Electronic Supplementary Information

Tailoring Phase Transition Temperature to Achieve High-Performance Cubic GeTe-based Thermoelectrics

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S1. Quality factor *B*, Transport Coefficients σ_{E_0}, and Weighted Mobility μ_W

To understand the nature of transport in more detail, we compute the σ_{E_0} from electrical conductivity σ, which can be expressed as:

$$\sigma = \sigma_{E_0} \ln(1 + e^{\eta}) \tag{1}$$

η can be obtained from experimental Seebeck coefficients via:

$$S = \pm \frac{k_B}{e}\left[\eta - \frac{(r+2.5)F_{r+1.5}(\eta)}{(r+1.5)F_{r+0.5}(\eta)}\right] \tag{2}$$

where r is the scattering exponent (r = -0.5 for acoustic phonon scattering). Essentially, $\sigma_{E_0}$is a convenient expression of electrical conductivity that is independent of carrier concentration. This is especially useful in our case since the carrier concentration values obtained via Hall measurements may not be accurate due to the non-linearity of the Hall voltage versus magnetic field. (i.e. the Hall carrier concentration is typically taken as the linear slope of Hall voltage versus magnetic field, non-linearity in Hall voltage versus magnetic field makes data interpretation inaccurate). Large σ_{E_0} can be associated with good crystalline quality and vice versa. Furthermore, the carrier mobility-equivalent for σ_{E_0} can be expressed as weighted-mobility μ_W. The relation between σ_{E_0} and μ_W can be expressed as:

$$\sigma_{E_0} = \frac{e(2m_e k_B T)^{3/2}}{3\pi^2\hbar^3}\mu_W \tag{3}$$

$$\mu_W = \mu_0 \left(\frac{m^*_{DOS}}{m_e}\right)^{3/2} \tag{4}$$

The main advantage of using weighted-mobility over inaccurately determined Hall mobility lies in the fact that weighted-mobility takes into account the m^*_{DOS} (density of states effective mass). Since the density of states effective mass provides a direct correlation to the Seebeck coefficient, the inverse correlation between electrical conductivity and Seebeck coefficient can be clearly accounted for by looking at the weighted mobility. Hence, it can be used as a robust indication of the thermoelectric power factor. It is important to note that while weighted mobility share some similarities with Hall mobility, their magnitude generally differs, especially for compounds with high band-degeneracy (high m^*_{DOS}). This comes from the fact that weighted mobility has a ${m^*_{DOS}}^{3/2}$ dependence whereas Hall mobility only depends on μ_0(intrinsic mobility) as well as the reduced Fermi level and scattering mechanism.

Lastly, the quality factor B can be evaluated from σ_{E_0} based on the following:

$$B = \left(\frac{k_B}{e}\right)^2 \frac{T}{k_L} \sigma_{E_0} \tag{5}$$

It is evident from equation 5 that in order to enhance the quality factor, σ_{E_0} must be enhanced, either via band convergence, resonant doping, energy filtering, or deformation potential engineering to increase m^*_{DOS}. Alternatively, k_L can be reduced via point defects, strain, dislocation, or stacking faults.

S2. Lorenz Number

The Lorenz number used in this work is calculated from the semi-classical Boltzmann Transport Equations:

$$L = \left(\frac{k_B}{e}\right)^2 \left[\frac{\left(r+\frac{7}{2}\right)F_{r+1.5}(\eta)}{\left(r+\frac{3}{2}\right)F_{r+0.5}(\eta)} - \left(\frac{\left(r+\frac{5}{2}\right)F_{r+1.5}(\eta)}{\left(r+\frac{3}{2}\right)F_{r+0.5}(\eta)}\right)^2\right] \quad (6)$$

Where *r* represents the carrier scattering exponent, set at -0.5 for acoustic phonon scattering.

S3. Tables

T (K)	a (Å)
300	6.167174
373	6.177666
473	6.190507
573	6.202146
623	6.210044
673	6.215292
700	6.219676

Table S1. Lattice parameters for $Ge_{0.4}Sn_{0.4}Bi_{0.02}Sb_{0.12}Te$ for temperature ranging from 300 K to 700 K.

Parameters	Values
vL, m/s	3270
vT, m/s	2040
vm, m/s	2248
Atomic mass, kg	1.91×10^{25}
Sample density, g/cm3	6.46
Debye T, K	213
γ	1.2
Poisson's ratio	0.18
Bulk modulus, GPa	33.2
Young's Modulus, GPa	63.5
Shear Modulus, GPa	26.9
Grain size, um	75
Prefactor of Umklapp process	0.16
Fraction of point defect, %	54

Table S2. Physical properties used to calculate κ_L in cubic $Ge_{0.49-x}Sn_{0.49-x}Bi_{0.02}Sb_{2x}Te$ based on various phonon scattering processes.

S4. Figures

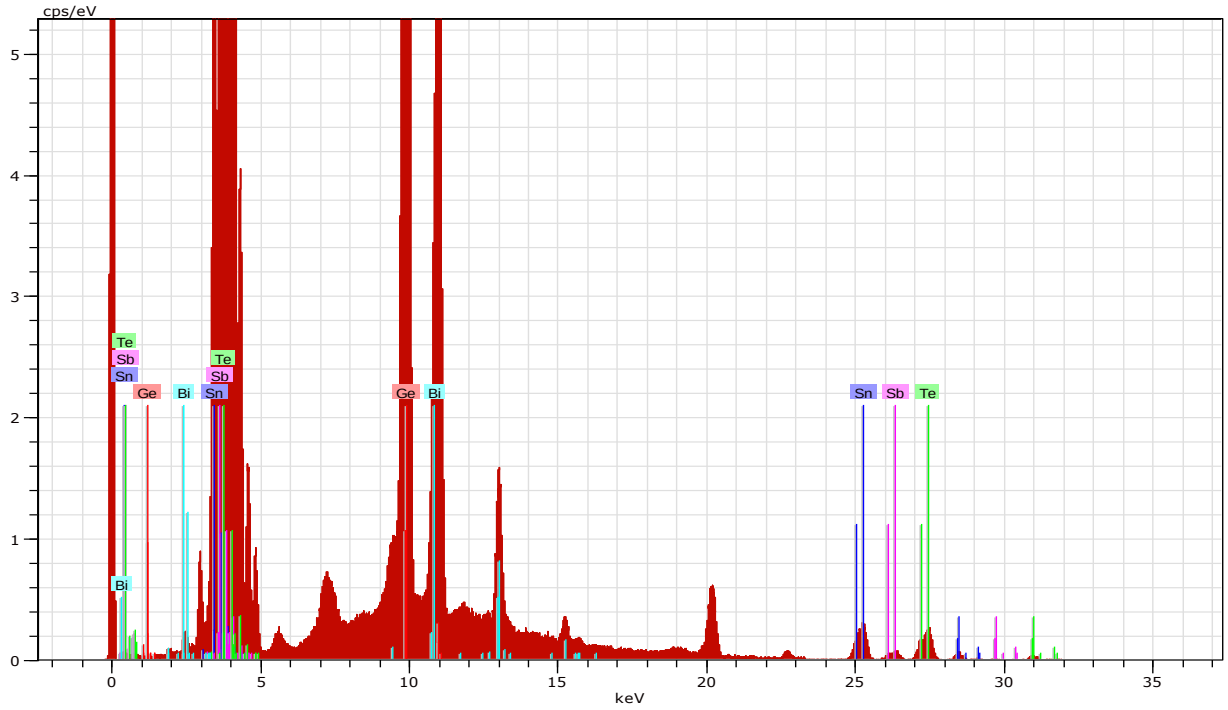

Figure S1. XRF data for $Ge_{0.4}Sn_{0.4}Bi_{0.02}Sb_{0.12}Te$ showing peaks belonging to Ge, Sn, Bi, Sb, and Te.

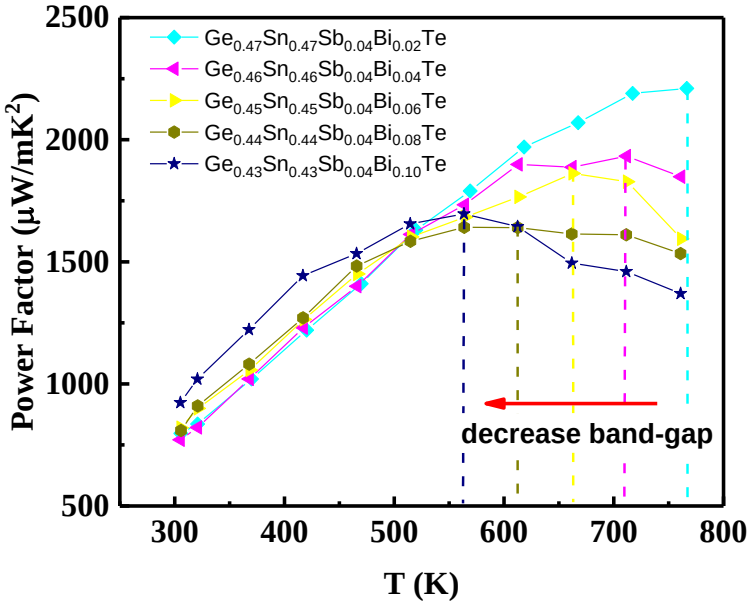

Figure S2. Power factor vs temperature for $Ge_{0.5}Sn_{0.5}Te$ samples with Bi doping ranging from 0.02 to 0.10 showing band-gap decrease with increasing Bi content.

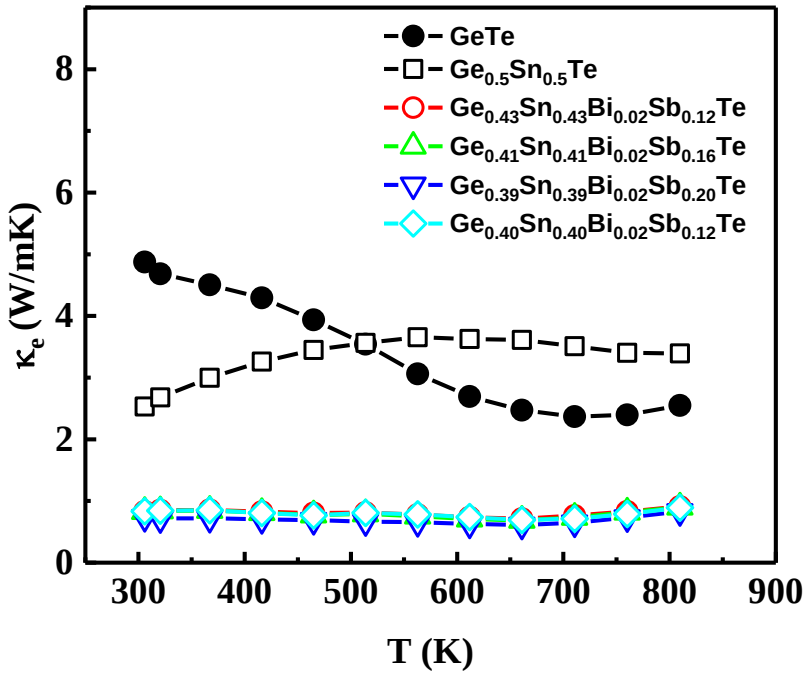

Figure S3. Electronic thermal conductivity of all samples in this work.

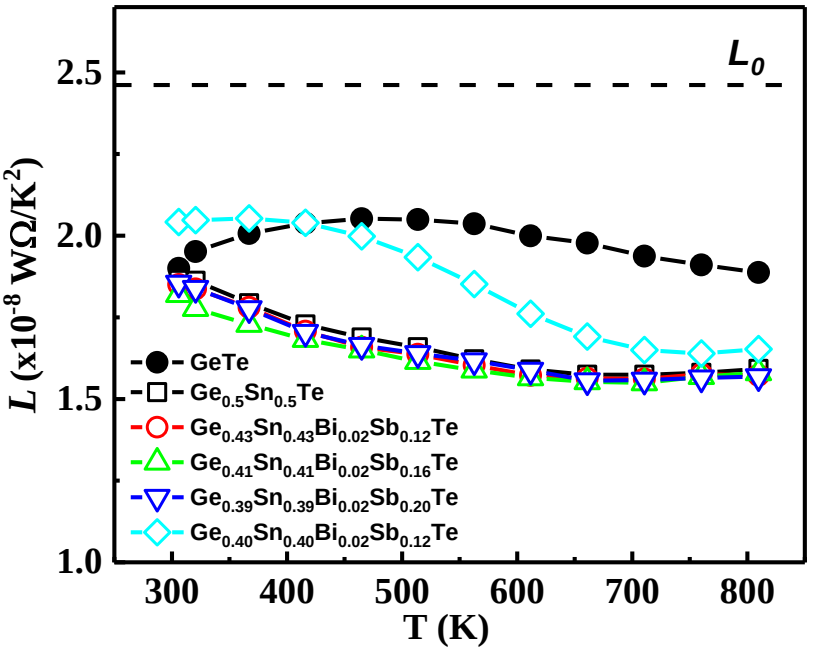

Figure S4. Lorenz number based on Boltzmann Transport Equations using experimental Seebeck coefficients data.

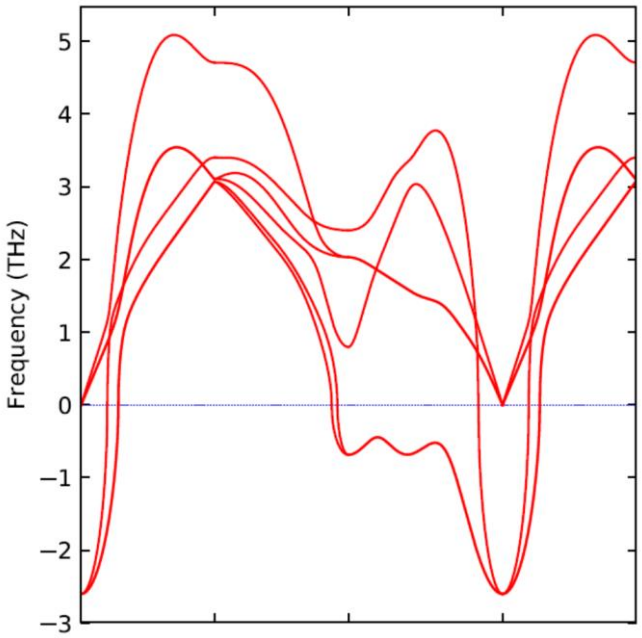

Figure S5. Phonon band structure of GeTe showing imaginary modes which hints at ferroelectric instability.

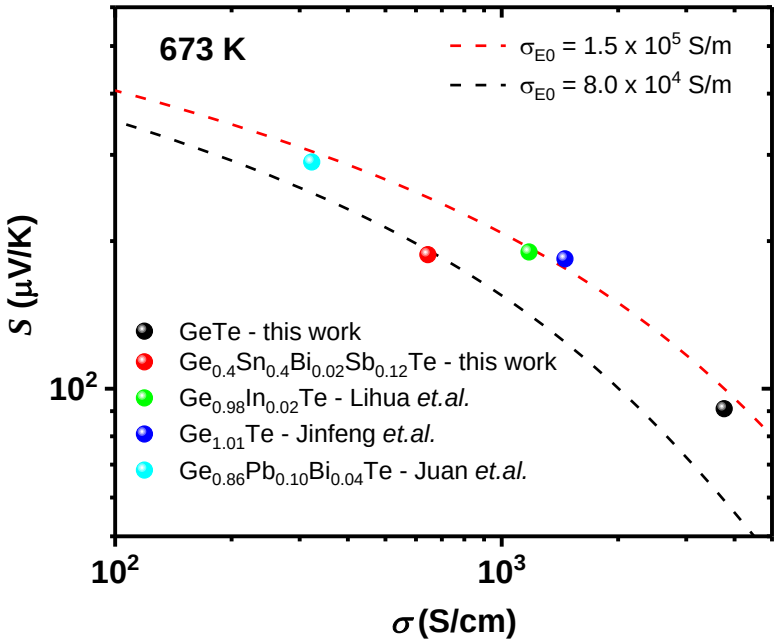

Figure S6. Transport coefficient for $Ge_{0.4}Sn_{0.4}Bi_{0.02}Sb_{0.12}Te$ compared to GeTe in the literatures.

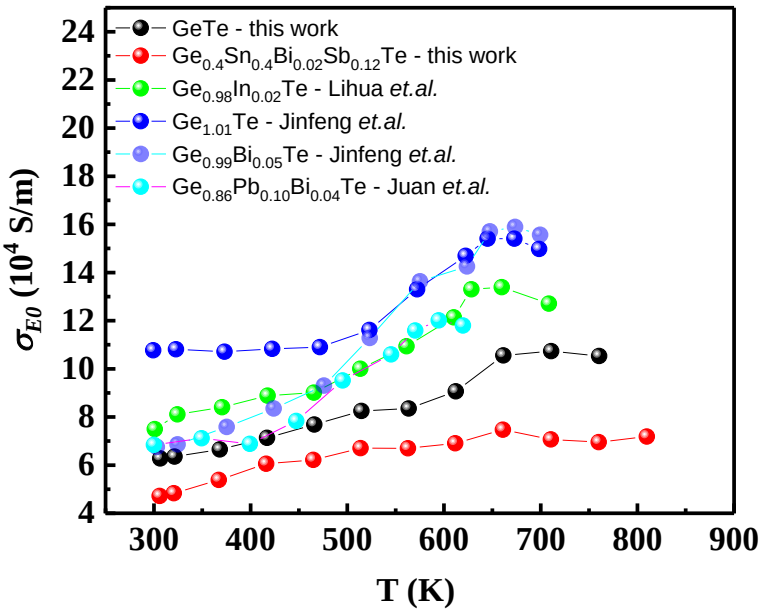

Figure S7. Transport coefficients vs temperature for $Ge_{0.4}Sn_{0.4}Bi_{0.02}Sb_{0.12}Te$ compared to GeTe in the literatures.

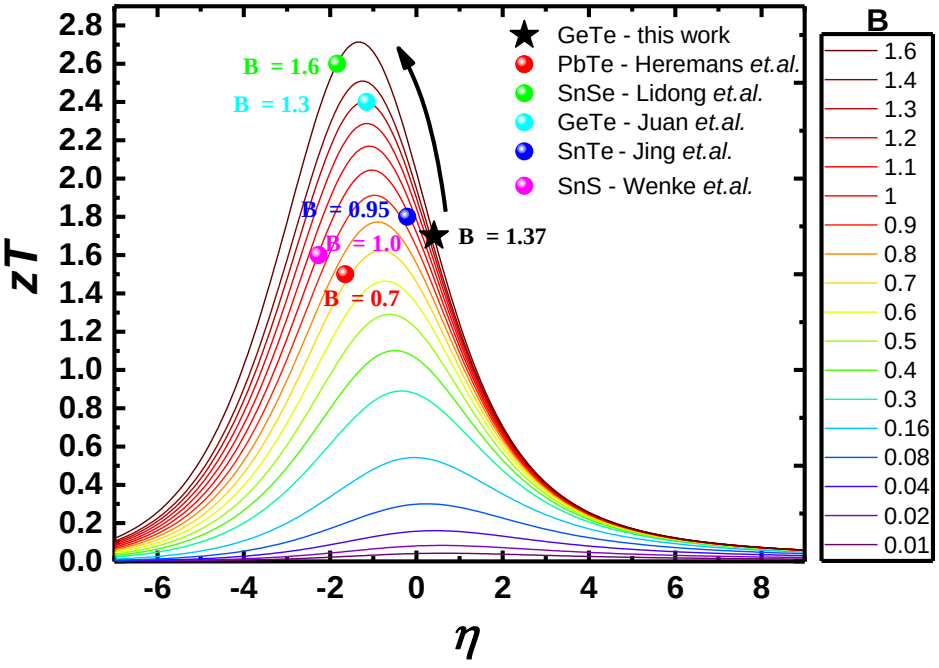

Figure S8. Thermoelectric quality factor of GeTe in this work as compared to other chalcogenides showing highest quality factor for SnSe and GeTe among binary chalcogenide class of materials.[1-5]

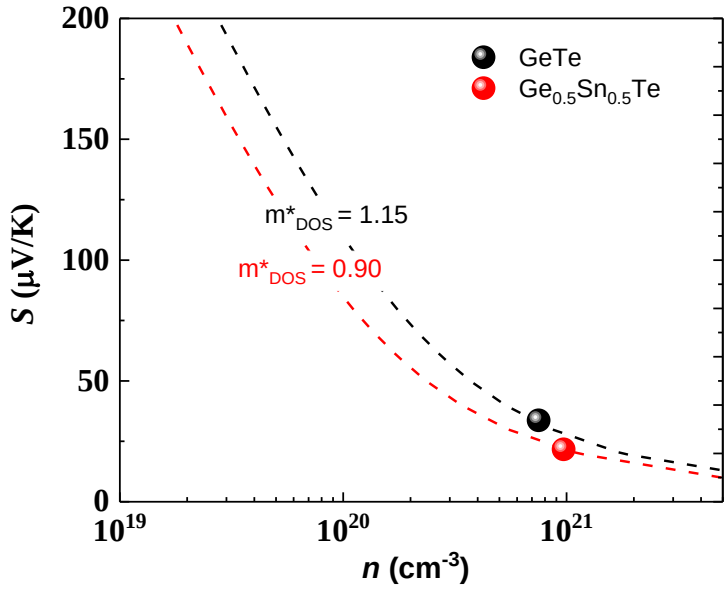

Figure S9. Room temperature Pisarenko plot showing slight decrease in effective mass of $Ge_{0.5}Sn_{0.5}Te$ as compared to pristine GeTe.

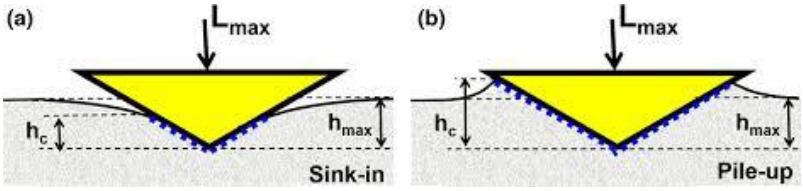

Figure S10. Illustration showing nano-indentation using Berkovich tip. [6]

References

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