, A.; Koo, H. C.; Nitta, J.; Frolov, S. M.; Duine, R. A. New Perspectives for Rashba Spin–Orbit Coupling. Nat. Mater. **2015**, *14* (9), 871-882. https://doi.org/10.1038/nmat4360.

[25] Zhang, X.; Bu, Z.; Lin, S.; Chen, Z.; Li, W.; Pei, Y. GeTe Thermoelectrics. Joule **2020**, *4* (5), 986-1003. https://doi.org/10.1016/j.joule.2020.03.004.

[26] Fahrnbauer, F.; Souchay, D.; Wagner, G.; Oeckler, O. High Thermoelectric Figure of Merit Values of Germanium Antimony Tellurides with Kinetically Stable Cobalt Germanide Precipitates. J. Am. Chem. Soc. **2015**, *137* (39), 12633-12638. https://doi.org/10.1021/jacs.5b07856.

[27] Zhu, T.; Liu, Y.; Fu, C.; Heremans, J. P.; Snyder, J. G.; Zhao, X. Compromise and Synergy in High-Efficiency Thermoelectric Materials. Adv. Mater. **2017**, *29* (14), 1605884. https://doi.org/10.1002/adma.201605884.

[28] Heremans, J. P.; Jovovic, V.; Toberer, E. S.; Saramat, A.; Kurosaki, K.; Charoenphakdee, A.; Yamanaka, S.; Snyder, G. J. Enhancement of Thermoelectric Efficiency in PbTe by Distortion of the Electronic Density of States. Science **2008**, *321* (5888), 554-557. https://doi.org/10.1126/science.1159725.

[29] Pei, Y.; Shi, X.; LaLonde, A.; Wang, H.; Chen, L.; Snyder, G. J. Convergence of Electronic Bands for High Performance Bulk Thermoelectrics. Nature **2011**, *473* (7345), 66-69. https://doi.org/10.1038/nature09996.

[30] Liu, H.; Shi, X.; Xu, F.; Zhang, L.; Zhang, W.; Chen, L.; Li, Q.; Uher, C.;

Day, T.; Snyder, G. J. Copper Ion Liquid-like Thermoelectrics. Nat. Mater. **2012**, *11* (5), 422-425. https://doi.org/10.1038/nmat3273.

[31] Liu, R.; Chen, H.; Zhao, K.; Qin, Y.; Jiang, B.; Zhang, T.; Sha, G.; Shi, X.; Uher, C.; Zhang, W.; Chen, L. Entropy as a Gene-Like Performance Indicator Promoting Thermoelectric Materials. Adv. Mater. **2017**, *29* (38), 1702712. https://doi.org/10.1002/adma.201702712.

[32] Zhao, L.-D.; Lo, S.-H.; Zhang, Y.; Sun, H.; Tan, G.; Uher, C.; Wolverton, C.; Dravid, V. P.; Kanatzidis, M. G. Ultralow Thermal Conductivity and High Thermoelectric Figure of Merit in SnSe Crystals. Nature **2014**, *508* (7496), 373-377. https://doi.org/10.1038/nature13184.

[33] Pei, Y.-L.; Wu, H.; Wu, D.; Zheng, F.; He, J. High Thermoelectric Performance Realized in a BiCuSeO System by Improving Carrier Mobility through 3D Modulation Doping. J. Am. Chem. Soc. **2014**, *136* (39), 13902-13908. https://doi.org/10.1021/ja507945h.

[34] Hong, M.; Lyv, W.; Li, M.; Xu, S.; Sun, Q.; Zou, J.; Chen, Z.-G. Rashba Effect Maximizes Thermoelectric Performance of GeTe Derivatives. Joule **2020**, *4* (9), 2030-2043. https://doi.org/10.1016/j.joule.2020.07.021.