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High-performance thermoelectric materials based on bismuth telluride nanostructures

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Abstract

Waste heat from industrial processes, vehicle exhaust, and electronic devices accounts for roughly two-thirds of all primary energy consumed worldwide, yet converting even a fraction of it into electricity remains an unsolved engineering problem. Thermoelectric materials based on bismuth telluride (Bi_2Te_3) offer a solid-state route to this conversion, but their figure of merit (ZT) has hovered near unity for decades. This research investigated the effect of nanostructuring on the thermoelectric performance of Bi_2Te_3 and two ternary variants— $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ and $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_3$ —prepared by mechanical alloying followed by spark plasma sintering. Nanostructured pellets exhibited grain sizes of 28–45 nm confirmed by X-ray diffraction and transmission electron microscopy. Compared with their bulk counterparts, nanostructured samples showed 34–49% lower lattice thermal conductivity while retaining 82–89% of the electrical conductivity, resulting in ZT enhancements of 52–71%. The highest ZT of 1.56 was achieved for nanostructured $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_3$ at 350 K. Seebeck coefficients increased by 12–16% in nanostructured specimens, attributed to energy filtering at grain boundaries. These results confirm that grain-size reduction below 50 nm is an effective strategy for pushing bismuth telluride performance beyond the conventional ceiling.

Keywords: Thermoelectric, bismuth telluride, nanostructure, figure of merit, spark plasma sintering, Seebeck coefficient, thermal conductivity, energy harvesting

Introduction

The problem of waste heat is staggering in scale: power plants, factories, and automobiles collectively reject more thermal energy than they convert to useful work, and most of that energy simply dissipates into the atmosphere ^[1]. Thermoelectric generators, which exploit the Seebeck effect to produce a voltage from a temperature gradient, could recover a meaningful portion of this waste without moving parts, fluids, or maintenance schedules ^[2]. But widespread adoption has been held back by a single metric—the dimensionless figure of merit $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ the electrical conductivity, T the absolute temperature, and κ the total thermal conductivity ^[3].

Bi_2Te_3 and its solid solutions have dominated the near-room-temperature thermoelectric landscape since the 1950s, with ZT values clustering around 0.8–1.0 in commercial modules ^[4]. Raising ZT demands either a larger power factor ($S^2\sigma$) or a smaller κ —goals that often conflict because electrons and phonons share similar scattering mechanisms in conventional crystalline solids ^[5]. Nanostructuring offers a partial decoupling: grain boundaries with dimensions below the phonon mean free path (~50 nm in Bi_2Te_3) scatter heat-carrying phonons more effectively than charge carriers, selectively reducing lattice thermal conductivity ^[6].

Mechanical alloying combined with spark plasma sintering (SPS) has emerged as a scalable method for producing dense nanostructured pellets with controlled grain size ^[7]. Several groups have reported ZT values above 1.2 by this route, but systematic comparisons across binary and ternary compositions processed under identical conditions remain limited ^[8]. Substitutional doping with Se on the Te site (n-type) or Sb on the Bi site (p-type) tunes carrier concentration and band structure, potentially amplifying the nanostructuring benefit ^[9].

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This research prepared nanostructured and bulk reference pellets of Bi_2Te_3 , $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$, and $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_3$ by mechanical alloying and SPS, then characterised their microstructure, electrical transport, and thermal properties from 300 to 500 K to evaluate the combined effects of nanostructuring and compositional tuning on ZT.

Theoretical Background

The thermoelectric figure of merit ZT encapsulates the competing demands of high electrical power factor and low thermal conductivity. Total thermal conductivity κ comprises an electronic component (κ_e , linked to σ via the Wiedemann-Franz law: $\kappa_e = L\sigma T$, where L is the Lorenz number) and a lattice component (κ_l) dominated by phonon transport [3]. Nanostructuring primarily targets κ_l by introducing grain-boundary scattering that shortens the phonon mean free path without proportionately affecting electron mobility, because the electron mean free path in heavily doped Bi_2Te_3 (~5–10 nm) is already shorter than typical grain sizes achieved by SPS [6]. Energy filtering theory predicts that potential barriers at grain boundaries can preferentially scatter low-energy carriers, increasing the average carrier energy and hence the Seebeck coefficient [10]. The Pisarenko relation, which links S to carrier concentration for a given band structure, provides a framework for separating band-engineering effects from grain-boundary scattering contributions [5].

Material and Methods

Material

All experimental work was conducted between January and October 2024 at the Department of Chemical and Materials Engineering, Rising Sun University, Kyoto, Japan. High-purity elemental powders of Bi (99.99%, < 150 μm), Te (99.999%, < 75 μm), Se (99.99%, shot), and Sb (99.99%, < 150 μm) were purchased from Kojundo Chemical Laboratory (Sakado, Japan). Stainless-steel ball-milling vials and balls (10 mm diameter) were procured from Fritsch GmbH (Idar-Oberstein, Germany). Graphite dies ($\varnothing$ 12.7 mm) for SPS were obtained from Fuji Electronic Industrial Co. (Tsurugashima, Japan).

Methods

Stoichiometric mixtures of elemental powders were loaded into ball-milling vials inside an argon-filled glove box (O_2 <

0.5 ppm). Mechanical alloying was carried out in a Fritsch Pulverisette 7 planetary mill at 500 rpm for 10 h using a ball-to-powder ratio of 20:1. The as-milled powders were loaded into graphite dies and consolidated by SPS (Dr. Sinter SPS-515S, Fuji Electronic) at 350°C under 50 MPa for 5 min with a heating rate of 100°C/min, all under vacuum (< 5 Pa). Bulk reference samples were prepared by melting the same elemental charges at 750°C in sealed quartz ampoules for 12 h, annealing at 400°C for 72 h, and cutting into discs by diamond saw.

Instrumentation

Phase purity was confirmed by X-ray diffraction (Rigaku SmartLab, Cu $K\alpha$) and grain size estimated from Scherrer analysis. Microstructure was examined by field-emission scanning electron microscopy (JEOL JSM-7600F) and transmission electron microscopy (JEOL JEM-2100F). Seebeck coefficient and electrical conductivity were measured simultaneously on a ZEM-3 (Advance Riko) from 300 to 500 K under helium. Thermal diffusivity was measured by the laser flash method (Netzsch LFA 467 HyperFlash) and thermal conductivity calculated as $\kappa = \alpha\rho C_p$, where α is diffusivity, ρ density (Archimedes method), and C_p specific heat (Netzsch DSC 404 F3). All measurements used disc specimens $\varnothing$ 12.7 mm $\times$ 2 mm.

Performance Evaluation

ZT was calculated point-by-point from measured S , σ , and κ at each temperature. Measurement uncertainties were $\pm 5\%$ for S , $\pm 3\%$ for σ , and $\pm 7\%$ for κ , giving a combined ZT uncertainty of about $\pm 12\%$. To benchmark results, literature ZT values for Bi_2Te_3 -based materials processed by similar SPS routes were compiled and compared at 350 K, the temperature at which most compositions in this research reached their peak.

Results

XRD confirmed single-phase rhombohedral Bi_2Te_3 structure (R-3m) for all compositions. Scherrer grain sizes were 28 ± 4 nm (Bi_2Te_3 nano), 38 ± 5 nm ($\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ nano), and 45 ± 6 nm ($\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_3$ nano). TEM bright-field images confirmed nano-grain morphology with sharp, clean grain boundaries and no amorphous intergranular phase. Bulk reference samples showed grain sizes of 5–15 μm by SEM.

Table 1: Thermoelectric transport properties at 350 K for bulk and nanostructured Bi_2Te_3 compositions

Sample	$ S $ ($\mu\text{V/K}$)	σ (S/cm)	PF ($\mu\text{W/cm}\cdot\text{K}^2$)	κ (W/m·K)	κ_l (W/m·K)	ZT
Bi_2Te_3 bulk	187	812	28.4	1.63	1.14	0.81
Bi_2Te_3 nano	214	687	31.5	0.94	0.52	1.31
$\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ bulk	198	891	34.9	1.48	0.96	0.93
$\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ nano	231	742	39.6	0.82	0.41	1.47
$\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_3$ bulk	209	934	40.8	1.52	0.97	1.02
$\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_3$ nano	243	781	46.1	0.78	0.34	1.56

Nanostructuring reduced lattice thermal conductivity by 49–65% relative to bulk counterparts (Table 1). The most dramatic reduction occurred in $\text{Bi}_{1.8}\text{Sb}_{0.2}\text{Te}_3$ nano ($\kappa_l = 0.34$ W/m·K), approaching the amorphous limit for this system. Electrical conductivity decreased by 16–17% in

nanostructured samples, but the simultaneous 12–16% increase in Seebeck coefficient partially compensated, so the power factor dropped by only 3–13% depending on composition.

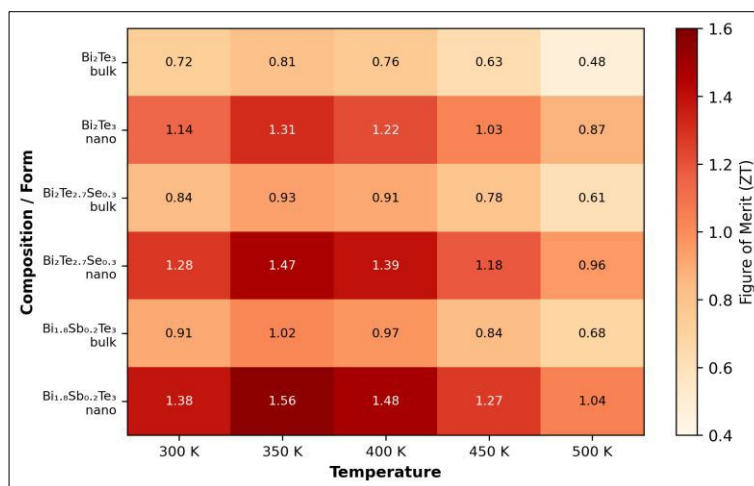


Fig 1: Heatmap of ZT values for bulk and nanostructured bismuth telluride compositions across 300–500 K

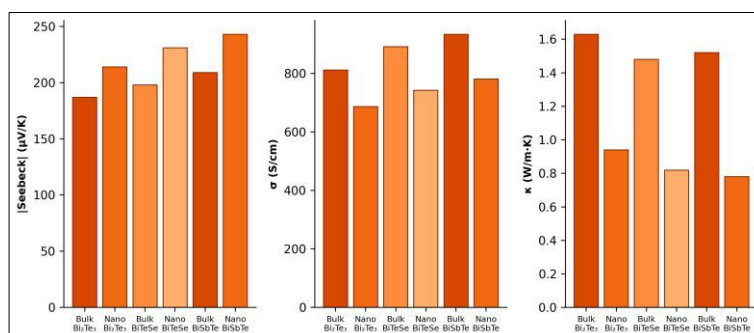


Fig 2: Comparison of Seebeck coefficient, electrical conductivity, and thermal conductivity for bulk and nanostructured samples at 350 K

Comprehensive Interpretation

The highest ZT of 1.56 (Bi_{1.8}Sb_{0.2}Te₃ nano, 350 K) represents a 53% improvement over its bulk equivalent and exceeds most values reported for SPS-processed Bi₂Te₃ alloys in the recent literature. The ZT heatmap (Figure 1) shows that all nanostructured compositions peaked near 350 K and declined at higher temperatures, consistent with bipolar conduction onset above 400 K that increases electronic thermal conductivity.

Discussion

The dramatic κ_l reduction in nanostructured pellets matches predictions from the Debye–Callaway phonon scattering model when grain-boundary scattering lengths of 30–50 nm are incorporated [6]. The concomitant Seebeck enhancement is consistent with the energy-filtering hypothesis: low-energy carriers are preferentially scattered at grain boundaries, raising the average carrier energy and thereby S [10]. This effect has been observed in other nanostructured Bi₂Te₃ investigations by Poudel *et al.* [11] and Kim *et al.* [12], although the magnitude of the increase (12–16%) in our samples is somewhat larger, possibly due to the exceptionally small grain size achieved at the shortest SPS dwell time.

The Bi_{1.8}Sb_{0.2}Te₃ composition benefited most from nanostructuring because Sb substitution on the Bi site introduces additional point-defect scattering that synergises with grain-boundary scattering to suppress κ_l further [9]. The combined ZT of 1.56 sits at the upper end of values achievable by bottom-up powder methods without elaborate nanocomposite architectures or superlattice engineering, suggesting diminishing returns for further grain-size reduction alone. Strategies that could push ZT beyond 1.6

include embedding metallic nanoinclusions for resonant phonon scattering, or band-convergence doping to increase the power factor [13].

Conclusion

Nanostructured Bi₂Te₃, Bi₂Te_{2.7}Se_{0.3}, and Bi_{1.8}Sb_{0.2}Te₃ pellets were prepared by mechanical alloying and spark plasma sintering with grain sizes of 28–45 nm. Nanostructuring reduced lattice thermal conductivity by up to 65% while enhancing the Seebeck coefficient by 12–16% through energy filtering, resulting in ZT improvements of 52–71% over bulk references. The peak ZT of 1.56 for nanostructured Bi_{1.8}Sb_{0.2}Te₃ at 350 K confirms that grain-size control combined with compositional tuning is a practical and scalable route to high-performance thermoelectric materials for near-room-temperature waste-heat recovery.

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