



Revolution in thermoelectric cooling using PbSe thermoelectrics by grid plainification

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Thermoelectric materials and devices enable direct conversion between heat and electricity, holding potential applications in thermoelectric power generation, localized cooling, and electronic thermal management [1]. However, despite widespread applications, thermoelectric technology remains constrained by material performance [2]. The performance of thermoelectric materials is dictated by the dimensionless figure of merit $ZT = S^2\sigma T/\kappa$, where S , σ , T , and κ represent the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity [2]. Enhancing power generation or thermoelectric cooling efficiency requires larger ZT values, necessitating a balance between electrical and thermal transport properties [2].

In the past few years, thermoelectric cooling technology has garnered considerable attention as a solution to heat dissipation issues in smart electronic devices [3]. It offers unique advantages such as noiselessness, adjustable size, fluorocarbon-free operation, and durability, making it highly promising in the refrigeration domain [3]. However, the increasingly prominent issue of cooling efficiency hampers its further development [3]. Currently, Bi_2Te_3 -based alloys are the only commercialized thermoelectric cooling materials [4], yet they suffer from poor cooling capacity, inability to operate in medium to high-temperature environments, scarcity of tellurium (Te) resources, poor processability, and high power consumption [2]. Therefore, research on alternative materials is needed to revolutionize the core thermoelectric materials of these cooling devices. In recent years, p-type SnSe crystals and n-type $\text{Mg}_3(\text{Bi,Sb})_2$ alloys have been developed in laboratories [5,6], demonstrating excellent cooling performance. However, the available thermoelectric cooling devices remain limited, far fewer than thermoelectric power generation devices [2], and their cooling effects still need further improvement. Hence, it is necessary to explore more efficient thermoelectric cooling materials to provide additional alternatives and meet the needs of various application scenarios within a wider temperature range.

Lead selenide (PbSe) is considered to be a promising alternative to traditional lead telluride (PbTe) as an effective new thermoelectric material without the expensive Te element [7]. The thermoelectric performance of PbSe has been significantly enhanced through various efforts, with peak ZT values reaching 1.8 at 900 K in n-type PbSe utilizing high-entropy strategies [8]. However, the reported performance of PbSe in the near-room temperature range still remains relatively low and notably

inferior to Bi_2Te_3 [4,8]. Therefore, there is an urgent need to further enhance the near-room temperature thermoelectric performance of PbSe while maintaining its high performance at elevated temperatures. To achieve this goal, Qin *et al.* [9] demonstrated how the lattice vacancy removal through grid design strategy transformed PbSe from a useful medium-temperature thermoelectric power generation material to an effective thermoelectric cooling material across the entire temperature range. At room temperature, the device based on 7 pairs of n-type PbSe and p-type SnSe generated a maximum cooling temperature difference ΔT of ~ 73 K, with a single-leg power generation efficiency approaching 11.2%. This result is attributed to a power factor of $>52 \mu\text{W cm}^{-1} \text{K}^{-2}$ achieved by enhancing the carrier mobility μ . This achievement provides a pathway for the commercial application of thermoelectric cooling based on earth-abundant Te-free selenide-based compounds.

Specifically, grid plainification achieves a clearer lattice structure with fewer defects [10]. The authors employed a grid design strategy to precisely manipulate the defects in the material by finely tuning the composition and preparation processes. By introducing additional Cu as a donor dopant, PbSe was converted into n-type semiconductor. Through process optimization, high-quality PbSe crystals were grown to enhance μ . Additionally, a small amount of extra Pb was introduced to further improve μ by compensating for inherent Pb vacancies and explicitly fixing the PbSe lattice, significantly reducing defect scattering of carriers. Electrical transport performance (power factor, $PF = S^2\sigma$) was optimized over a wide temperature range, particularly near room temperature, with a maximum PF exceeding $52 \mu\text{W cm}^{-1} \text{K}^{-2}$ (Fig. 1a). The high PF value along with a relatively low intrinsic κ facilitated ultrahigh ZT values across the entire temperature range (Fig. 1b), achieving a room temperature ZT value of 0.9 and a peak ZT of ~ 1.8 at 623 K, especially compared with currently reported n-type PbSe thermoelectrics [7].

Additionally, the ultrahigh ZT values over a wide temperature range greatly contribute to the power generation and cooling performance of the device. At a ΔT of 420 K, the maximum thermoelectric conversion efficiency of the single-leg device approaches $\sim 11.2\%$. Furthermore, by coupling the n-type Pb_{1+x}Se with the previously developed p-type SnSe crystal, a thermoelectric device consisting of 7 pairs of selenide-based legs

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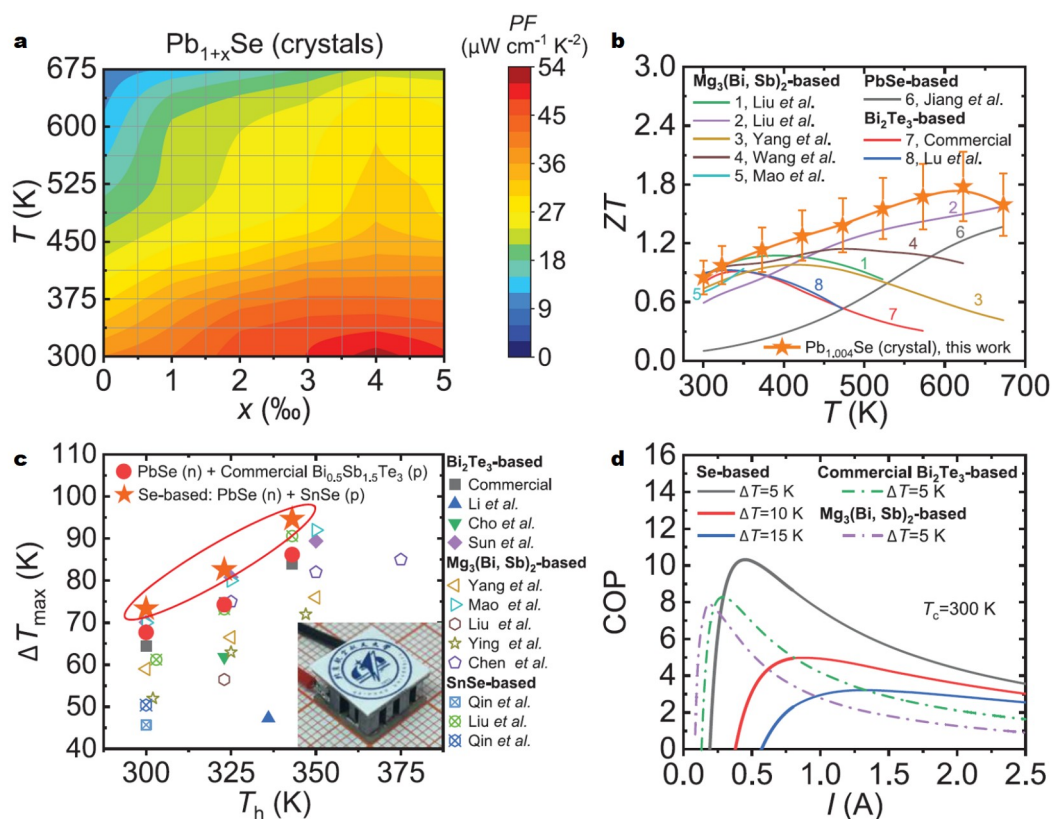


Figure 1 (a) Distribution mapping of the PF values as functions of temperature (T) and the excess Pb content (x) in n-type Pb_{1+x}Se crystals with an additional 0.08 mol% Cu, showing an enhanced PF, particularly near ambient temperature. (b) Comparison of overall ZT values from 300 to 673 K for the $\text{Pb}_{1.004}\text{Se}$ crystal with an additional 0.08 mol% Cu, with high-entropy PbSe and various n-type thermoelectric cooling candidates, including commercial Bi_2Te_3 and recently developed $\text{Mg}_3(\text{Bi}, \text{Sb})_2$ alloys. (c) Maximum cooling temperature difference (ΔT_{max}) versus the hot-side temperature (T_h) for the selenide-based thermoelectric cooler, with comparison to other systems such as commercial $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ and laboratory-made Bi_2Te_3 , $\text{Mg}_3(\text{Bi}, \text{Sb})_2$, and SnSe crystals. The inset illustrates the fabricated 7-pair selenide-based thermoelectric cooling device comprising n-type PbSe and p-type SnSe . (d) Comparison of the calculated coefficient of performance (COP) for the selenide-based cooler at ΔT s of 5, 10, and 15 K, along with commercial Bi_2Te_3 -based and recently developed $\text{Mg}_3(\text{Bi}, \text{Sb})_2$ -based devices, based on a fixed cold-side temperature (T_c) of 300 K. Reproduced with permission from Ref. [9]. Copyright 2024, American Association for the Advancement of Science.

was constructed. The device exhibits high cooling capacity, with a cooling performance of ~ 73 K at ambient temperature (Fig. 1c), and a theoretical maximum coefficient of performance (COP) of 10 (Fig. 1d).

In conclusion, the high thermoelectric performance within a wide temperature range of Pb_{1+x}Se crystals makes them promising candidates for Te-free thermoelectric cooling applications. This work demonstrates the effectiveness of grid-plainification strategies in developing superior thermoelectric materials, along with the potential applications in thermoelectric cooling. However, it is noteworthy that lead (Pb), being a toxic element, requires additional attention to environmental and human health concerns during the use of thermoelectric materials and devices, necessitating effective encapsulation. Furthermore, due to the volatility of Selenium (Se) at high temperatures (e.g., above 800 K) [5], aside from effective encapsulation, enhancing the stability of materials and devices is crucial, especially at high temperatures.

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