

could enable transformation of the world's energy from carbon based to nitrogen based.

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Preview

A Game-Changing Strategy in SnSe Thermoelectrics

Ananya Banik¹ and Kanishka Biswas^{1,2,*}

Tin selenide (SnSe) has emerged as a hotspot of thermoelectric research since the discovery of an exceptionally high thermoelectric figure of merit (ZT) in single crystals of SnSe. In the issue of Joule, Lee et. al. unveil the ultralow thermal conductivity and unprecedented ZT in the polycrystalline SnSe by employing an oxide removal strategy.

Rising global demand for energy in conjunction with a greater emphasis on increasing efficiency has driven researchers to look for clean and renewable energy sources. As one of the most accessible renewable energy sources, heat holds promise in view of its ubiquitous and ineluctable nature. A major percentage (~65%) of used energy is inevitably lost through heat dissipation. One efficient way to advance the sustainability of our electricity base is the recovery of this waste heat with thermoelectric (TE) generators due to their reversible heat-to-electricity conversion efficiency.¹ Additional advantages arise from their reliable, robust, and environmentally friendly nature.

The hunt for efficient TE materials in the past decade has been intense, orga-

nized, and multifaceted; it has thrived, discovering several new materials with outstanding performance.¹ Lead chalcogenides (PbTe/PbSe/PbS) and their alloys have been widely contemplated as the leading material for mid- to high-temperature (600–900 K) thermoelectric power generation application.² Recently, tin chalcogenides have received enormous attention from the TE community as potential alternatives to lead chalcogenide because of their unique electronic structures and phonon dispersions.³ In particular, layered tin chalcogenides have emerged as a hotspot of TE research because of their anisotropic crystal structure, weak interlayer van der Waals interaction, and phase stability.³ Tin selenide (SnSe), a layered semiconductor from the tin chalc-

genide family, has recently stimulated huge interest among the TE community due to superior thermoelectric properties originating from its significant lattice anharmonicity, ultra-low thermal conductivity (κ_{tot}), chemical stability, earth abundance, and low toxicity.^{4,5} Although SnSe was neglected by the TE community until 2013 due to its high electrical resistance, an outstanding thermoelectric figure of merit (ZT) of ~2.6 has been recently realized in *p*-type single crystalline pristine SnSe. Furthermore, Br-doped *n*-type crystals exhibit a ZT of 2.8 at 773 K along the *a*-axis. Such a record high ZT value is imputed to intrinsically ultra-low lattice thermal conductivity, κ_{lat} (~0.20 $Wm^{-1}K^{-1}$), which stems from a layered structure, soft chemical bonding and lattice anharmonicity.⁶ Despite its extraordinary properties, the use of layered single crystalline SnSe in thermoelectric devices is obstructed by its poor mechanical stability, tedious synthesis procedure

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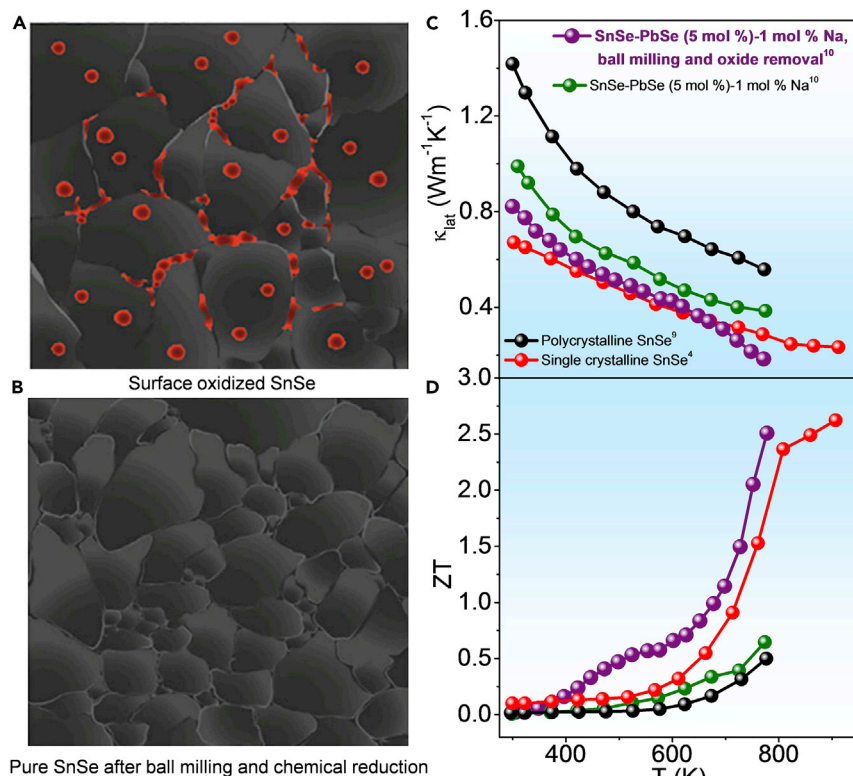


Figure 1. Enhancement of Thermoelectric Performance of Polycrystalline SnSe by the Removal of Surface Oxides

Schematic of SnSe samples (A) with and (B) without tin oxides. Tin oxides are marked in red. Temperature-dependent (C) lattice thermal conductivity, κ_{lat} and (D) thermoelectric figure of merit, ZT of polycrystalline SnSe with 5% PbSe and 1% Na before and after ball milling and tin oxide coating removal. For comparison, κ_{lat} and ZT of single crystalline and polycrystalline SnSe are also given.

and processability.⁵ Thus, for TE application, development of high-performance polycrystalline SnSe is imperative due to the ease of its production and its better mechanical stability and processability.^{7,8} However, the major challenge in polycrystalline SnSe relies on its higher κ_{lat} values compared to single crystals.⁵ Thus, bulk polycrystalline SnSe-based material shows a peak ZT of ~ 1.2 , which is far below the ZT (~ 2.6) of the SnSe single crystal.⁹

The recent paper published in *Joule* reports record high thermoelectric performance of bulk polycrystalline SnSe by addressing the long-term thermal conductivity problem of polycrystalline SnSe.¹⁰ Two mechanisms have been

proposed for this anomalously higher κ_{lat} of polycrystalline SnSe as compared to the single crystal.⁵ First, chalcogenides are susceptible to surface oxidation when exposed to air. Thus, tin chalcogenide materials need special care to prohibit surface oxidation and spontaneous formation of oxide thin films. Additionally, tin (Sn) can adopt both divalent and stable tetravalent formal oxidation states, which can create unavoidable cation-site lattice defects. Near room temperature, SnO₂ shows a κ_{tot} of ~ 98 and $\sim 55 \text{ Wm}^{-1}\text{K}^{-1}$ along the crystallographic *c* and *a* axes, respectively. Interestingly, SnO has a much lower κ_{tot} ($\sim 2 \text{ Wm}^{-1}\text{K}^{-1}$) than SnO₂ at room temperature, and it transforms into SnO₂ with temperature and/or time.

Thus, its presence even in a very low concentration can increase κ_{tot} significantly and degrade electrical conductivity arising from carrier scattering at the interface, leading to poor TE performance. Besides, as-grown SnO₂ exhibits *n*-type conductivity, which can also have a negative impact on the electrical transport properties of *p*-type pristine SnSe. Since the presence of SnO and SnO₂ is the main reason for the apparent higher κ_{tot} of the polycrystalline SnSe, surface oxide removal should reveal the true intrinsic ultra-low thermal conductivity in polycrystalline SnSe, which will be lower than the thermal conductivity of single crystals.

Lee et al.¹⁰ have experimentally confirmed that tin oxide layers on the surface of SnSe powder are the origin of the paradoxically higher κ_{lat} in polycrystalline samples over the single crystal (Figure 1). Since the oxygen concentration is much higher at the edges than at the central part of the powder sample, the consolidation process (spark plasma sintering, SPS) spreads the oxide films on grain boundaries throughout the pellets (Figure 1A). Presence of tin oxides on grain boundaries can uplift the phonon transport because of very high thermal conductivity of tin oxide itself. Chung and co-workers reported successful chemical removal of the tin oxide layers from the powdered polycrystalline SnSe, certainly uncovering the intrinsic ultra-low κ_{lat} and realizing an extraordinarily high ZT comparable to that of the single crystals.

In this work, Lee et al.¹⁰ have prepared an oxide-free, nanostructured bulk sample via additional thermal treatment of ball-milled polycrystals of SnSe with 5% PbSe and 1% Na under H₂/Ar atmosphere (Figure 1B). The ball milling and the subsequent chemical reduction process significantly enhance the carrier mobility, electrical conductivity, and Seebeck coefficient of the polycrystalline SnSe-

based materials. The most striking changes brought about by the chemical reduction process on the polycrystalline SnSe samples have been observed in the κ_{lat} . After chemical reduction, the κ_{lat} reaches a minimum of $\sim 0.11 \text{ Wm}^{-1}\text{K}^{-1}$ at 773 K, which is about one-third of previously reported pristine polycrystalline SnSe and one-half of SnSe single crystal (Figure 1C). These results validate that ultra-low κ_{lat} is intrinsic for SnSe; in the polycrystalline form, it indeed shows lower κ_{lat} than the corresponding single crystals originating from strong grain boundary scattering.

Rapid advancement in the thermoelectric performance of SnSe makes this material promising for waste heat recovery application. However, a major restricting factor is the surface oxidation of SnSe polycrystals, which degrades thermoelectric performance. In this article, Lee et al.¹⁰ have reported a unique approach to remove tin oxide film growth by playing with simple solid-state chemistry and uncovering its ultra-low κ_{lat} . Their results validated the previous prediction regarding the role of present tin oxides on the κ_{lat} of polycrystalline SnSe.⁵ Thus, after chemical reduction, the simultaneous enhancement in carrier mobility, elec-

trical conductivity, and Seebeck coefficient, coupled with the lowest κ_{lat} for polycrystalline SnSe with 5% PbSe and 1% Na, leads to an remarkably high ZT of ~ 2.5 at 773 K.¹⁰ We believe that the work of Chung and co-workers has provided a new direction to the field of polycrystalline thermoelectrics that can advance the prospects for realizing efficient thermoelectric devices using polycrystalline SnSe. The exceptionally high ZT of these samples resulting from the removal of surface tin oxides hints at the presence of enormous room for further enhancement in TE performance of other polycrystalline materials via the application of new strategies and intricate preparation techniques.

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