This ESI for *J. Mater. Chem. A*, 2019, DOI: 10.1039/C9TA05115E, originally published on 20th June 2019, was updated on 10th July 2019 to fix an error in the legend of Fig. S3 ('Cu 4d' was corrected to 'Cu 3d').

Electronic Supporting information for

Significant average *ZT* enhancement in Cu_3SbSe_4-based thermoelectric material via softening *p-d* hybridization

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1) Effective mass and Lorenz number calculation based on SPB model

The effective mass (m^*) and Lorenz number (L) are calculated according to the following equations [1-2]:

$$S = \pm \frac{\kappa_B}{e}\left(\frac{(r+5/2)F_{r+3/2(\eta)}}{(r+3/2)F_{r+1/2(\eta)}} - \eta\right) \quad (1)$$

$$F_n(\eta) = \int_0^\infty \frac{x^n}{1+e^{x-n}}\mathrm{d}x \quad (2)$$

$$m^* = \frac{h^2}{2k_B T}\left[\frac{n}{4\pi F_{1/2}(\eta)}\right]^{2/3} \quad (3)$$

$$L = \left(\frac{\kappa_B}{e}\right)^2\left\{\frac{(r+7/2)F_{r+5/2(\eta)}}{(r+3/2)F_{r+1/2(\eta)}} - \left[\frac{(r+5/2)F_{r+3/2(\eta)}}{(r+3/2)F_{r+1/2(\eta)}}\right]^2\right\} \quad (4)$$

Where η is the reduced Fermi energy, $F_n(\eta)$ is the n^{th} order Fermi integral, κ_B is the Boltzmann constant, e is the electron charge, h is the Planck constant and r is the scattering factor. The scattering factor (r) is -1/2 as the acoustic phonon scattering is

independent of the grain size and is generally assumed to be the main scattering mechanism at room temperature.

2) Callaway model calculation

The Debye-Callaway model is used to describe the influence of point defects on the lattice thermal conductivity. Following equations [3-5] are used for the modeling of the composition-dependent lattice thermal conductivity:

$$\frac{\kappa_L^{cal}}{\kappa_L^{pure}} = \frac{tan^{-1}(U)}{U} \tag{5}$$

$$U = \left(\frac{\pi^2 \theta_D \Omega}{h v^2} \kappa_L^{pure} \Gamma\right)^{\frac{1}{2}} \tag{6}$$

$$\Gamma = \Gamma_m + \Gamma_s = x(1-x)\left[\left(\frac{\Delta M}{M}\right)^2 + \varepsilon\left(\frac{\Delta r}{r}\right)^2\right] \tag{7}$$

Where κ_L^{pure} is the lattice thermal conductivity of the parent sample, $\kappa_L^{cal}$is the calculated lattice thermal conductivity, θ_D is the Debye temperature calculated from the sound velocity measurement, h is the Planck constant, Ω is the average volume per atom, v is the average sound velocity, Γ is the total disorder parameter which includes the mass fluctuation part (Γ_m) and strain field fluctuation part (Γ_s), M is the average atomic mass, ΔM is the mass difference, r is the average atomic radius, Δr is the atomic radius difference, ε is the lattice anharmonic parameter estimated by the method from refs [6].

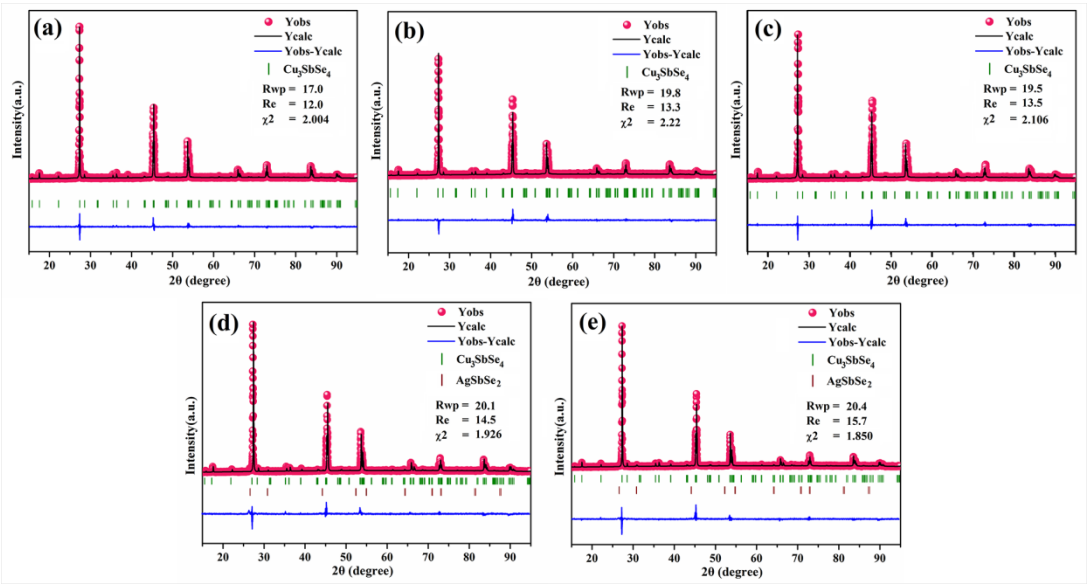

Fig. S1. Rietveld refinement using X-ray diffraction data for $Cu_{3-3x}Ag_{3x}SbSe_4$ samples: (a) x = 0.02; (b) x = 0.03; (c) x = 0.04; (d) x = 0.05; (e) x = 0.06.

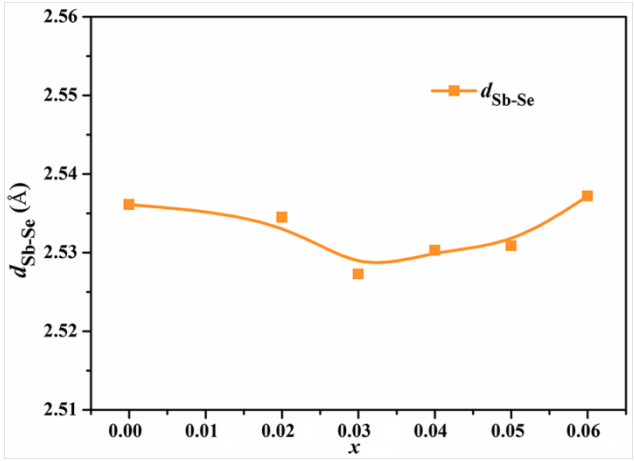

Fig. S2. The calculated distance between Sb site and Se site for $Cu_{3-3x}Ag_{3x}SbSe_4$ (x = 0, 0.02, 0.03, 0.04, 0.05, 0.06) samples.

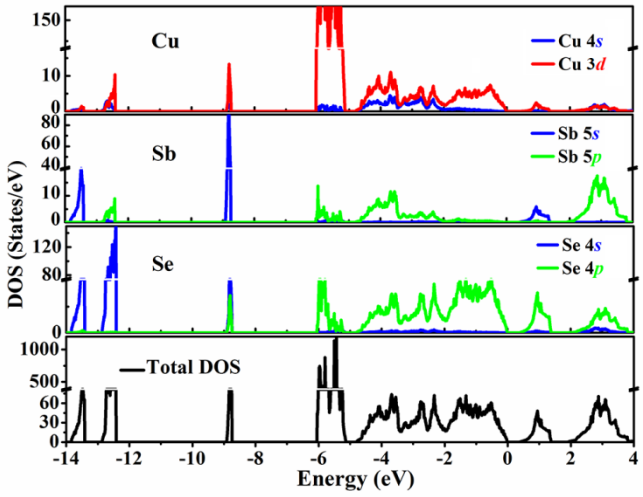

Fig. S3. The calculated total and partial density of states (PDOS) for pristine Cu_3SbSe_4.

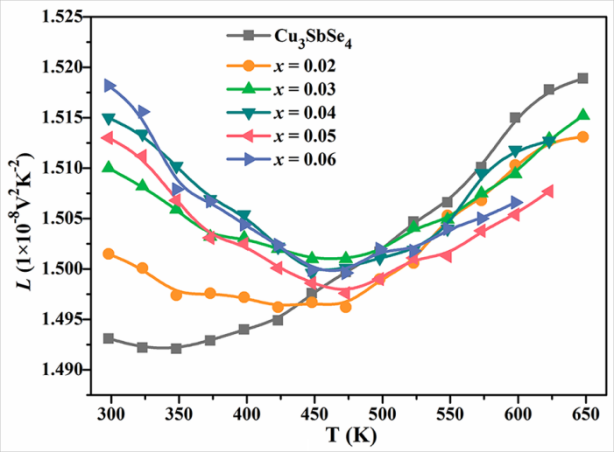

Fig. S4. Temperature dependence of the calculated Lorenz number.

Tab. S1. The relative content of $AgSbSe_2$, calculated carrier effective mass (m^*), and measured density for $Cu_{3-3x}Ag_{3x}SbSe_4$ samples (x= 0, 0.02, 0.03, 0.04, 0.05 and 0.06).

Sample	$AgSbSe_2$ (*wt.*%)	m^* (m_e)	Density (g.cm^{-3})	Theoretical Density (%)
***x* = 0.00**	--	1.40	5.60	96.6
***x* = 0.02**	--	1.46	5.55	95.7
***x* = 0.03**	--	1.80	5.67	97.8
***x* = 0.04**	--	1.60	5.56	95.9
***x* = 0.05**	0.48	1.41	5.61	96.7
***x* = 0.06**	1.29	1.21	5.58	96.2

Tab. S2. Physical parameters (average sound velocity v_a, Debye temperature θ, Poisson ratio ε, bulk modules B and Grüneisen parameter γ) calculated from the measured longitudinal (v_L) and transverse (v_T) sound velocity at room temperature for $Cu_{3-3x}Ag_{3x}SbSe_4$ samples (x = 0, 0.02, 0.03, 0.04, 0.05 and 0.06)

Sample	v_L （m/s）	v_T （m/s）	v_a（m/s）	θ(K)	ε	B (GPa)	γ
***x* = 0.00**	3976	2012	2256	238	0.3	62.4	1.96
***x* = 0.02**	3896	1963	2201	232	0.3	59.4	1.97
***x* = 0.03**	3896	1955	2193	231	0.3	59.1	1.99
***x* = 0.04**	3899	1989	2229	235	0.3	60.8	1.93
***x* = 0.05**	3889	1964	2202	232	0.3	59.5	1.97
***x* = 0.06**	3862	1955	2192	231	0.3	58.9	1.96

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