Seebeck and Figure of Merit Enhancement in Nanostructured Antimony Telluride by Antisite Defect Suppression through Sulfur Doping

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ABSTRACT: Antimony telluride has a low thermoelectric figure of merit (ZT < ~0.3) because of a low Seebeck coefficient $\alpha$ arising from high degenerate hole concentrations generated by antimony antisite defects. Here, we mitigate this key problem by suppressing antisite defect formation using subatomic percent sulfur doping. The resultant 10−25% higher $\alpha$ in bulk nanocrystalline antimony telluride leads to ZT > 0.95 at 423 K, which is superior to the best non-nanostructured antimony telluride alloys. Density functional theory calculations indicate that sulfur increases the antisite formation activation energy and presage further improvements leading to ZT ∼ 2 through optimized doping. Our findings are promising for designing novel thermoelectric materials for refrigeration, waste heat recovery, and solar thermal applications.

KEYWORDS: Nanobulk thermoelectrics, sulfur doping, antimony telluride, antisite defects, first principle transport calculations, high figure of merit ZT
by using a combination of doping and nanostructuring for refrigeration, waste heat recovery, and solar thermal applications.

We synthesized sulfur-doped nanoplates of Sb$_2$Te$_3$ by a microwave-stimulated solvothermal approach$^{13,14}$ (Figure 1a TEM inset). The nanocrystals were consolidated into nanostructured bulk pellets by cold compaction and sintering (Figure 1a inset and b). X-ray diffractograms of the nanobulk pellets confirm the retention of the rhombohedral R$3m$ structure, with no observable traces of extraneous phases (Figure 1a). Energy and wavelength dispersive X-ray spectroscopy (EDX and WDX) confirm 0.1–0.5 at. % sulfur and stoichiometric Sb$_2$Te$_3$ with 40 ± 1 at. % Sb and 60 ± 1 at. % Te. The sintered nanobulk pellets have ∼92 ± 3% of the theoretical density. We measured $\kappa$ and $\alpha$ of the nanobulk pellets by a steady state method described in detail elsewhere.$^{14,15}$ A four-probe tool in the van der Pauw configuration was used to measure $\sigma$. Our measurements of $\alpha$, $\sigma$, and $\kappa$ along axial and radial directions yielded identical values within instrumental uncertainty, confirming the isotropic properties of our nanobulk Sb$_2$Te$_3$. Hole concentrations $h$ and mobility $\mu$ were determined from Hall measurements.

We obtain high room-temperature electrical conductivity in the $90 \leq \sigma \leq 150$ k$\Omega^{-1}$·m$^{-1}$ range (see Figure 1c), comparable to the lower $\sigma$ ranges reported for single crystal Sb$_2$Te$_3$, but hundred- to thousand-fold higher than that of other reports on nanocrystal assemblies.$^{16,17}$ Our nanobulk Sb$_2$Te$_3$ show $110 \leq \alpha \leq 135$ $\mu$V·K$^{-1}$, which is more than 50% higher than that of non-nanostructured stoichiometric Sb$_2$Te$_3$, and approximately 10–25% higher than the highest $\alpha$ observed for off-stoichiometric non-nanostructured Sb$_2$Te$_3$. Our isotropic nanobulk Sb$_2$Te$_3$ has ∼10% higher $\alpha$ than the highest $\alpha$ in single crystals with similar carrier concentration but lower than that of p-type Sb-rich Sb–Bi–Te alloys.$^{7,8}$ Previous reports of nanostructured Sb$_2$Te$_3$ with unknown or nondeliberate doping have either not shown increases in $\alpha$ (Figure 2b) or the $\alpha$ increase compromises $\sigma$ significantly. For example, microwave synthesized nanostructured Sb$_2$Te$_3$ with unknown doping chemistry$^{19,20}$ reports similar or higher $\alpha$ as exhibited by our S-doped Sb$_2$Te$_3$, but the
σ is more than 10- to 100-fold lower than both conventional non-nanostructured and our doped nanobulk Sb₂Te₃, which translates to at least 2-3 fold lower ZT than ours.

Our nanobulk Sb₂Te₃ exhibit room-temperature thermal conductivity in the 0.7 ≤ κ ≤ 1.1 W m⁻¹K⁻¹ range, which is ~40-70% lower than that of the single- or polycrystalline Sb₂Te₃. This κ decrease corresponds to about 60-75% diminution in the lattice thermal conductivity κₗ due to phonon scattering by the ~20-50 nm nanograins and nanopores. The high α, ultralow κ, and enhanced α in nanobulk Sb₂Te₃ yield ZTₓ₀ₓ₀ₓₚ ≈ 0.75, which is more than 2- to 4-fold that of non-nanostructured poly- or single-crystalline antimony telluride, which is more than 10- to 100-fold lower than both conventional non-nanostructured and our doped nanobulk Sb₂Te₃, which translates to at least 2-3 fold lower ZT than ours.

The ZT of our nanobulk Sb₂Te₃ increases monotonically between 300 ≤ T ≤ 423 K, reaching ZTₓ₀ₓ₀ₓₚ ≈ 0.95, which is ~35% higher than ZTₓ₀ₓ₀ₓₚ ≈ 0.7 reported for non-nanostructured Sb₁₋ₓBiₓTe₃ alloys. This ZT increase is mainly due to the monotonic α increase with temperature, yielding values as high as αₓ₀ₓ₀ₓₚ ≈ 150 μV K⁻¹ (Figure 1c). We expect α to peak at higher temperatures than that of Sb₁₋ₓBiₓTe₃ alloys and Bi₂Te₃, because of the higher temperature onset of bipolar conduction arising from the larger bandgap of Sb₂Te₃. Both σ and κ remain relatively unchanged within ~20% in the 300 ≤ T ≤ 423 K range (see Figure 1c). The weaker-than-typical temperature dependence of σ, reminiscent of degenerate doping implies significant scattering due to grain boundaries and/or point defects, leaving open the scope for further ZT improvements by optimizing grain size and/or defect concentrations. The insensitivity of κ is expected above the Debye temperature Θ_D (~160 K for antimony telluride) for nanostructured materials. These effects combined with the higher α endow our nanobulk Sb₂Te₃ with high ZT without alloying.

Room-temperature Hall measurements on the nanobulk pellets reveal hole concentrations of 10¹⁹ ≤ h ≤ 10²⁰ cm⁻³ that are about 10- to 100-fold smaller than that reported for both polycrystalline and single-crystal non-nanostructured Sb₂Te₃. The hole mobilities of 75 ≤ μ ≤ 250 cm² V⁻¹ s⁻¹ are lower than that of single crystals as expected, but higher than non-nanostructured Sb-rich Sb−Bi−Te alloys (Figure 2a) probably because the low <1 at. % sulfur doping levels diminish impurity scattering of holes. This behavior is in contrast to dopants such as Bi, Tl and In that are known to degrade μ at even low concentrations. The low decrease in μ thus offsets decreases in h to maintain a high α in our nanobulk Sb₂Te₃. The α is isotropic and varies rather weakly with h in the measured range of 3 × 10¹⁹ ≤ h ≤ 10²⁰ cm⁻³, contrary to the strong α−h dependence expected (see Figure 2b). Isotropic α is consistent with the lack of crystallographic texture but unlike anisotropic α seen in single-crystal Sb₂Te₃ due to holes from two bands. The weak dependence of α on h is contrary to the more usual variation found in the theoretical result, may be due to spatial inhomogeneities in stoichiometry and sulfur doping giving rise to regions of varying carrier concentration, considering the lack of second phase within the detection limit of our X-ray diffraction experiments. In general, the nanoscale regions of highest σ will preferentially determine the measured α, provided such regions exceed the percolation threshold. This suggests optimizing the spatial distribution of dopants could further improve α.

The 10–25% increase in α can be traced to the effect of sulfur doping on the antisite defect chemistry in Sb₂Te₃. The similar electronegativities of Sb and Te facilitates Sb′⁻Te⁻ and Sb⁻Te⁻ antisite defect formation. Each Sb′⁻Te⁻ generates a hole by the reaction

\[ 2\text{Sb} + 3\text{Te} + 2\text{h} + V^- + 2V'' + 3/2\text{Te}_2 \]

Figure 2. Plots of (a) hole mobility μ and (b) Seebeck coefficient α, as a function of hole concentration h, in our nanobulk Sb₂Te₃ pellets (blue circles). For comparison, data from ref 8 are shown for undoped bulk single-crystal Sb₂Te₃ (SC) for two crystallographic directions (red and maroon) and from ref 18 for undoped nanostructured Sb₂Te₃ (black diamonds).
where $V_{Te}$ and $V_{Sb}$ are vacancies. The consequent high hole concentrations decrease $\alpha$. We propose that doping with sulfur, which has a higher electronegativity than Te, decreases $h$ by suppressing $Sb_{Te}$ formation, thereby offering a means for increasing $\alpha$. This hypothesis is supported by the sulfur core-level band structure of the nanoplates and the nanobulk pellets measured by X-ray photoelectron spectroscopy (XPS) as described below.

The $S$ 2p band at 162 eV indicates thioligation of $Sb_{2}Te_{3}$ nanoplate surfaces with thioglycolic acid (TGA) used in our synthesis; unfettered TGA has a higher binding energy peak at 164 eV (Figure 3a). Synchrotron XPS of the nanobulk pellets reveals three $S$ 1s sub-bands at 2477, 2471, and 2468 eV whose intensities scale with the sulfur doping level measured by WDX (Figure 3b). All three sub-bands correspond to $S^{2-}$ states (higher oxidation numbers are expected only above 2480 eV) and can be identified with sulfur occupancy of specific sites based on the inverse correlation between valence electron density and core-level binding energy. Sulfur at the Te 3a site, bound to two layers of electropositive Sb (see Figure 3d), would have the highest electron density and the lowest core-level binding energy. Sulfur at the $Sb 6c$ site bound to two layers of isovalent Te would have a higher binding energy. Sulfur at the Te 6c site would have the highest binding energy because of a heterocovalent bond with one layer of Sb and weakly bound to Te atoms in the adjacent layer of the $R3m$ structure via van der Waals bonding.

We note that only the Te 6c sub-band intensity of $S$ 1s strongly correlates with increasing $\alpha$ (Figure 3b), suggesting that this state exerts the largest influence on the hole concentration. The Te 3a and Sb 6c sites appear to be filled only after the Te 6c sites are first filled to a threshold concentration. Such hierarchical site occupancy reported in selenium-alloyed bismuth telluride may be associated with the ease of interlayer sulfur incorporation in the $R3m$ structure and lattice strain effects. Considering $x$ moles of sulfur and $y$ moles of decrease in $Sb_{Te}$ and hence $h$, per mole of $Sb_{2}Te_{3}$ at equilibrium, we can write

$$\frac{d}{dx}$$

Figure 3. (a) Core-level $S$ 2p band structure obtained by XPS from as-synthesized $Sb_{2}Te_{3}$ nanoplate powders. A baseline spectrum from neat TGA is shown for reference. (b) Core-level $S$ 1s band structure obtained by synchrotron XPS from sintered nanostructured bulk pellets of $S$-doped $Sb_{2}Te_{3}$ with different $\alpha$ values, shown alongside the spectra. The sub-bands are labeled with Wyckoff sites that specify sulfur occupancy; see text for details. (c) Core-level Sb 3d band structure with sub-bands from unoxidized and oxidized $Sb_{2}Te_{3}$ and the overlapping O 1s indicated. (d) Schematic atomic structures of $Sb_{2}Te_{3}$ with Wyckoff site labels depicting mixed ionic-covalent bonded quintet layers held by interlayer van der Waals bonding in the undoped, defect-free configuration (left), with an antisite $Sb_{7}Te$ defect (center), and with sulfur doping (right). The Wyckoff site notations are indicated on the left. We used supercells of these structures for our DFT calculations.
Figure 4. Density of states computed using DFT calculations for (a) undoped and (b) sulfur-doped Sb$_2$Te$_3$. The energy scale is referred to the valence band maximum and $E_F$, arbitrarily set to zero, connotes the Fermi level. Sulfur doping increases the density of states in the valence band as can be clearly seen in (c) a magnified view of superimposed density of states of undoped (gray) and S-doped (red). (d) Valence band spectra obtained by synchrotron XPS from our nanobulk S-doped Sb$_2$Te$_3$ pellets.

Figure 5. (a) Planar $[\bar{1}1\bar{0}]$ Seebeck coefficient $\alpha$ for three different carrier concentrations (in cm$^{-3}$), and peak ZT, calculated as a function of temperature. The black circles represent experimentally measured $\alpha$ in our isotropic nanobulk. (b) Pisarenko plot of the planar $[\bar{1}1\bar{0}]$ $\alpha$ and (c) estimated ZT of nanobulk Sb$_2$Te$_3$, both calculated by DFT as a function of hole concentration for various temperatures. Experimental data from sulfur-doped nanobulk Sb$_2$Te$_3$ at 300 K (black circles) and 400 K (red square) are also shown for comparison, along with 300 K data for bulk single-crystal Sb$_2$Te$_3$ from ref 8 for two crystallographic directions $[0001]$ (magenta diamonds) and planar $[\bar{1}1\bar{0}]$ (purple triangles).
\[ xS + 2Sb_{3b} + 3Te_{3c} \]
\[ \Leftrightarrow ySb'_{3c} + xS'^{4+}Te + (2 - y)Sb_{3c} + (2 - y)h \]
\[ + (1 + x - y)V^{**}_{Te} + (2 - y)V^{**}_{Sb} + 3/2Te_{3c}(g) \]

Although we expect \( x = y \), our experimental result shows that the \( h \) decrease exceeds sulfur doping by 15–20\% that is, \( y > x \). We attribute this greater-than-anticipated effectiveness of sulfur doping to a higher activation energy \(^{3,10,29}\) for creating \( Sb_{3c} \) defects in sulfur-doped \( Sb_{2}Te_{3} \) than its undoped counterpart. The increase in activation energy for \( Sb'_{3c} \) formation \( \Delta E_{a} \) due to sulfur doping can be estimated by recognizing that

\[ [Sb'_{3c}]\alpha(c_{Sb} - c_{S})_{\text{exp}} - [(E_{0} + \Delta E_{a})/(kT_{m})] \]

where \( c_{Sb} \) and \( c_{S} \) are \( Sb \) and \( S \) concentrations, respectively, \( T_{m} \) the melting point, and \( E_{0} \) the activation energy \(^{3,10,29}\) in undoped \( Sb_{2}Te_{3} \). Setting \( [Sb'_{3c}] = h \) from Hall measurements of nanobulk pellets with different \( c_{Sb} \) and \( c_{S} \) quantified by WDX, we obtain \( \Delta E_{a} \sim 0.06 \text{ eV} \) connoting a 17% increase over \( E_{0} \sim 0.35 \text{ eV} \). This result is corroborated by density functional theory (DFT) calculations showing \( \Delta E_{a} \sim 0.05 \text{ eV} \) for sulfur doping to the Te 6\% site (see Figure 3d). Calculations with singly charged antisite defects in sulfur-doped \( Sb_{2}Te_{3} \) yield \( \Delta E_{a} \sim 0.17 \text{ eV} \), suggesting that the antisite defects are predominantly uncharged. This result is also consistent with all of the \( Sb \) 3\% core-level bands being attributable to \( Sb-\text{Te bonds}^{14} \) (Figure 3c) and residual surface oxide and the lack of charged state signatures expected at \( >530 \) eV. We are thus persuaded to conclude that subatomic percent doping of substitutional \( Sb \)—supposed to be electronically inactive in pnictogen chalcogenides \(^{26}\)—is more effective in tuning carrier concentration than adding tens of atomic percent of alloying elements \(^{11,23,29}\) which degrade the charge carrier mobility.

Our DFT supercell calculations also reveal that sulfur doping increases the density of states close to the valence band maximum (Figures 4a–c) and creates an additional peak in the \( 1 \to 2.5 \) at. \% doping range. This result suggests the possibility of resonant states \(^{8}\) that can lead to increased \( \alpha \), although this could also be due to limitations of the supercell approximation. The valence band spectra obtained by synchrotron XPS \(^{31}\) (see Figure 4d) agree with envelope profiles of the discrete structure obtained by the DFT calculations, but no resonant states are discernible (see Figure 4d). The absence of an \( O \) 2p peak at \( \sim 5 \text{ eV} \) in the valence band points to inhibited oxidation \(^{26}\) and absence of oxygen doping. The above results confirm sulfur doping is responsible for the observed \( \alpha \) increase, but the question of whether or not there are resonant states remains open.

The high \( ZT \sim 0.95 \) at 420 K despite a comparatively low \( \alpha \sim 150 \mu V\text{K}^{-1} \) suggests the possibility of accessing even higher \( ZT \) through optimized doping. To estimate optimal doping, results of first principles band structure calculations carried out using the linearized augmented plane wave method (see Supporting Information) were used to determine \( \alpha \) as a function of doping and temperature based on Boltzmann transport theory. Our calculations indicate a substantial increase in \( \alpha \) at \( h < 10^{19} \text{ cm}^{-3} \) for a wide temperature range of \( 300 \to 800 \text{ K} \) (Figures 5a,b) with \( \alpha \) maxima \( \geq 200 \mu V\text{K}^{-1} \), without entering the bipolar regime at 300 K. The theoretical calculations agree well with experimentally determined \( \alpha \) in the 300–450 K range (Figure 5a,b), confirming the applicability of our approach.

We calculated \( ZT \) as a function of temperature and hole concentration from experimentally measured \( \kappa_{T} \) and \( \mu \) as a function of \( h \), and theoretically determined \( \alpha \), Lorenz number and \( \kappa_{T} \) using first principles transport calculations. We find \( 1.7 \leq \text{peak } ZT \leq 2 \) for \( 400 \leq T \leq 600 \text{ K} \) for \( h < 3 \times 10^{19} \text{ cm}^{-3} \) (Figure 5b,c). For example, peak \( ZT \sim 2 \) at 500 K for \( h \sim 1.4 \times 10^{19} \text{ cm}^{-3} \) and decreases to 1.2 at 800 K due to bipolar conduction. For nanobulk \( Sb_{2}Te_{3} \) with higher \( h \), the \( ZT \) peaks at higher temperatures, and for a factor of 10 increase in \( h \) the peak \( ZT \) shifts from 300 to 800 K. These results predict unprecedented \( ZT \sim 2 \) without alloying if the antisite defects can be suppressed further by optimal sulfur doping. Furthermore, as mentioned earlier, the weak temperature-dependence of \( \sigma \) suggests that the power factor \( \alpha^2 \sigma \) and \( ZT \) can be improved further via optimization of the grain size and nanostructure.

In summary, we have demonstrated a novel approach for producing high \( ZT \) thermoelectrics by the use of subatomic percent sulfur doping. Sulfur substitution of isovalent Te 6\% sites suppresses antisite defect formation. The resultant 10- to 100-fold decrease in the hole concentration increases \( \alpha \) by 10–25\% over the highest observed in nondoped counterparts. Subatomic sulfur doping also fosters high \( \sigma \) due to the diminished effect of impurity scattering of holes, while nanostructuring results in ultralow \( \kappa \). Cumulatively, we obtain 3-fold higher \( ZT \sim 0.95 \) than non-nanostructured analogues at 423 K and the state-of-art alloys. Our experimental results and theoretical predictions presage that further gains in \( \alpha \), and hence \( ZT \), are possible by manipulating dopant type, level, and site occupancy. Our approach of doping-induced \( \alpha \) increase and nanostructuring-induced \( \kappa \) diminution, without compromising \( \sigma \), opens up new opportunities for obtaining \( ZT > 2 \) and transforming thermo-electric refrigeration and energy-harvesting.