Supporting Information

Significant improvement in thermoelectric performance of Cu-deficient Cu$_{4-\delta}$Ga$_4$Te$_8$ ($\delta=1.12$) chalcogenide through an addition of Sb

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Figure S1 (a) XRD patterns of the powders Cu$_{4-\delta}$Ga$_4$Sb$_x$Te$_8$ ($x=0, 0.1, 0.25, 0.4, 0.5, 0.6, 0.7$) 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$_4$Sb$_x$Te$_8$ 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 $\sim$0.34 nm.
**Figure S3**  The results from the first principles calculation. (A) Upper panel: the crystal structures of \( \text{Cu}_{24}\text{Ga}_{32}\text{Sb}_{y}\text{Te}_{64} \) \((y=0, 2, 4, 6, 8)\) 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 \( \text{Cu}_{24}\text{Ga}_{1-x}\text{Sb}_{0.6}\text{Te}_{x} \); (b) Corresponding lattice constants \( a \) and \( c \) at different temperatures.