Electronic Supplementary Information

Calculations for the Grüneisen parameter in Cu_8GeSe_6:

The Grüneisen parameter is estimated by [1]

$$\kappa_L = A\frac{M_{avg}\Theta_D^3\delta}{\gamma^2 n^{2/3}T} \quad , \quad (1)$$

where κ_L is the lattice thermal conductivity, M_{avg} is the average mass per atom, δ^3 is the average volume per atom, n is the number of atoms in the primitive unit cell (n = 90 for Cu_8GeSe_6), and A is a collection of physical constants ($A = 3.1\times10^{-6}$ if κ is in W m^{-1} K^{-1}, M_{avg} is in amu, and δ is in Angstroms).

Table S1 Chemical composition of Cu_8GeSe_6, $Cu_8GeSe_{5.1}Te_{0.9}$ and $Cu_{7.6}Ag_{0.4}GeSe_{5.1}Te_{0.9}$ measured by EDS at 10 randomly selected locations.

Nominal composition: Cu_8GeSe_6 **Actual composition: $Cu_{7.95}GeSe_{5.98}$**										
elements	**Atomic percent concentration (normalized to 100%)**									
Cu	53.28	53.35	53.05	53.38	53.21	53.19	53.46	53.26	53.32	52.92
Ge	6.49	6.81	6.59	6.75	6.53	6.74	6.82	6.77	6.72	6.75
Se	40.24	40.02	40.36	39.87	40.26	40.08	39.72	39.96	39.96	40.29
Nominal composition: $Cu_8GeSe_{5.1}Te_{0.9}$ **Actual composition: $Cu_{7.86}GeSe_{5.03}Te_{0.88}$**										
elements	**Atomic percent concentration (normalized to 100%)**									
Cu	52.99	54.19	53.74	53.56	52.12	53.48	52.98	53.23	53.11	53.09
Ge	6.94	6.70	6.98	7.00	6.60	6.62	6.82	6.60	6.59	6.83
Se	34.22	33.14	33.47	33.45	35.24	33.90	34.63	33.87	34.57	33.92
Te	5.85	5.98	5.81	5.99	6.04	6.01	5.98	6.30	5.73	6.15
Nominal composition: $Cu_{7.6}Ag_{0.4}GeSe_{5.1}Te_{0.9}$ **Actual composition: $Cu_{7.45}Ag_{0.37}GeSe_{5.04}Te_{0.86}$**										
elements	**Atomic percent concentration (normalized to 100%)**									
Cu	50.33	50.44	50.30	50.39	50.87	50.58	50.63	50.72	50.70	50.66
Ag	2.65	2.55	2.44	2.43	2.49	2.50	2.51	2.58	2.48	2.51
Ge	6.78	6.71	6.86	6.75	6.73	6.86	6.73	6.84	6.68	6.92
Se	34.47	34.53	34.35	34.37	34.10	34.19	34.25	34.00	34.19	34.00
Te	5.78	5.78	5.80	5.82	5.81	5.86	5.88	5.87	5.96	5.92

Table S2 Parameters used to fit the heat capacity (C_P) data of Cu_8GeSe_6, $Cu_8GeSe_{5.1}Te_{0.9}$, and $Cu_{7.6}Ag_{0.4}GeSe_{5.1}Te_{0.9}$ by using a Debye and two Einstein modes. R^2 stands for the correlation coefficient. The Debye temperature (Θ_D) is derived by the equation $\Theta_D = (12\pi^4 pR/5\beta)^{1/3}$, where R is the gas constant and p is the number of atoms in each molecule (p = 15 for our samples).

Fitting parameters	Cu_8GeSe_6	$Cu_8GeSe_{5.1}Te_{0.9}$	$Cu_{7.6}Ag_{0.4}GeSe_{5.1}Te_{0.9}$
φ (10^{-3}Jmol^{-1}K^{-2})	26.68±2.79	49.76±3.01	42.01±2.79
β (10^{-4}Jmol^{-1}K^{-4})	10.5±0.332	11.1±0.332	12.1±0.318
A (Jmol^{-1}K^{-1})	16.335±0.597	14.094±0.642	14.196±0.548
Θ_{E1} (K)	36.426±0.419	35.953±0.515	33.812±0.363

B (Jmol^{-1}K^{-1})	78.851±1.697	77.774±1.584	79.023±1.457
Θ_{E2} (K)	82.110±0.920	79.854±0.921	76.170±0.765
Θ_D (K)	302.81	297.3	288.83
R^2	0.99994	0.99988	0.99986
χ^2	0.0000585	0.000111	0.000148

Table S3 Parameters used to fit the heat capacity (C_P) data of Cu_8GeSe_6 by using different methods (one Debye and one Einstein modes, one Debye and two Einstein modes, one Debye and three Einstein modes).

Fitting parameters	One Debye+ One Einstein	One Debye+ Three Einstein
φ (10^{-3}Jmol^{-1}K^{-2})	80.43±14.62	11.38±3.76
β (10^{-4}Jmol^{-1}K^{-4})	19.2±0.822	8.7±0.385
A (Jmol^{-1}K^{-1})	46.088±2.303	4.202±1.399
Θ_{E1} (K)	53.908±1.084	26.722±2.021
B (Jmol^{-1}K^{-1})		24.552±1.844
Θ_{E2} (K)		47.957±2.773
C (Jmol^{-1}K^{-1})		82.919±1.792
Θ_{E3} (K)		92.645±2.267
Θ_D (K)	247.63	322.40
R^2	0.99618	0.99998
χ^2	0.00362	0.0000173

Table S4 Parameters used to fit the lattice thermal conductivity (κ_L) of $Cu_{7.6}Ag_{0.4}GeSe_{5.1}Te_{0.9}$.

Fitting parameters	**$Cu_{7.6}Ag_{0.4}GeSe_{5.1}Te_{0.9}$**
L (μm)	0.634
A (10^{-41} s^3)	14.304
B (10^{-17} s K^{-1})	2.8848
C_1 (10^{36} s^{-3})	0.1206
ω_1 (THz)	3.442
C_2 (10^{36} s^{-3})	19.55
ω_2 (THz)	6.889
R^2	0.99800
χ^2	0.005987

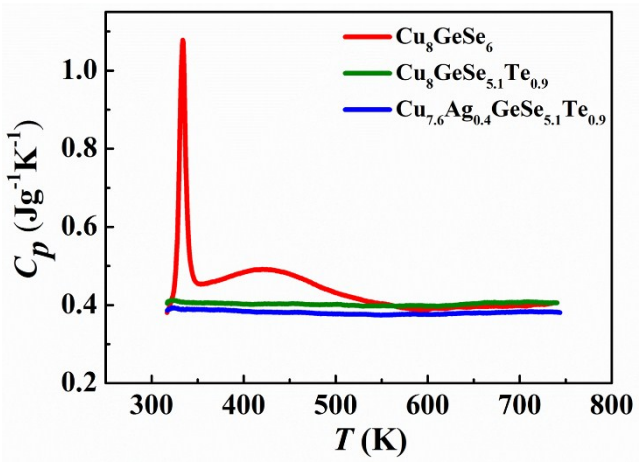

Fig. S1 Temperature dependence of the heat capacity for Cu_8GeSe_6, $Cu_8GeSe_{5.1}Te_{0.9}$ and $Cu_{7.6}Ag_{0.4}GeSe_{5.1}Te_{0.9}$ at constant pressure.

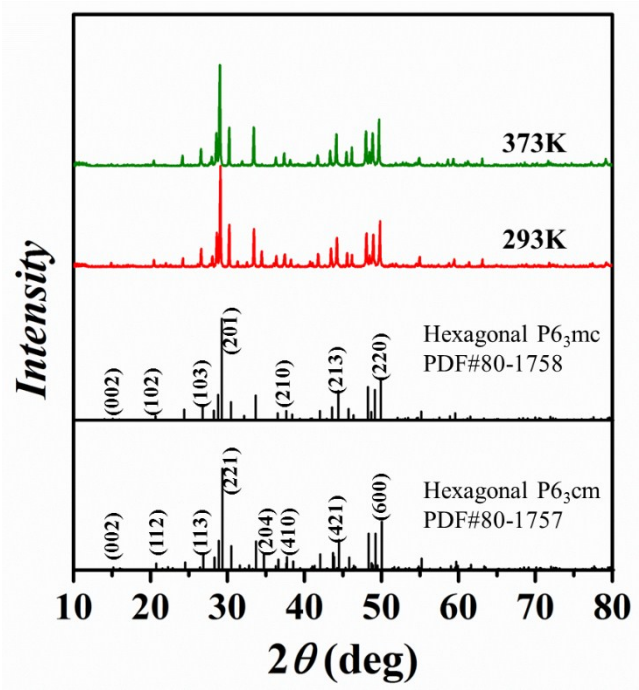

Fig. S2 XRD patterns for Cu_8GeSe_6 at 293K and 373K.

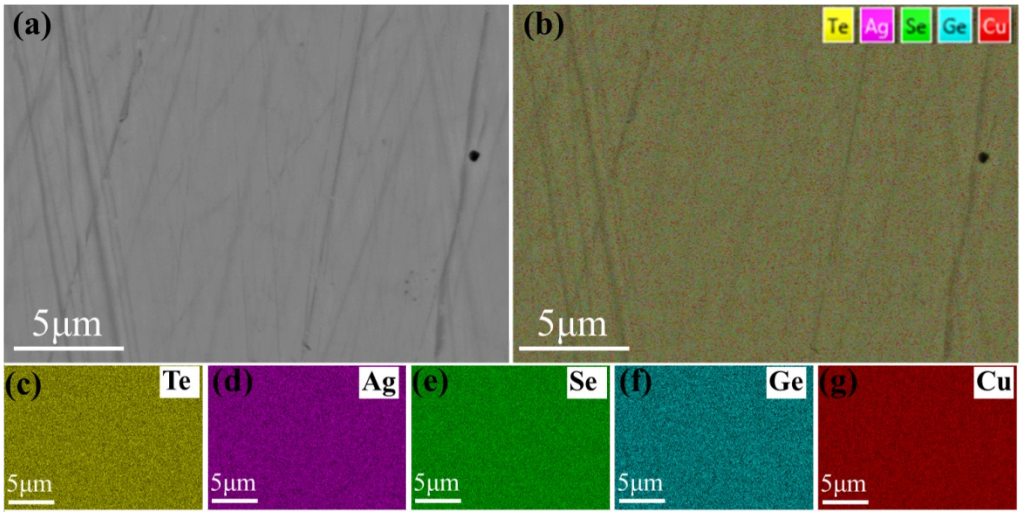

Fig. S3 Scanning electron microscopy (SEM) images of $Cu_{7.6}Ag_{0.4}GeSe_{5.1}Te_{0.9}$. (a) Backscattered electron imaging map, (b) all elements, (c) Te, (d) Ag, (e) Se, (f) Ge, and (g) Cu mappings.

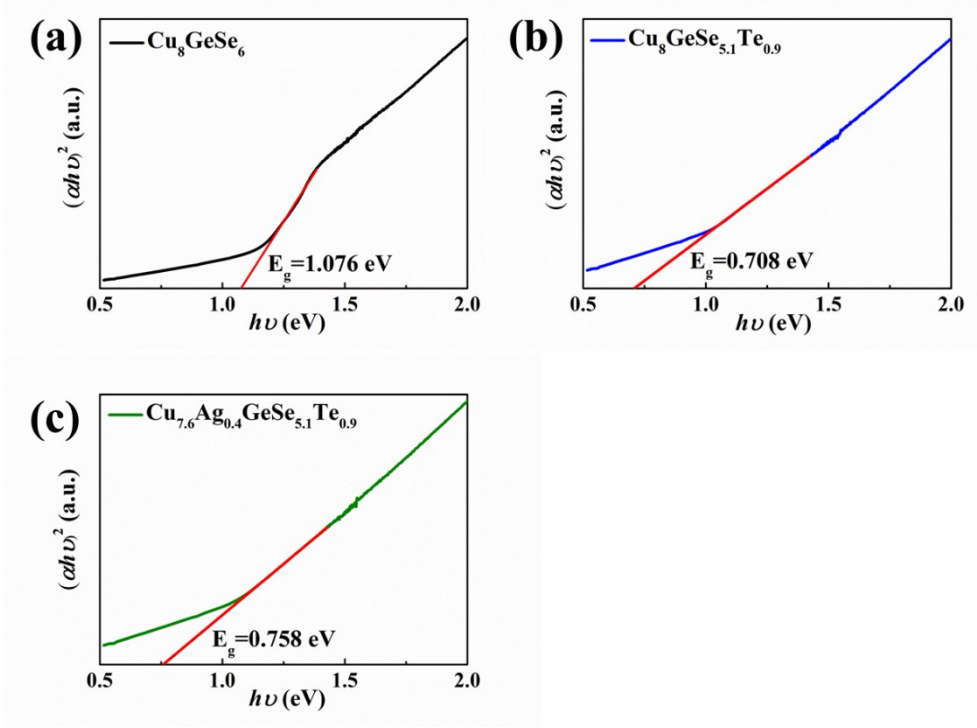

Fig. S4 $(\alpha h\upsilon)^2$ as a function of photon energy $h\upsilon$. An extrapolation of the spectra (red lines) is used to estimate optical band gap values for Cu_8GeSe_6, $Cu_8GeSe_{5.1}Te_{0.9}$ and $Cu_{7.6}Ag_{0.4}GeSe_{5.1}Te_{0.9}$.

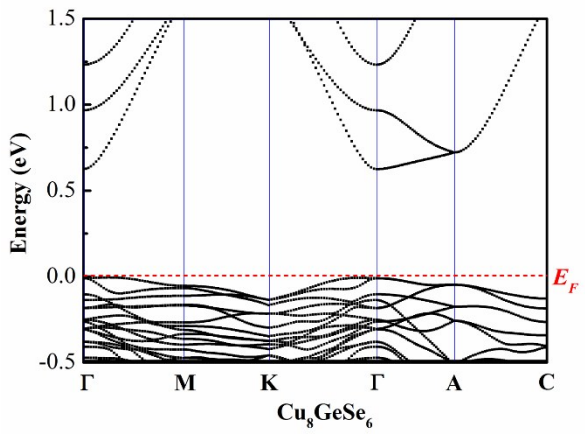

Fig. S5 Calculated band structure of low temperature phase Cu_8GeSe_6 using revised PBE + 6U method. The Fermi level is set to zero. The calculated band structure indicates a direct transition. The CBM is mainly dominated by Se-4s and 4p bands, and the VBM is mainly from the Cu-3d and Se-4p bands, which indicates a direct allowed transition.

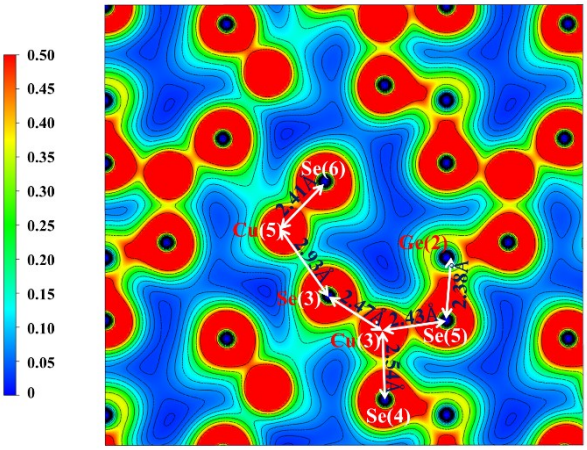

Fig. S6 Total charge density map of low-temperature phase Cu_8GeSe_6. The plot is on the Se(6)-Cu(5)-Se(3) plane. The unit is e/ Å^3. The contour lines are plotted from 0 to 0.50 e/ Å^3 with 0.05 e/ Å^3 intervals.

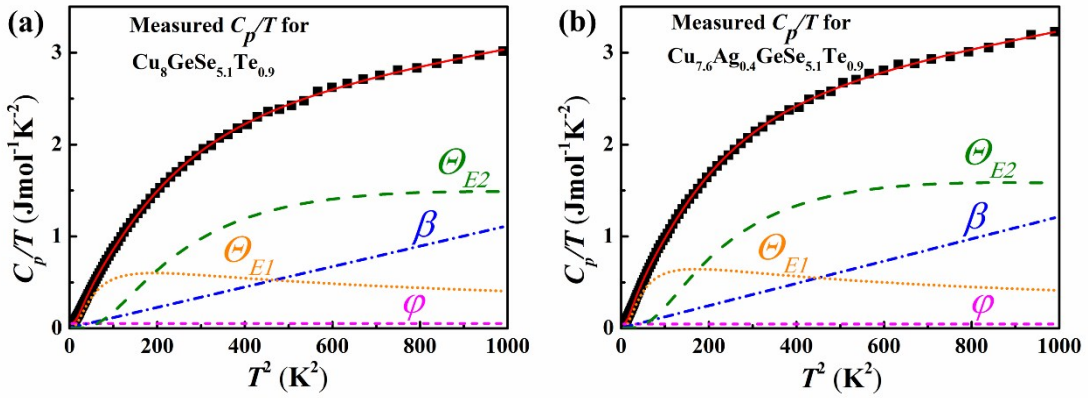

Fig. S7 Measured C_p/T versus T^2 for $Cu_8GeSe_{5.1}Te_{0.9}$ and $Cu_{7.6}Ag_{0.4}GeSe_{5.1}Te_{0.9}$ (black

squires). The red solid line represents the fitted curve by using one Debye mode and two Einstein modes. The other lines represent the electronic term φ, Debye term β, and two Einstein terms, Θ_{E1} and Θ_{E2}.

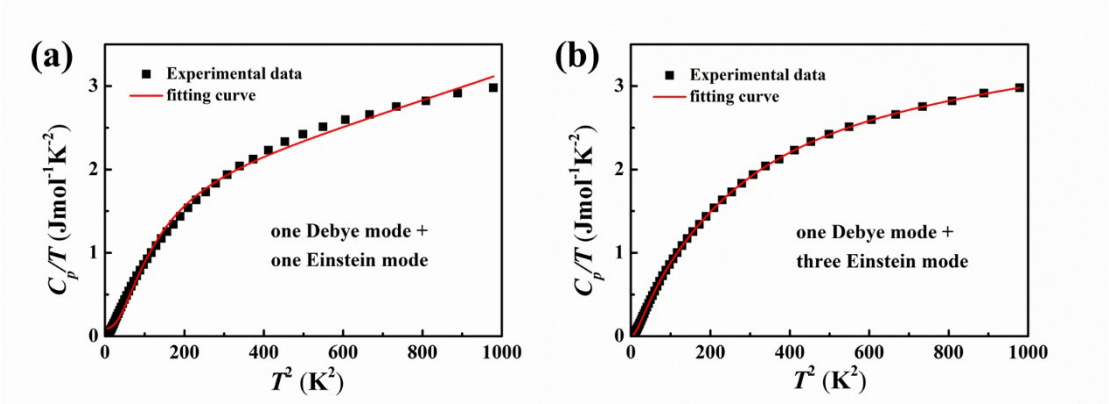

Fig. S8 Measured C_p/T versus T^2 for Cu_8GeSe_6 (black squires). The red solid line represents the fitted curve by using different methods, (a) one Debye and one Einstein mode, (b) one Debye and three Einstein modes.

References

1 D. T. Morelli, V. Jovovic, J. P. Heremans, *Phys. Rev. Lett.* 2008, **101**, 035901.