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Supporting Information:

Hierarchical structures lead to high thermoelectric performance in $Cu_{m+n}Pb_{100}Sb_mTe_{100}Se_{2m}$ (CLAST)

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Experimental details

Put purity elements into quartz tubes according to the corresponding stoichiometric ratio including Pb pieces (99.99%, Aladdin element, China), Cu granules (99.9%, Alfa Aesar, China), Sb pieces (99.99%, Aladdin element, China), Te pieces (99.999%, Aladdin element, China), Se pieces (99.999%, Aladdin element, China) and seal the quartz tubes under 10^{-4} Pa. Then heat them from room temperature to 1323 K for 24 h, wait 10 h at 1323 K, and let them cool down with furnace. Then, ground the obtained ingots into powder respectively, and some block samples were prepared by spark plasma sintering (SPS-211Lx, Dr. Sinter). The phase identification was analyzed by X-ray diffraction (XRD, D/max 2200pc, Japen) operating at 40 KV and 20 mA with the Cu Kα radiation (λ = 1.5418 Å). The electrical transport performance was detected by Cryoall CTA. Calculate the total thermal conductivity (κ) according to the formula $\kappa = D \times C_p \times \rho$. The thermal diffusivity (D) was measured using Netzsch LFA 457. Use the mass and volume of the sample to calculate the sample density (ρ). The specific heat capacity (C_p) was evaluated by Debye law. The carrier concentration (n) was tested with the Lake Shore 8400 Series instrument, and the carrier mobility (μ) was calculated by $\mu = \sigma /(e \times n)$, where e was electrical conductivity and e was unit charge. Samples used for TEM and STEM were prepared by traditional mechanical polishing and ion milling. TEM imagines, STEM imagines and EDS mappings were carried out by JEOL F200 and JEOL ARM 200F equipped with a probe corrector operated at 200kV.

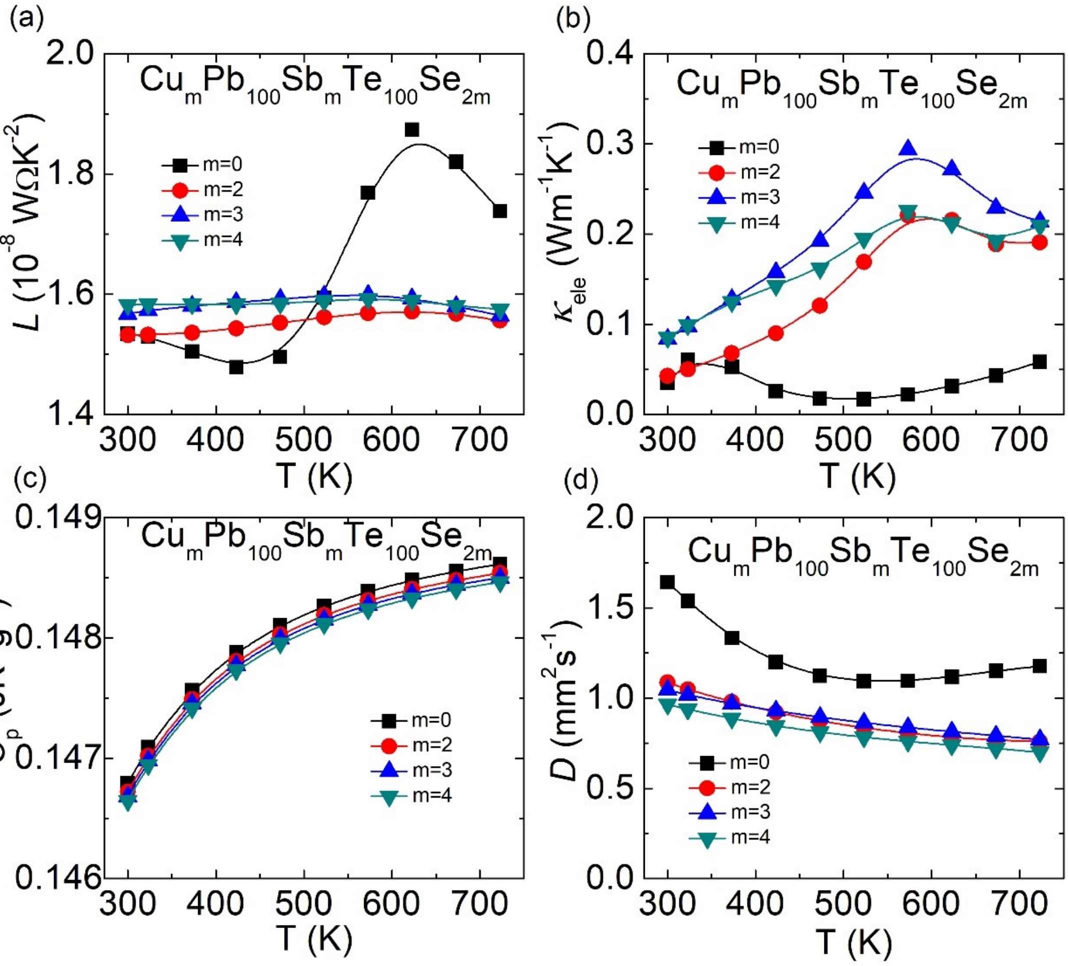

Fig. S1 Thermoelectric transport properties as a function of temperature for $Cu_mPb_{100}Sb_mTe_{100}Se_{2m}$ (m = 0-4): (a) Lorenz number; (b) Electronic thermal conductivity; (c) Heat capacity; (d) Thermal diffusivity.

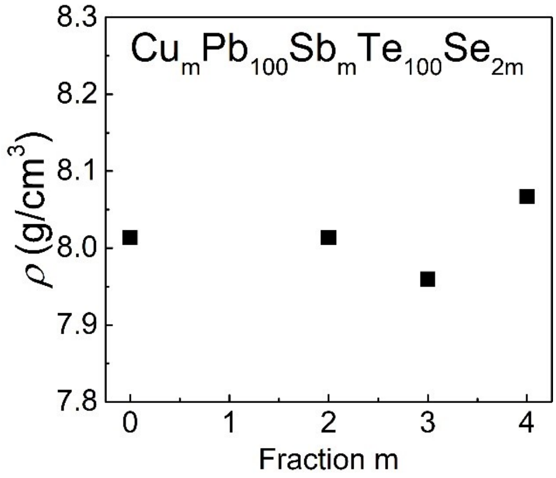

Fig. S2 Sample density of $Cu_mPb_{100}Sb_mTe_{100}Se_{2m}$ (m = 0-4).

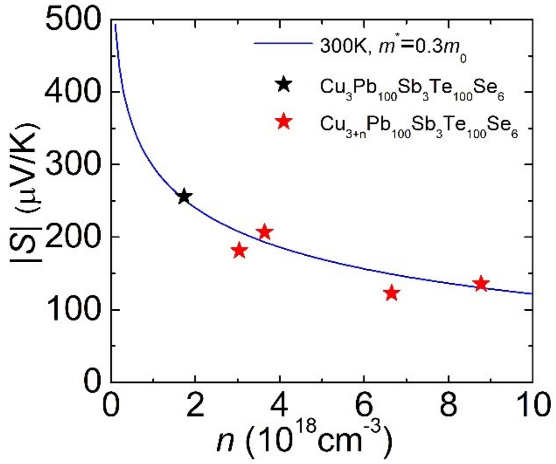

Fig. S3 Room-temperature Pisarenko plots of $Cu_{3+n}Pb_{100}Sb_3Te_{100}Se_6$.

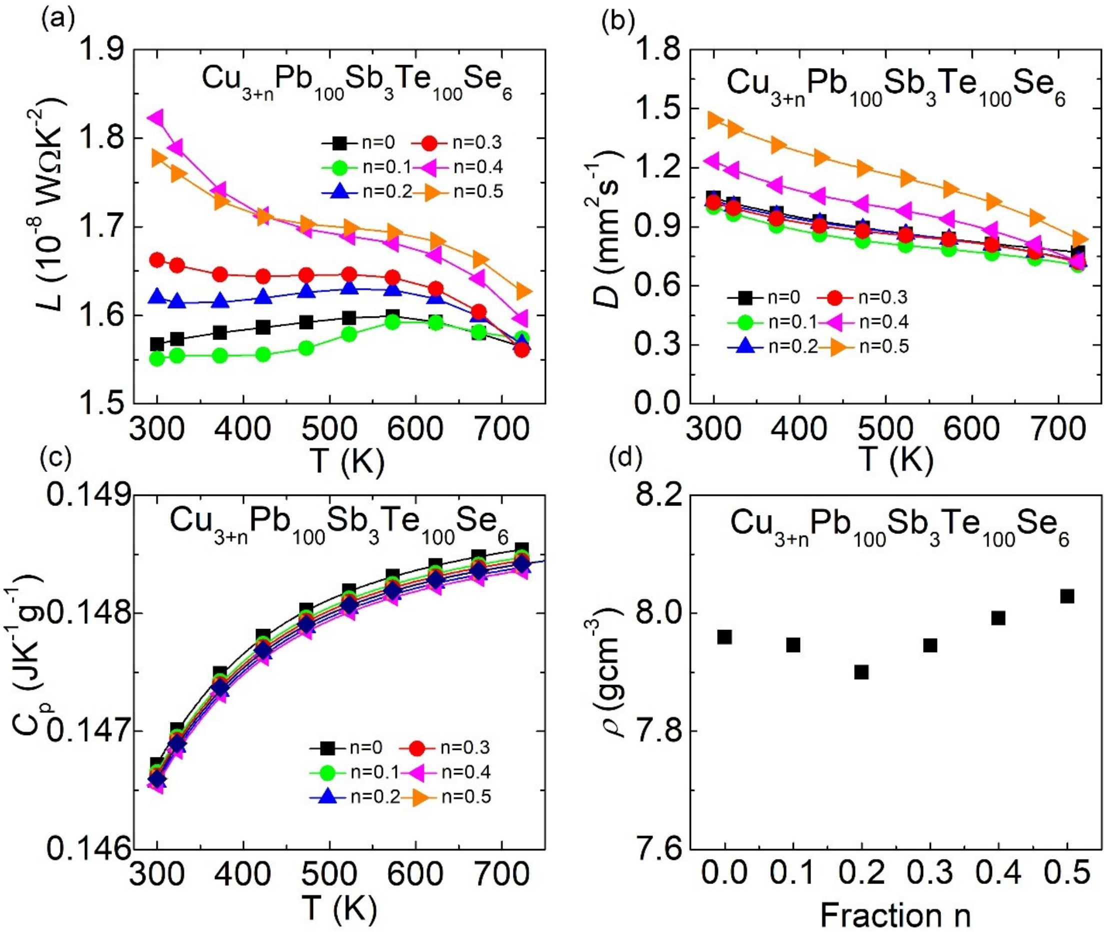

Fig. S4 Thermoelectric transport properties as a function of temperature for $Cu_{3+n}Pb_{100}Sb_3Te_{100}Se_6$ (n = 0-0.5): (a) Lorenz number; (b) Thermal diffusivity; (c) Heat capacity; (d) Sample density.

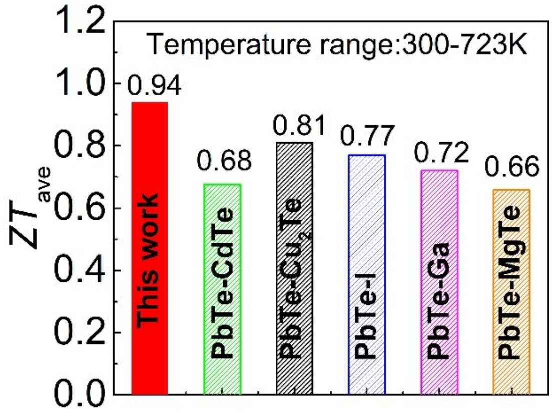

Fig. S5 Comparisons of ZT_{ave} values in *n*-type PbTe-based thermoelectric materials (PbTe-CdTe[1], PbTe-Cu_2Te[2], PbTe-I[3], PbTe-Ga[4], PbTe-MgTe[5]).

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