Supporting Information

Significant improvement in thermoelectric performance of Cu-deficient $Cu_{4-\delta}Ga_4Te_8$ (δ=1.12) chalcogenide through an addition of Sb

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Figure S1 (a) XRD patterns of the powders $Cu_{4-\delta}Ga_4Sb_xTe_8$ (x=0, 0.1, 0.25, 0.4, 0.5, 0.6, 0.7) at RT; (b) The lattice constants a and c as a function of x value.
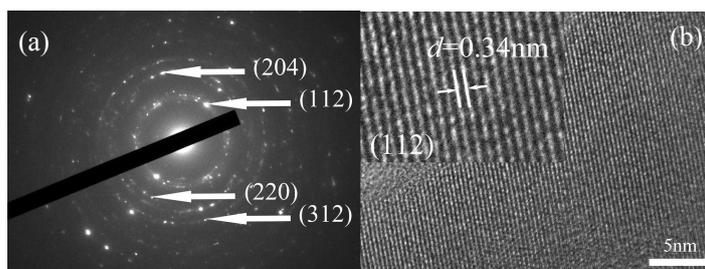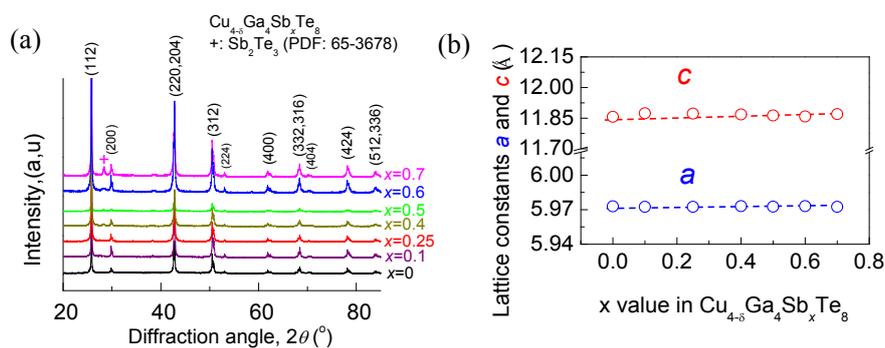
Figure S2   (a) Selected area electron diffraction (SAED) pattern of the sample $Cu_{4-\delta}Ga_4Sb_xTe_8$ at x=0.6; (b) High resolution TEM (HRTEM) image, an inset is an magnified image, where the d spacing between the (112) crystal planes is ~0.34 nm.

(A)

(B)

$Cu_{24}Ga_{32}Te_{64}$

E_f

$Cu_{24}Ga_{32}Sb_2Te_{64}$
$d_H = -2.18$ eV

E_f

$Cu_{24}Ga_{32}Sb_4Te_{64}$
$d_H = -2.82$ eV

E_f

$Cu_{24}Ga_{32}Sb_6Te_{64}$
$d_H = -3.37$ eV

E_f

$Cu_{24}Ga_{32}Sb_8Te_{64}$
$d_H = -3.62$ eV

E_f

Energy, eV

Te Sb Cu Ga
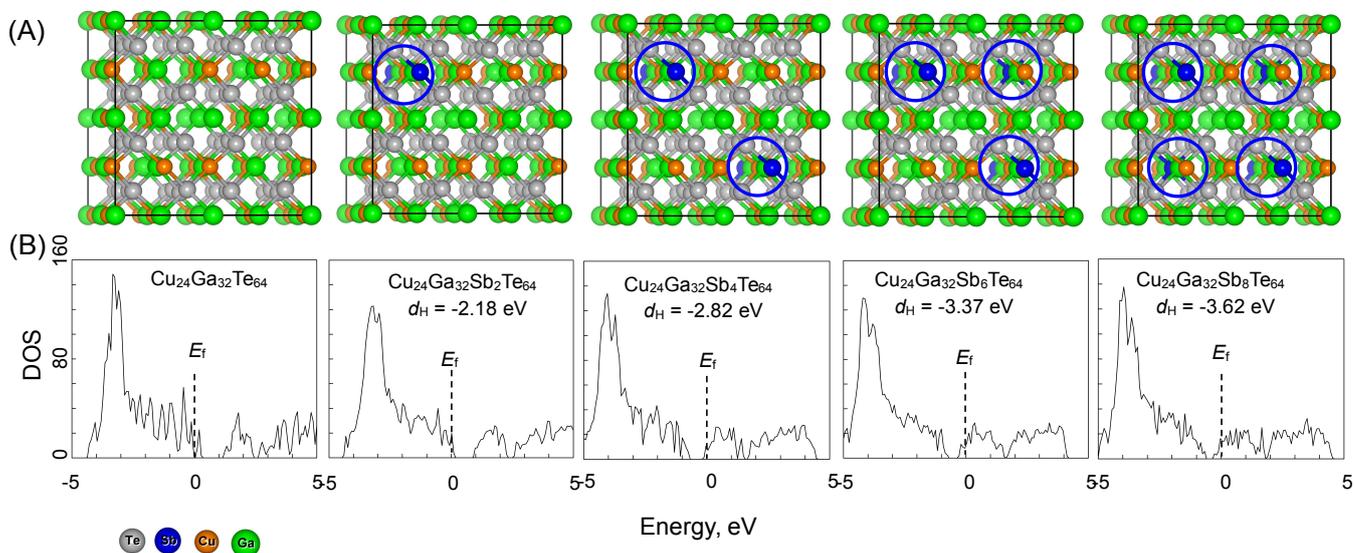
Figure S3   The results from the first principles calculation. (A) Upper panel: the crystal structures of $Cu_{24}Ga_{32}Sb_yTe_{64}$ (y=0, 2, 4, 6, 8) upon occupation of Sb in the Cu sites. The structures from left to right in sequence correspond to y=0, 2, 4, 6 and 8. Blue balls circled represent Sb atoms that occupy Cu sites; (B) Lower panel: the density of States (DOS) with different Sb atoms in the unit cell. It was observed that the Fermi level (E_f) gradually moves to the inner side of the conduction band, and the bandgap narrows gradually with an increase in Sb content. d_H represents the formation of energy.
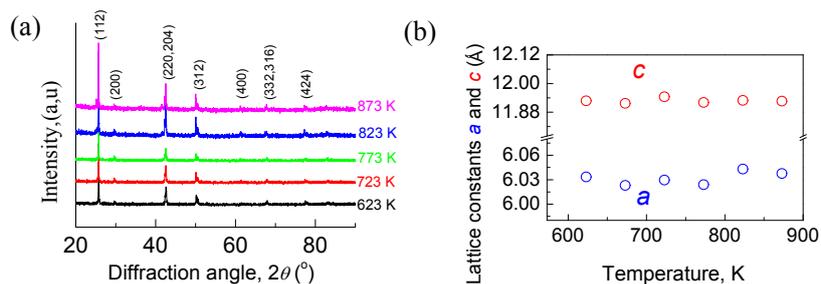
Figure S4   (a) High temperature XRD patterns of the $Cu_{4-\delta}Ga_4Sb_{0.6}Te_8$; (b) Corresponding lattice constants a and c at different temperatures.