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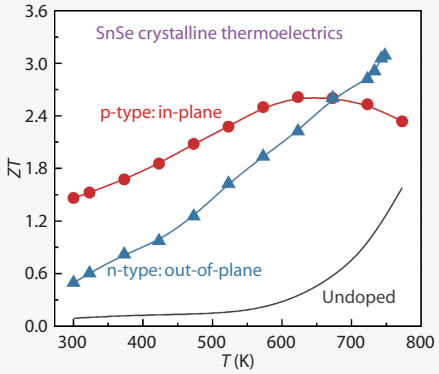
PERSPECTIVE

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SnSe crystalline thermoelectrics

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Thermoelectric materials are increasingly crucial in addressing energy challenges for enabling conversion between heat and electricity. Crystalline tin selenide (SnSe) has gained significant attention since 2014 when its high-temperature thermoelectric performance was first reported. Based on unique characteristics in phonon and electron transports, numerous investigations have been conducted to promote the development of SnSe crystals for low- to mid-temperature waste recovery and electronic cooling applications. Herein, we concisely summarize the significant advancements for SnSe crystalline thermoelectrics, covering material performance optimization and full-scale thermoelectric device development. We then emphasize that the multiple valence bands and high in-plane carrier mobility promote high-performance p-type materials. Additionally, we highlight the critical role of three-dimensional (3D) charge and two-dimensional (2D) phonon transports for promising n-type out-of-plane conduction. Finally, personal insights into future research directions of enhancing performance of SnSe materials and devices are proposed, with the goal of advancing their practical applications.



The rising requirements for sustainable energy solutions have brought increased attention to new technologies for energy conversion, particularly in the field of thermoelectric (TE) technology, which plays a critical role in energy conversion between heat and electricity.[1] TE technology not only facilitates energy recovery, thus enhancing the efficiency of existing energy systems by utilizing waste heat, but also offers a promising alternative to traditional compression refrigeration technology, reducing environmental pollution through solid-state cooling.[2, 3] However, the large-scale implementations for TE materials are hindered due to its low efficiency, primarily determined by the dimensionless figure of merit ZT value, defined as $ZT = (S^2\sigma)T/\kappa$, in which S, σ, T, and κ represent the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively.[4-6]

The interdependence between electrical transports (power factor, $PF = S^2\sigma$) and thermal transports (κ, comprising lattice thermal conductivity (κ_{lat}) and electronic thermal conductivity (κ_{ele})) makes it challenging to independently optimize each aspect to achieve overall enhancement in TE performance.[7, 8] Therefore, it becomes crucial to seek a synergistic approach for coordinating the contradiction between the competing electrical and thermal transports.[9] Over decades of research, various strategies have been established, including tuning carrier concentration,[10, 11] optimizing carrier mobility,[12, 13] engineering electronic band structures,[14-16] constructing microstructure at different scales,[17-19] discovering new systems with intrinsic low thermal transport,[20] etc. Resultantly, TE systems with impressive performance have been developed, such as Bi_2Te_3 and $Mg_3(Bi, Sb)_2$ for room-temperature TE cooling and low-grade heat harvesting,[21-24] lead and tin chalcogenides for mid-temperature power generation,[18, 25-28] and SiGe,[29] Cu_2Se,[30] and half-Heusler alloys[31] for high-temperature applications. In addition to the above bulk thermoelectrics, TE technology has critical application scenarios to produce wearable electronics by utilizing flexible or organic thermoelectrics.[32-34] These achievements have extended the application of TE materials and technology across a wide range of temperatures and diverse fields.

Recently, the non-toxic, stable, and cheap crystalline SnSe thermoelectrics have been regarded as prominent research focuses, demonstrating exceptional potential not only for waste-heat power generation, but also for electronic cooling.[35-40] Initially, SnSe was primarily considered as an ideal material for solar photovoltaic applications, rather than a potential TE material due to its relatively wide bandgap and extremely low carrier concentration (~10^{17} cm^{-3}).[41] However, in 2014, Zhao *et al.* discovered the efficient high-temperature TE performance of SnSe, with robust bonding anharmonicity and ultralow thermal conductivity, attributed to its complex

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layered crystal structure.[35] Thereafter, significant advancements have been realized to optimize the in-plane properties of p-type crystalline SnSe through leveraging complex electronic band structure,[36] promoting multiband synglisis (Synglisis, a convergence of energies and momentum in the bands, further maximizes thermoelectric performance. This is the distinguish from the generally used "band convergence" in TE research which involves convergence in energy but not momentum),[38] and adopting lattice plainification strategy,[40] as shown in Fig. 1. Meanwhile, n-type high-performance out-of-plane SnSe crystals have been achieved through establishing 3D charge and 2D phonon transports,[37] as well as manipulating layered phonon-electron decoupling[39] as Fig. 1 depicts. Gradually, both p-type and n-type SnSe were developed with ultrahigh TE performance over wide temperature ranges, with average ZT (ZT_{ave}) values substantially surpassing 1.0 among 300 to 773 K, demonstrating great potential of SnSe crystals for mid-temperature applications.

Moreover, the thermoelectric transport properties of p-type SnSe crystals, particularly at ambient temperature, have been significantly enhanced. The achieved ZT values at 300 K have progressively exceeded 1.0,[38, 40, 42] approaching and even surpassing those of the commercial Bi_2Te_3.[21] This promising development highlights the potential of p-type SnSe crystals for near-room temperature TE cooling applications, which may help overcome the challenges associated with existing Bi_2Te_3-based alloys, including limited material properties, extreme scarcity of Te reserves, and inadequate processability.[40] Building upon these advancements in material properties, researchers have also conducted extensive investigations into full-scale TE devices based on SnSe crystals, leading to promising outcomes in both power generation efficiency and cooling performance.[38, 40, 42] These achievements further propel the practical applications of thermoelectrics in power generation and solid-state cooling.

In this perspective, the concise and systematic outlines on significant research progress in SnSe crystalline thermoelectrics are proposed, with a particular focus on studies conducted within our group, as illustrated in Fig. 1. We cover various aspects, including the investigation of undoped SnSe, which exhibits intrinsic low thermal conductivity attributed to strong anharmonicity. Additionally, we delve into the studies on p-type SnSe that demonstrates high-ranged TE performance along the in-plane direction resulting from its complicated valence band structure, multiband synglisis, and the utilization of lattice plainification strategy, and the studies on the comparable out-of-plane performance for n-type SnSe achieved through 3D charge-2D phonon transports and layered phonon-electron decoupling. The ongoing efforts towards developing full-scale TE devices composed of SnSe crystals are also presented. Lastly, we offer personal insights and perspectives on future directions of enhancing the performance of SnSe crystalline materials and devices, as well as promoting their practical applications. These outlooks might provide guidance for the future research and potential practical applications of the SnSe system.

Undoped SnSe: Anharmonicity

As a traditional semiconductor, SnSe possesses a bandgap higher than 0.85 eV and exhibits excellent light-absorption characteristics, making it a promising candidate in photovoltaic research.[43, 44] Undoped SnSe was initially considered unsuitable for TE applications due to its poor electrical transport properties, with the inferior hole carrier concentration lower than 10^{18} cm^{-3} and electrical conductivity below 10^{-1} S cm^{-1} at 300 K.[41] This concept changed in 2014 when researchers discovered that undoped SnSe crystals display ultralow thermal conductivity resulting from strong anharmonic bonding.[35] Combined with admirable in-plane carrier mobility, the remarkable ZT_{max} ~2.6 in the b-axis direction at 923 K was achieved,[35] as shown in Fig. 1a. This breakthrough caused a significant stir in thermoelectric community and sparked the increasing interest in exploring promising TE performance of

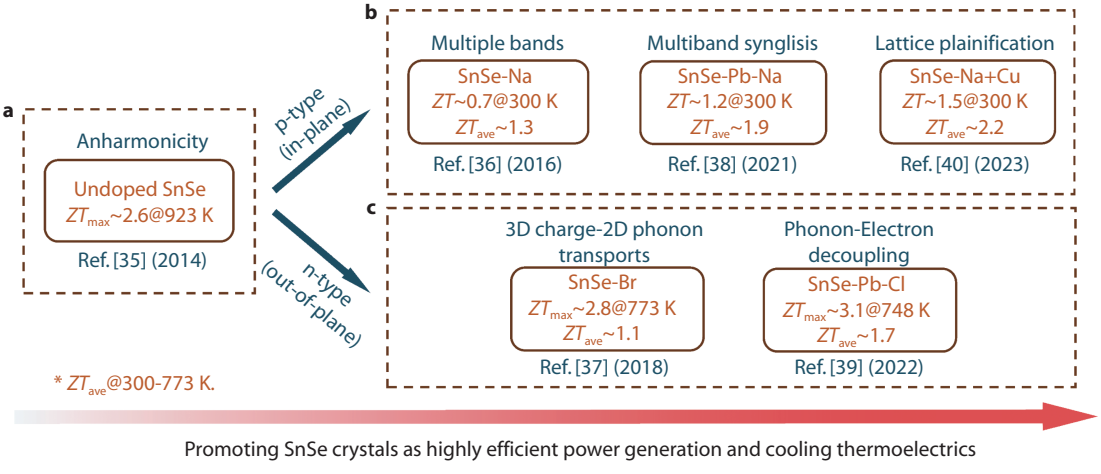


Fig. 1 Timeline of the significant achievements for SnSe crystalline thermoelectrics. **a** Undoped SnSe exhibits exceptional ZT_{max} ~2.6, originating from extremely low thermal conductivity and strong anharmonicity.[35] **b** p-type SnSe crystals with continuous achievements on both room-temperature ZT and ZT_{ave} along the in-plane direction through the utilization of multiple valence bands transport,[36] promotion of multiband synglisis,[38] and implementation of lattice plainification strategy,[40] respectively. **c** n-type SnSe crystals with continuous achievements on both ZT_{max} and ZT_{ave} in the out-of-plane direction by utilizing 3D charge and 2D phonon transports,[37] and manipulating layered phonon-electron decoupling,[39] respectively.

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crystalline SnSe.

Subsequent experimental and theoretical investigations of the thermal transport performance in SnSe elucidated the origin of its strong anharmonicity.[45] Theoretical calculations of phonon and Grüneisen dispersions revealed that the phonon dispersion is significantly softened along all crystallographic directions, leading to large Grüneisen parameters and strong phonon anharmonicity.[35] Additionally, analysis on the unique crystal structure of SnSe, characterized by distorted $SnSe_7$ polyhedron and jagged *b*-*c* plane, unveiled that the soft lattice and weak interlayer bonding contributed to the strong anharmonicity.[35] Inelastic neutron scattering (INS) experiments further confirmed this strong anharmonicity.[46] Qualitative analysis revealed that this anharmonicity originated from resonant bonding caused by the *p* orbitals of Se atoms, which coupled with 5*s* orbitals of Sn, weakening the coordination of $5s^2$ lone-pair electrons in Sn^{2+}. The dynamic deformation of the coordination polyhedron of local Sn further contributed to lattice softening and destabilization.[46] In essence, the unique layered crystal structure results in lattice instability and soft bonding of SnSe, thus causing strong anharmonicity as well as extremely low thermal conductivity.

While lattice instability and strong anharmonicity are the inherent mechanisms resulting in the ultralow thermal conductivity in SnSe, external factors such as stoichiometric ratio, internal microcracks between cleavage planes, and oxidation could also influence its thermal transport properties.[45, 47] To summarize, undoped crystalline SnSe has demonstrated great application prospects in thermoelectric field, and the most fundamental origin of its efficient TE performance is the intrinsic low thermal conductivity caused by the unique physical and chemical properties, layered crystal structure and strong anharmonicity.

P-Type SnSe: In-Plane Direction

As mentioned above, undoped SnSe crystals exhibit remarkable TE performance and peak *ZT* values due to their extremely low thermal conductivity. However, this exceptional performance is limited to a narrow temperature range, with the in-plane and out-of-plane ZT_{ave} values among 300 to 773 K only reaching ~0.4 and 0.1, respectively,[35] as depicted in Fig. 2. However, the practical application of TE technology requires promising material performance across wide temperature ranges. Therefore, optimizing the wide-range TE performance is crucial for further advancements in SnSe crystalline thermoelectrics. Theoretical studies have revealed that SnSe, as a simple compound, possessed a complex electronic band structure, and the boosted electrical performance was expected to realize when multiple bands participated into carrier transport.[36] Combined with intrinsic low thermal transport, significant improvements could be achieved in wide-range TE performance of SnSe.

In experimental investigations, researchers initially focused on tuning the carrier concentration by selectively doping Sn with typically Li, Na, K, and Ag, to introduce more hole carriers, among which Na doping exhibited optimal efficiency in SnSe.[36, 48, 49] Results demonstrated an enhanced hole carrier concentration of ~4×10^{19} cm^{-3}, leading to the deepening of Fermi level and activation of more valence bands for carrier

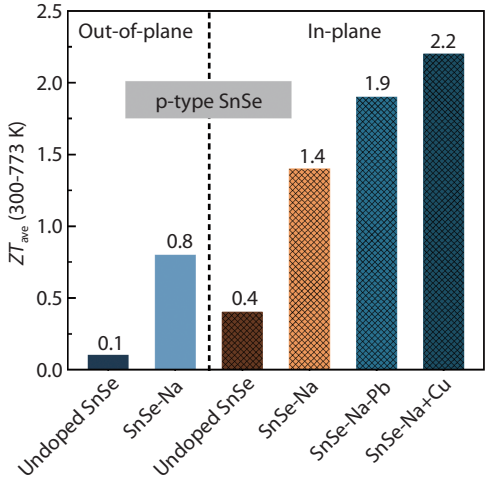


Fig. 2 ZT_{ave} (300-773 K) of typical p-type crystalline SnSe samples along out-of-plane and in-plane directions.[35, 36, 38, 40]

transport.[36] The resultant synergistic effect of enlarged band effective mass and maintained high in-plane carrier mobility facilitated an obvious improvement in *PF* of p-type SnSe crystals across the wide temperature range. Consequently, overall *ZT* of ~0.7 to 2.0 from 300 K to 773 K was realized, with an extraordinary ZT_{ave} of ~1.4 along *b*-axis direction,[36] as shown in Fig. 1b and Fig. 2. These findings greatly promote the potential utilization of p-type SnSe crystals for mid-temperature power generation.

Building upon effective hole doping, the wide-range TE properties for p-type crystalline SnSe have been progressively improved via increasing carrier mobility by modifying crystal structure with Te alloying,[50] and through enhancing the effective mass by producing extrinsic vacancies,[51] respectively. Additionally, researchers focused on the complex valence band structure and its evolution behavior with temperature in SnSe, to increase the weighted mobility μ_W, a comprehensive parameter accounting for both carrier mobility and effective mass.[52, 53] Resultantly, the multiband synglisis at momentum and energy spaces in p-type SnSe were proposed and effectively facilitated by Pb alloying, leading to significantly enhancements in the *PF* and *ZT* values across a wide temperature range, with the peak room-temperature *ZT* approaching ~1.2 and ZT_{ave} (300-773 K) ~1.9,[38] as shown in Fig. 1b and Fig. 2. Based on the optimized material properties, researchers constructed a full-scale TE device based on p-type SnSe crystals coupled with n-type commercial Bi_2Te_3, exhibiting a considerable power generation efficiency ~4.4% at the temperature difference ΔT ~210 K, along with a maximum cooling ΔT_{max} ~45.7 K at ambient temperature.[38] Expanding upon Pb alloying, further enhancements in the conversion efficiency and cooling performance were achieved through dual modulation of crystal and electronic band structures through Sr alloying. These results not only underscore the promising potential of wide-bandgap SnSe crystals for power generation but also confirm their applicability for TE cooling.[42]

For SnSe thermoelectrics, both undoped and doped crystals exhibit numerous non-stoichiometric defects that strongly hinder carrier transport, particularly in the case of Sn

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vacancies in p-type SnSe.[54, 55] Researchers have emphasized the criticality of enhancing carrier mobility in the optimization of room-temperature TE performance through manipulating the intrinsic defects.[13] Motivated by the strategy of compositional plainification for investigating structural alloys,[56] the lattice plainification strategy has been proposed for TE functional materials, by fixing the intrinsic defects in materials, thereby facilitating carrier transport,[40, 57] as schematically shown in Fig. 3. For p-type SnSe, the introduction of Cu was observed to compensate intrinsic Sn vacancies and weaken defects scattering, favoring a substantial increase of carrier mobility.[40] Moreover, the additional Cu atoms also acted as hole dopants by substituting Sn in the lattice, which effectively promoted the multiband synglisis, leading to a substantial enhancement of effective mass as well as carrier mobility. Consequently, remarkable room-temperature *PF* of approximately 100 μW cm^{-1} K^{-2} was achieved, alongside the room-temperature *ZT* ~1.5 and ZT_{ave} (300-773 K) ~2.2, as depicted in Fig. 1b and Fig. 2. In addition to performance enhancement of materials, the interfacial structure of TE devices was carefully designed to reduce contact resistance, resulting in excellent device performance with an exceptional power generation efficiency ~12.2% at the temperature difference ΔT ~300 K, along with the promising cooling ΔT_{max} ~61.2 K near ambient temperature.[40]

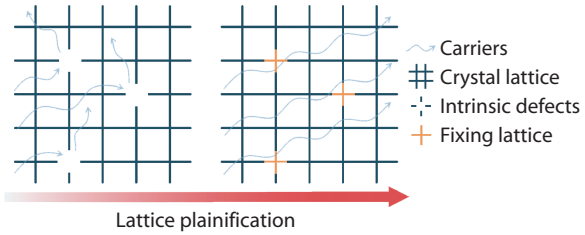


Fig. 3 Schematic of the Lattice Plainification Strategy. The intrinsic defects in materials strongly scatter carriers and impede carrier transport. Lattice plainification by fixing lattice defects could improve carrier mobility and electrical properties, contributing to high-ranged TE performance especially near room temperature.[40, 57]

It is worth noting that the experimental power generation efficiency and cooling performance attained in current devices still fall short of 80% of the theoretical values,[40] which is mainly attributed to the relatively high contact resistance and the absence of geometric design in crystalline SnSe-based TE devices. Given the unique orientation and structure of crystalline materials, achieving activation and close contact between TE elements and barrier layers poses a technical challenge. Moreover, future electronic devices are trending towards higher integration and miniaturization, which presents an additional obstacle for the processing of SnSe crystals and the maintenance of performance after miniaturization.

N-Type SnSe: Out-of-Plane Direction

Significant advancements have been achieved in research on p-type SnSe crystals, as discussed above. However, high-efficiency TE devices require suitable and compatible p-type and n-type materials. Therefore, investigating highly effective n-type SnSe is crucial. Nevertheless, the studies on n-type crystalline SnSe are not merely a replication of its p-type counterpart. Despite sharing the same crystal structure, n-type SnSe possesses distinct conduction band structures, resulting in completely different transport properties.[36, 58] After researchers have developed p-type SnSe crystals with ultrahigh in-plane performance, the different optimal direction for n-type SnSe was discovered.[37] This mainly originates from the much higher interlayer charge density than that of p-type doping, facilitating the 3D charge transport for out-of-plane n-type SnSe crystals.

Researchers initially achieved n-type transport in SnSe crystals through doping with Bi or Br, and realized admirable performance along the in-plane and out-of-plane directions for Bi-doped and Br-doped SnSe crystals, respectively.[37, 59] Furthermore, in Br-doped SnSe crystals, by employing first-principles calculations and scanning tunneling microscopy (STM), high charge density between layers for n-type SnSe was observed, facilitating effective charge transport between crystalline layers and enabling 3D charge transport.[37] Further experiments revealed the converging and diverging processes for the conduction bands of SnSe. Coupled with the continuous phase transition inducing high carrier mobility, n-type crystalline SnSe maintained high out-of-plane *PF* values across the entire temperature range. Meanwhile, it exhibits lowest thermal conductivity value among all crystalline directions due to the strong interlayer phonon scattering (2D phonon transport).[37] Ultimately, the n-type crystalline SnSe achieved an extraordinary interlayer ZT_{max} ~2.8 at 773 K, as Fig. 1c depicts, along with the moderate ZT_{ave} (300-773 K) ~1.1, as depicted in Fig. 4.[37] To further optimize wide-range thermoelectric properties for n-type SnSe crystals, Pb alloying was employed to promote the continuous phase transition, resulting in a higher ZT_{ave} ~1.4,[60] as presented in Fig. 4.

The achievements for p-type crystalline SnSe thermoelectrics highlights the significance of increasing carrier mobility to achieve promising ZT_{ave} among wide temperature ranges. Building upon this, researchers devised a strategy to manipulate layered phonon-electron decoupling, further enhancing carrier mobility and *PF* in n-type SnSe crystals, thereby resulting in a significant increase of ZT_{ave}.[39] By substituting Cl doping for Br doping, the deformation potential was notable de-

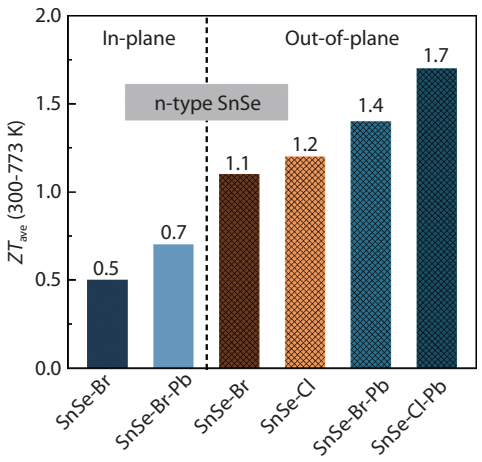


Fig. 4 ZT_{ave} (300-773 K) of typical n-type crystalline SnSe samples along in-plane and out-of-plane directions.[37, 39, 60, 61]

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creased, leading to prominent weakening of phonon-electron coupling and interlayer carrier scattering in n-type SnSe crystals.[39] Resultantly, higher carrier mobility and average *PF* (PF_{ave}) were achieved, ultimately yielding a ZT_{ave} ~1.2 (300-773 K), as shown in Fig. 4. Additionally, Pb alloying was employed to enhance electrical transport properties by promoting the conduction band degeneration and continuous phase transition processes. This approach ultimately resulted in an exceptional out-of-plane ZT_{max} ~3.1 at 748 K, with the ZT_{ave} of approximately 1.7 for n-type Cl-doped $Sn_{0.9}Pb_{0.1}Se$ crystals,[39] as shown in Fig. 1c and Fig. 4. These findings present a critical step towards the realization of all-crystalline-SnSe-based TE devices for potential applications.

However, it is important to note that the weak interlayer bonding poses significant challenges to the preparation process of TE devices based on n-type out-of-plane SnSe crystals. In comparison, in-plane crystalline samples exhibit superior mechanical properties and processability, making the construction of TE devices relatively easier. Consequently, researchers have also conducted relevant investigations and performance optimizations of in-plane n-type SnSe crystals, initially achieving a moderate ZT_{ave} of ~0.7,[61] as depicted in Fig. 4. Nonetheless, the current in-plane n-type performance still lags those of p-type SnSe crystals. Therefore, future studies on n-type crystalline SnSe should primarily focus on performance optimization across a wide temperature range, especially near room temperature, at the material level. Simultaneously, it is essential to explore the preparation process of TE devices consisting of out-of-plane crystalline samples, to realize the construction and enhance efficiency within all-crystalline-SnSe-based TE devices.

Summary and Outlook

During the last few years, significant advancements have been realized for discovering and developing high-performance SnSe crystalline thermoelectrics. Particularly, extraordinary n-type samples achieved out-of-plane ZT_{max} surpassing 3.0, while p-type crystalline SnSe achieved not only the overall ZT_{ave} > 2.0 among 300 to 773 K, but also extraordinary room-temperature *ZT* approaching 1.5. These advancements in material performance also led to the design and construction of crystalline-SnSe-based TE devices, especially for p-type SnSe-based TE devices, in which power generation efficiency exceeding 10% at a temperature difference ~300 K was achieved, highlighting their potential for mid-temperature energy harvesting applications. Furthermore, full-scale TE cooling devices based on highly effective p-type SnSe crystals demonstrated a cooling ΔT_{max} exceeding 60 K near ambient temperature, indicating promising prospects of SnSe-based TE devices as alternatives to the current Bi_2Te_3-based TE cooling devices. Future research on SnSe crystalline thermoelectrics should focus on optimizing material properties and enhancing device efficiency, as well as addressing critical challenges such as large-scale production that determine practical applications. To this end, several personal outlooks are proposed.

1. Material properties optimization: carrier mobility majorization. For p-type crystalline SnSe, the strategy of lattice plainification achieved through bringing in additional Cu was proved effective.[40] Exploring other atoms or approaches to manipulate intrinsic defects and fix SnSe lattice might offer more efficient means to increase carrier mobility by weakening carrier scattering, as Fig. 3 illustrates. Modifying crystal growth process could provide an alternative method.[13] Moreover, combining the multiband synglisis with lattice plainification is expected to have a dual effect on performance optimization. In the case of n-type SnSe crystals, the strategies employed for improving p-type SnSe, particularly the lattice plainification strategy, should also be referenced to optimize n-type transport, considering the existence of extensive lattice imperfections in n-type SnSe. At present, the optimal directions are different in p-type and n-type crystalline SnSe, making it challenging to achieve a balance in mechanical properties on both sides of the p-n junctions for TE devices. So, enhancing the thermoelectric properties of n-type SnSe along the in-plane direction becomes rather crucial for effectively matching the p-type counterparts. Furthermore, the topological states provide an essential guidance for enhancing carrier mobility. The molecular beam epitaxy-grown cubic SnSe films with a dozen atomic layers was verified to exhibit topological features,[62] laying important foundation for developing high-performance bulk SnSe thermoelectrics with topological states.

2. Device efficiency enhancement: interfacial and geometrical design. Following the successful synthesis of high-performance crystalline SnSe samples, the next crucial step towards practical applications is the construction of high-efficiency devices. However, designing efficient devices for SnSe crystalline thermoelectrics presents several challenges compared to traditional TE systems, mainly including: 1) the strong Fermi pining effect at the contact surface between wide-bandgap SnSe crystals and metallic electrodes hinders carrier transport, thereby negatively impacting the device efficiency; 2) the diffusion between TE elements and electrodes, especially at high temperatures, deteriorates device performance, reduces its lifetime, and may even lead to service failure. To address these challenges, optimizing and matching the p-type and n-type properties alone remains not sufficient. It is crucial to reduce contact resistance through interfacial designs that incorporate appropriate barrier and welding layers. Moreover, TE device design encompasses not only the selection of suitable TE elements and interfacial structures, but also involves geometry design. This could be achieved through a combination of experiments and finite element analysis, taking into consideration of various factors such as the sizes of p/n legs, spacings between TE legs, and even multi-stage design.[63]

3. Practical application promotion: large-scale production, performance homogenization, and processability improvement. In addition to outstanding performance, the practical large-scale application of innovative TE materials, such as crystalline SnSe, must consider the time and cost involved in the production process. Currently, the modified vertical Bridgman method for growing SnSe crystals is time-consuming (~10 days) and poses challenges for realizing large-size and batch production. Particularly in p-type SnSe crystals, the high-temperature reaction between the dopant Na and quartz crucibles further limits the size of the grown SnSe samples to the centimeter level. This necessitates the im-

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provement of crystal growth techniques, and researchers have recently made progress with vapor deposition and horizontal Bridgman methods for growing larger SnSe crystals.[64-66] Moreover, the vertical Bridgman method inevitably results in concentration gradients of doping and alloying elements along the vertical direction. Combined with composition segregation during crystal growth, this may cause compositional and TE performance inhomogeneity within the bulk samples, which is detrimental to practical applications. The horizontal growth method, along with annealing treatment, provides important solutions to address this issue. Moreover, the increasing integration and miniaturization of electronic devices have placed higher demands on the mechanical properties and processability of TE materials, with sizes of the processed features reaching below 100 μm. For SnSe crystalline thermoelectrics, it is crucial to improve the interlayer bonding force through strategies such as atomic intercalation, which is expected to effectively promote the practical utilizations by enhancing their macroscopic processability.

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■ AUTHOR CONTRIBUTIONS

Conceptualization, L.-D.Z.; Writing-Original Draft, B.Q., D.L., Q.C.; Writing-Revised Draft, B.Q., X.Z.; Sketching Fig. 1 and Fig. 3, D.L. All authors discussed the results, read the paper, and commented on the text.

■ CONFLICT OF INTEREST

The authors declare no conflict of interest.

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