Supporting Information

Promoted thermoelectric performance in cubic-phase GeTe *via* grain-boundary phase elimination under phase diagram guidance

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Experimental details

Materials fabrication:

Ge (pieces, 99.99 %), Te (particle, 99.99 %), Ag (chunks, 99.99 %) and Sb (granules, 99.99 %) were used as raw materials to synthesize $(GeTe)_x(Ag_{0.8}Sb_{1.2}Te_{2.2})_{100-x}$ (x = 75, 76, 77, 78, 79) and $(GeTe)_{78}(Ag_{1-\delta}Sb_{1+\delta}Te_{2+\delta})_{22}$ (δ = 0.2, 0.21, 0.22, 0.23, 0.24) (written as: δ-TAGS-78) utilizing melting and quenching method. These mixtures were load into evacuated quartz tubes and encapsulated with 10^{-4} Pa, following put into the furnace and heated up to 1173K in 12 h and kept there for 12 hours before being quenched in water. Then, the as-obtained ingots were annealed at 773 K for 24 h. After that, the obtained ingots were hand-ground into powders in agate mortar, then poured into a ϕ15 mm graphite die and sintered using spark plasma sintering (SPS) method (Sinter Land INC, Japan) under 50 MPa and 723K in vacuum (< 6 Pa) for 5min.

The obtained bulk samples were cut into a block with cross section of 3×3×12 mm^3 for electrical transport measurements and 6×6×2 mm^3 for thermal diffusion coefficient (D) measurements.

Thermoelectric properties measurements:

The commercial ZEM-3 apparatus (Ulvac-Riko, Japan) was performed to measure the Seebeck coefficient and electrical conductivity under dilute helium atmosphere. The uncertainties of measurements were estimated to be about 5%. The thermal conductivity κ was calculated *via* $\kappa = D\, C_p \rho$, where D is thermal diffusivity coefficient can be obtained using the LFA-467 (Netzsch, Germany) laser flash under nitrogen atmosphere, ρ is the mass density measured using the Archimedes method (Mettler Toledo, Model XSE105DU), and C_p is the heat capacity which was estimated by the Dulong-Petit limit. The uncertainty of thermal conductivity was estimated to be about 7%. The electronic thermal conductivity (κ_{ele}) was calculated according to Wiedemann-Franz law: $\kappa_{ele} = \sigma LT$, where the Lorenz factor (L) was roughly calculated by the equation: $L = 1.5 + \exp(-|S|/116)$.[1] Considering the uncertainties of all the parameters, the uncertainty of the calculated ZT was about 13%. Room temperature carrier concentration and carrier mobility were measured with Van der Pauw method (Lake Shore 8400 Series, Model 8404, USA), with an uncertainty of about 10%.

Structural characterization

Powder X-ray diffraction using a diffractometer (MiniFlex600, Rigaku, Tokyo, Japan) was conducted to analyze the crystal structures. With Cu Kα radiation (λ = 1.5418 Å, 40 kV, 40 mA), while the scanning rate of 10° min^{-1} from 2θ = 20° to 80°.

Transmission electron microscopy (TEM), Cs-corrected high-angle angular dark field-scanning transmission electron microscopy (HAADF-STEM) and energy dispersive X-ray mapping (EDX) experiments were performed using a FEI Titan Themis 60-300 kV microscope equipped with a Super-X detector and operating at 300 kV.

Mechanical properties

The Vickers hardness and Young's modulus were measured through a nano-indentation technique (iMicro KLA, USA).

The temperature-dependent relative length variation was measured on a thermal dilatometer (DIL 402 Expedis Supreme, Netzsch), where the slope of corresponding curves indicates the coefficient of thermal expansion.

Weighted mobility

The temperature-dependent weighted mobility (μ_w) was derived from the experimental electrical conductivity σ and Seebeck coefficient S proposed by G. J. Snyder et al:[2]

$$\mu_w = 331\left(\frac{1}{\rho}\right)\left(\frac{1}{300}\right)^{-\frac{3}{2}}\left[\frac{\exp\left[\frac{|S|}{k_B/e} - 2\right]}{1+\exp\left[-5\left(\frac{|S|}{k_B/e} - 1\right)\right]} + \frac{\frac{3}{\pi^2}\frac{|S|}{k_B/e}}{1+\exp\left[5\left(\frac{|S|}{k_B/e} - 1\right)\right]}\right]$$

where μ_w is the weighted mobility, ρ is the electrical resistivity measured in mΩ cm, T is the absolute temperature in K, S is the Seebeck coefficient, and k_B/e = 86.3 μV K^{-1}.

Thermoelectric generator fabrication

The thermoelectric power generator (TEG) with an overall size of 20×20 mm^2, in which composed of eight-pair of p-type legs $(GeTe)_{78}(Ag_{0.77}Sb_{1.23}Te_{2.23})_{22}$ and n-types leg $Pb_{0.985}Sb_{0.015}Te$. The SPS-sintered p- and n-type bulk was cut into thermoelectric legs with geometric dimensions sizes of ~3.5×3.5mm^2, and Ni as a diffusion barrier material was electroplated to the as-obtained legs. The TEG was assembled with soldering the thermoelectric pairs onto a copper-clad plate at the hot side using tin-based high-temperature solder, whereas directly bonding a copper substrate at the cold side. The TEG performance is characterized by a commercial instrument (PEM-2, Riko), with the cold-side temperature is fixed at 293 K and the hot-side temperature is varied from 473 K to 773 K. The asbestos blanket was further used as heat insulator to reduce the radiant heat.

Supporting Figures

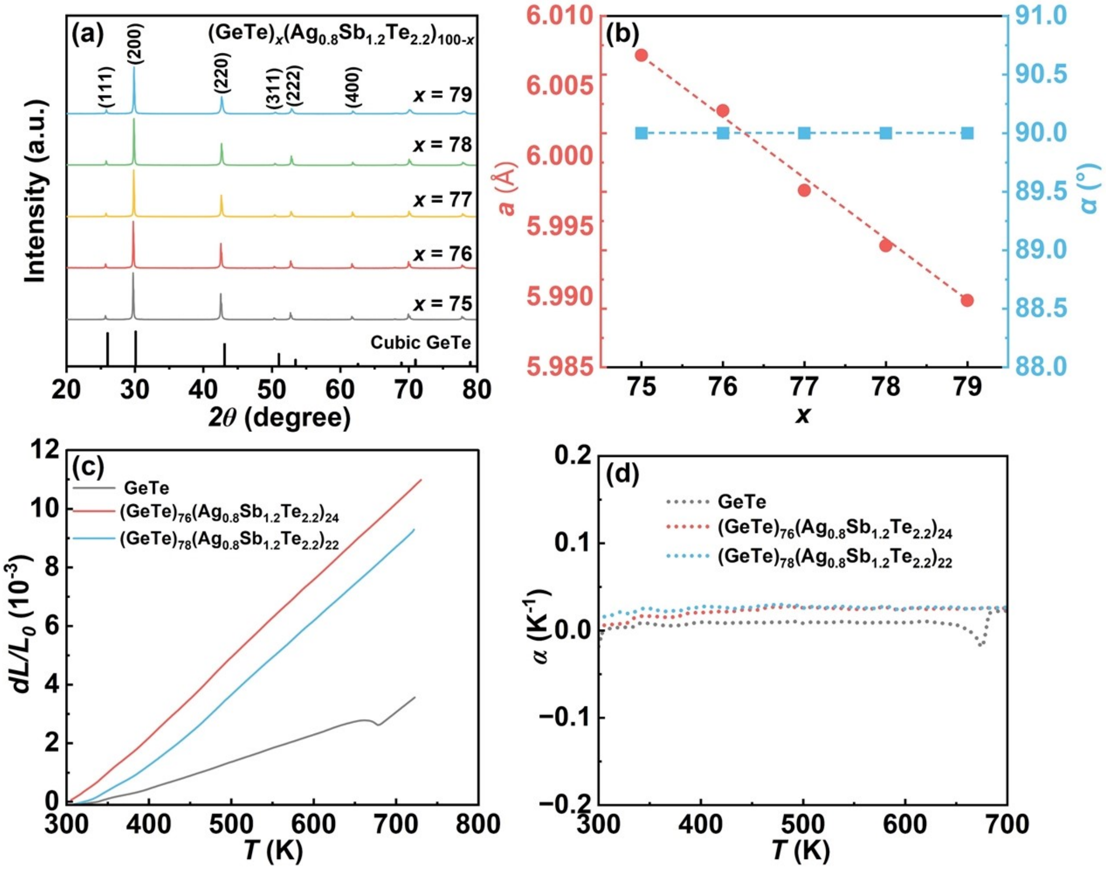

Figure S1 (a) Room-temperature powder XRD patterns, (b) calculated lattice parameters and interaxial angles α of $(GeTe)_x(Ag_{0.8}Sb_{1.2}Te_{2.2})_{100-x}$ (x = 75, 76, 77, 78, 79). (c) Temperature-dependent thermal expansion rate (dL/L_0), and (d) calculated coefficient of thermal expansion for x = 76, 78 (δ = 0.2) as compared with pristine GeTe.

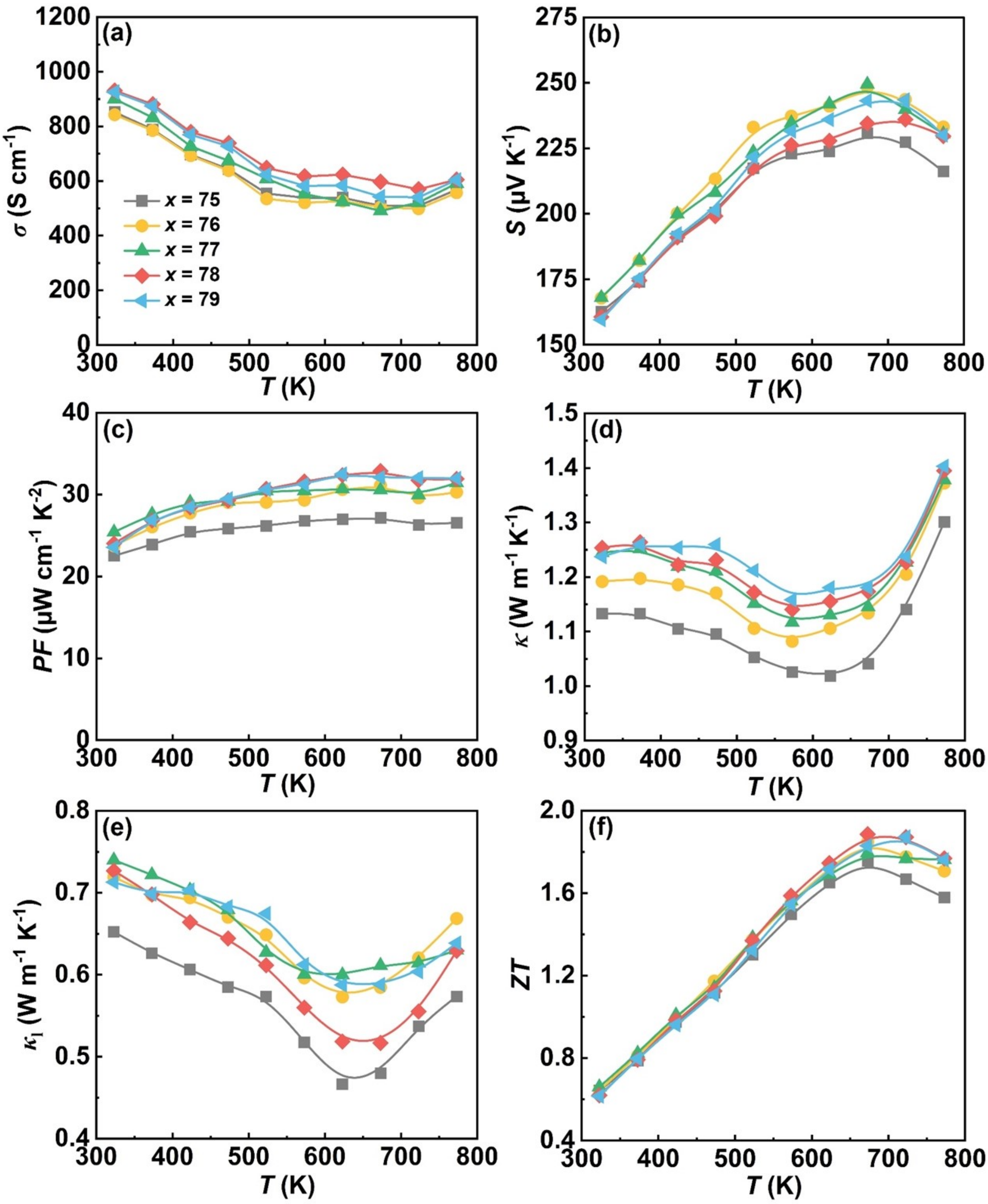

Figure S2 Thermoelectric properties of $(GeTe)_x(Ag_{0.8}Sb_{1.2}Te_{2.2})_{100-x}$ (x = 75, 76, 77, 78, 79). Temperature-dependent (a) electrical conductivity, (b) Seebeck coefficient, (c) power factor, (d) total thermal conductivity, (e) lattice thermal conductivity and (e) *ZT* values.

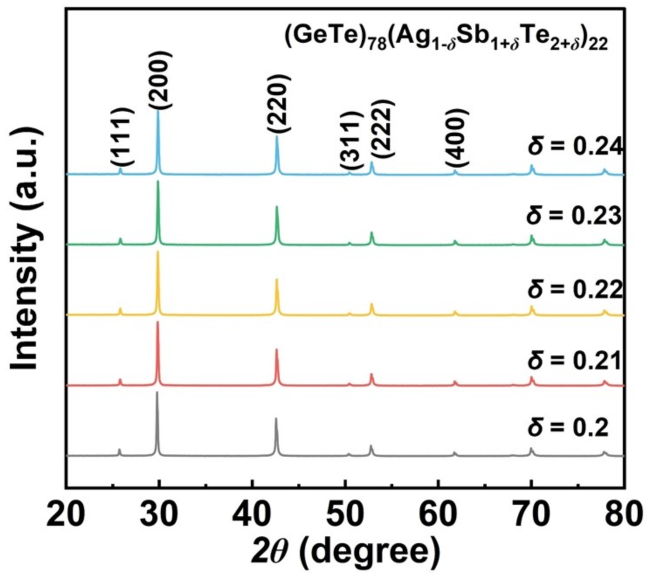

Figure S3 Room-temperature powder XRD patterns of $(GeTe)_{78}(Ag_{1-\delta}Sb_{1+\delta}Te_{2+\delta})_{22}$ (δ = 0.2, 0.21, 0.22, 0.23, 0.24).

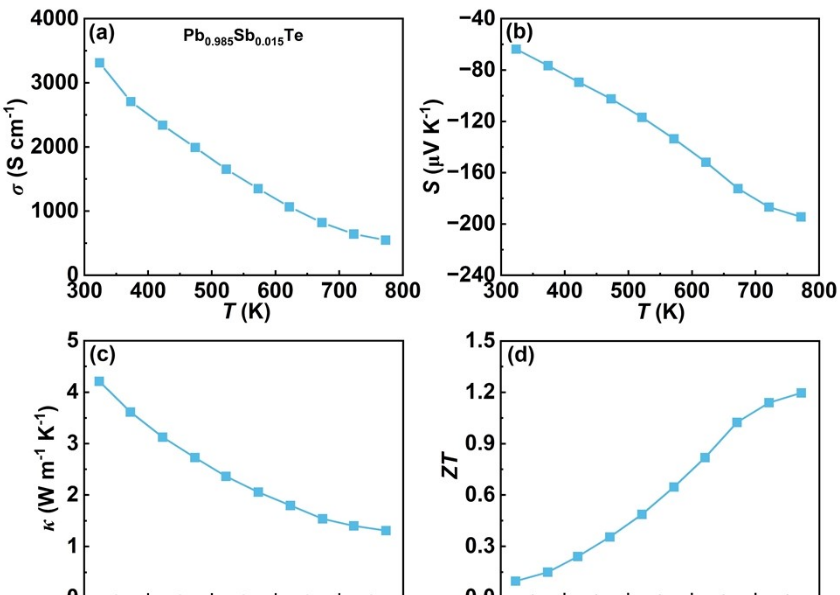

Figure S4 Thermoelectric properties of *n*-type $Pb_{0.985}Sb_{0.015}Te$. Temperature-dependent (a) electrical conductivity, (b) Seebeck coefficient, (c) total thermal conductivity, and (d) *ZT* value.

References

[1] H. S. Kim, Z. M. Gibbs, Y. Tang, H. Wang and G. J. Snyder, *APL Mater*., 2015, **3**, 041506.

[2] G. J. Snyder, A. H. Snyder, M. Wood, R. Gurunathan, B. H. Snyder, and C. Niu, *Adv. Mater*., 2020, **32**, 2001537.