Supporting Information

Band and Phonon Engineering for Thermoelectric Enhancements of Rhombohedral GeTe

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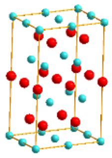
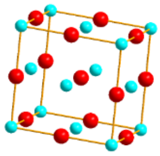
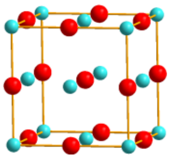
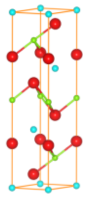
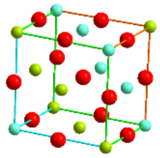
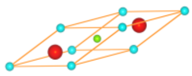
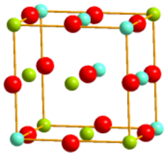
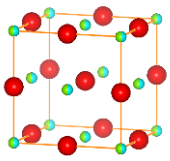
Table S1. Crystal structures, lattice parameters and interaxial angles for GeTe and $AgBiSe_2$.

	Space group	**Crystal Structure** 	**Lattice Parameters and Interaxial Angles**	**Distorted Crystal Structure from Cubic Lattice** 	**Lattice Parameters and Interaxial Angles**
Rhombohedral GeTe	R$\bar{3}$m		a=b=8.3580 Å, c=10.7070 Å α=β=90° γ=120°		a=b=c=6.0019 Å, α=β=γ=88.258°
Cubic GeTe	Fm$\bar{3}$m		a=b=c=5.9860 Å α=β=γ=90°		
Hexagonal $AgBiSe_2$	P$\bar{3}$m1		a=b=4.18 Å, c=19.67 Å α=β=90° γ=120°		a=5.8163 Å, b= 5.7944 Å, c=5.8942 Å, α=91.89°, β=92.34°, γ=90.33°
Rhombohedral $AgBiSe_2$	R$\bar{3}$m		a=b=c=7.02 Å α=β=γ=34.5°		a=b=c=5.8316 Å, α=β=γ=91.15°
Cubic $AgBiSe_2$	Fm$\bar{3}$m		a=b=c=5.83 Å α=β=γ=90°		

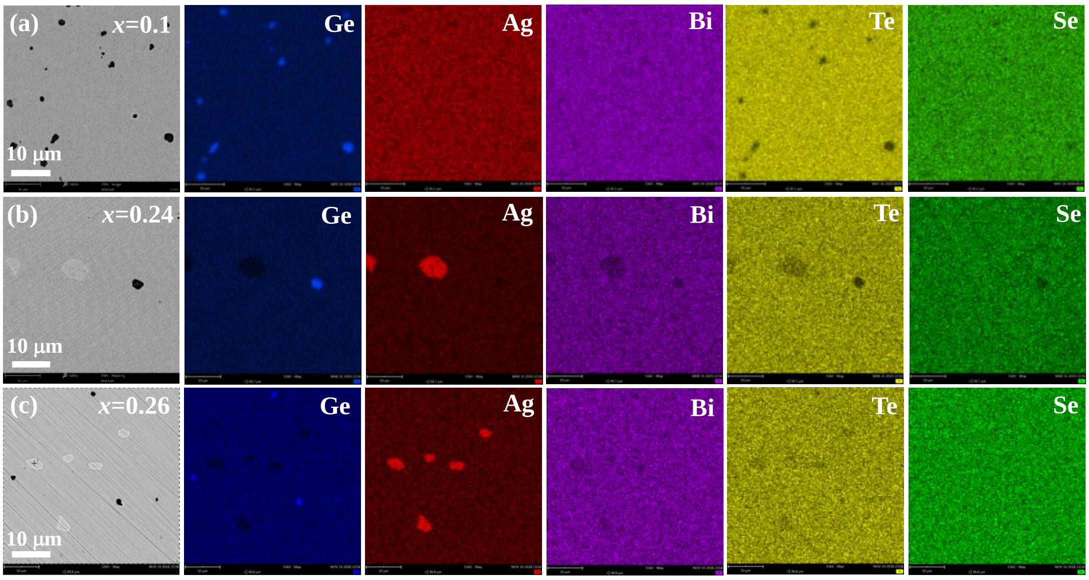


Figure S1. Back-scattering SEM images and corresponding EDS mappings for the samples with x=0.1 (a), x=0.24 (b) and x=0.26 (c).

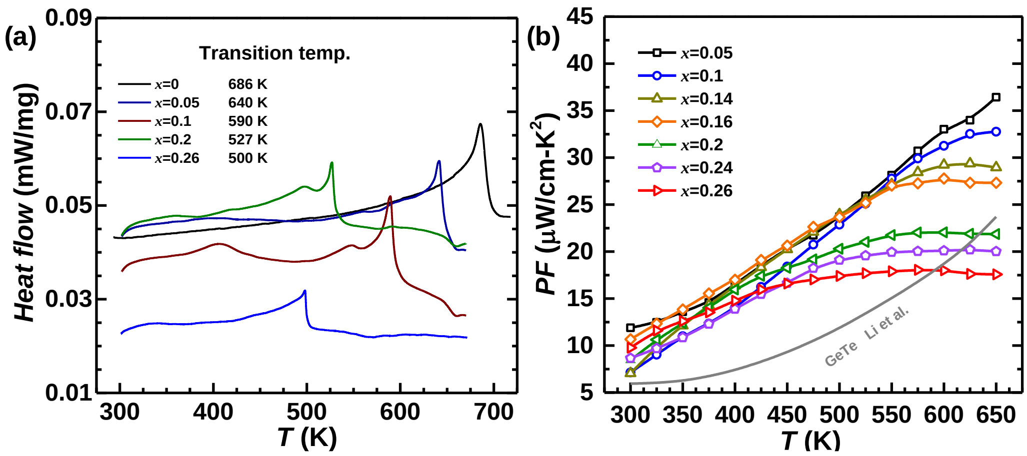


Figure S2. Temperature dependent power factor (a) and heat flow (b) for $(GeTe)_{1-x}(Ag_{0.5}Bi_{0.5}Se)_x$.

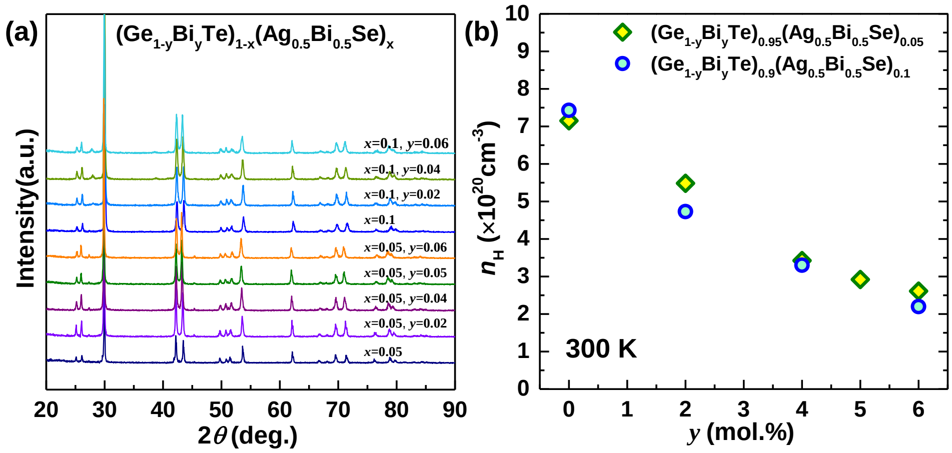


Figure S3. Room temperature powder XRD patterns (a), and composition dependent Hall carrier concentration for $(Ge_{1-y}Bi_yTe)_{1-x}(Ag_{0.5}Bi_{0.5}Se)_x$ (b).

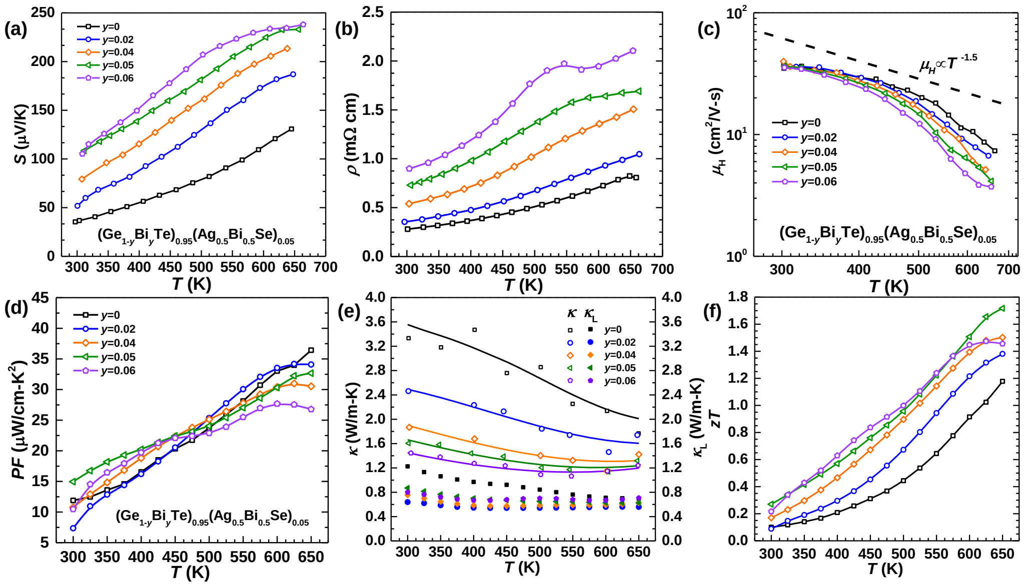


Figure S4. Temperature dependent Seebeck coefficient (a), resistivity (b), Hall mobility(c), power factor(d), total and lattice thermal conductivity (e) and *zT* (f) for $(Ge_{1-y}Bi_yTe)_{0.95}(Ag_{0.5}Bi_{0.5}Se)_{0.05}$.

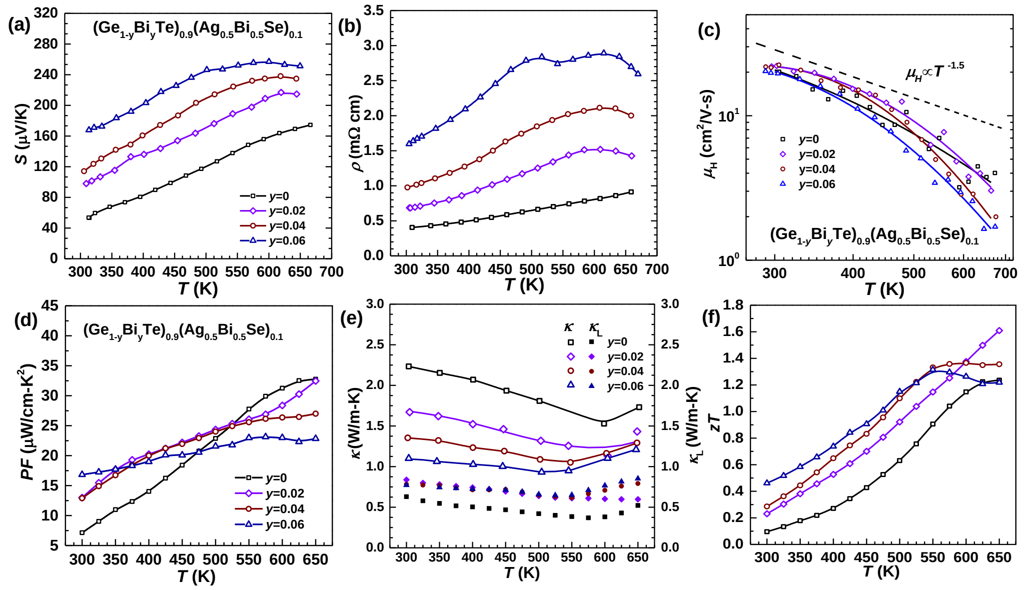


Figure S5. Temperature dependent Seebeck coefficient (a), resistivity (b), Hall mobility(c), power factor(d), total and lattice thermal conductivity (e) and *zT* (f) for $(Ge_{1-y}Bi_yTe)_{0.9}(Ag_{0.5}Bi_{0.5}Se)_{0.1}$.

Using the measured longitudinal (v_L) and transverse (v_T) sound velocities, the corresponding physical parameters including Debye temperature (θ_D), Poisson ratio (ε), bulk modulus (B) and Grüneisen parameter (γ) are estimated according to the equations as below[1-2]:

$$v_s^2 = \frac{v_L^2 + 2v_T^2}{3} \qquad (1)$$

$$\theta_D = \frac{h}{k_B}\left[\frac{3N}{4\pi v_s^2}\right]^{-1/3} \qquad (2)$$

$$\left(\frac{v_L}{v_T}\right)^2 = \left(\frac{2\text{-}2\varepsilon}{1\text{-}2\varepsilon}\right) \qquad (3)$$

$$B = \frac{d(3v_L^2 - 4v_T^2)}{3} \qquad (4)$$

$$\gamma_D = \frac{3}{2}\frac{3v_L^2 - 4v_T^2}{v_L^2 + 2v_T^2} \qquad (5)$$

where v_s is the mean sound velocity, $\hbar$ is the Planck constant, k_B is the Boltzmann constant, N is the Avogadro constant, d is the density.

References:

1. Sanditov, D. S.; Belomestnykh, V. N., Relation between the parameters of the elasticity theory and averaged bulk modulus of solids. *Tech Phys+* **2011,** *56* (11), 1619-1623.

2. Roufosse, M.; Klemens, P. G., Thermal Conductivity of Complex Dielectric Crystals. *Phys Rev B* **1973,** *7* (12), 5379-5386.