Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
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Supporting information

The role of excess Sn in $Cu_4Sn_7S_{16}$ for the modification in band structures and reduction in lattice thermal conductivity

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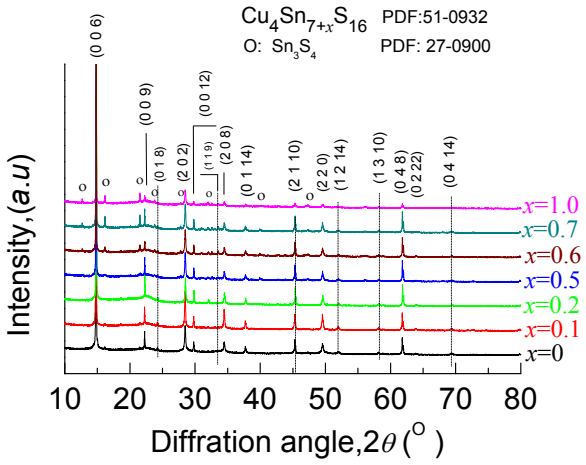

Fig.S1 X-ray diffraction patterns of the $Cu_4Sn_{7+x}S_{16}$ (x=0, 0.1, 0.2, 0.5, 0.6, 0.7, 1.0)

Table S1 Chemical compositions (relative molars) identified for x=0, 0.5 (taken from mappings)

Compounds	Cu	Sn	S
$Cu_4Sn_7S_{16}$	3.98	7.18	16.0
$Cu_4Sn_{7.5}Se_{16}$	3.94	7.78	16.0

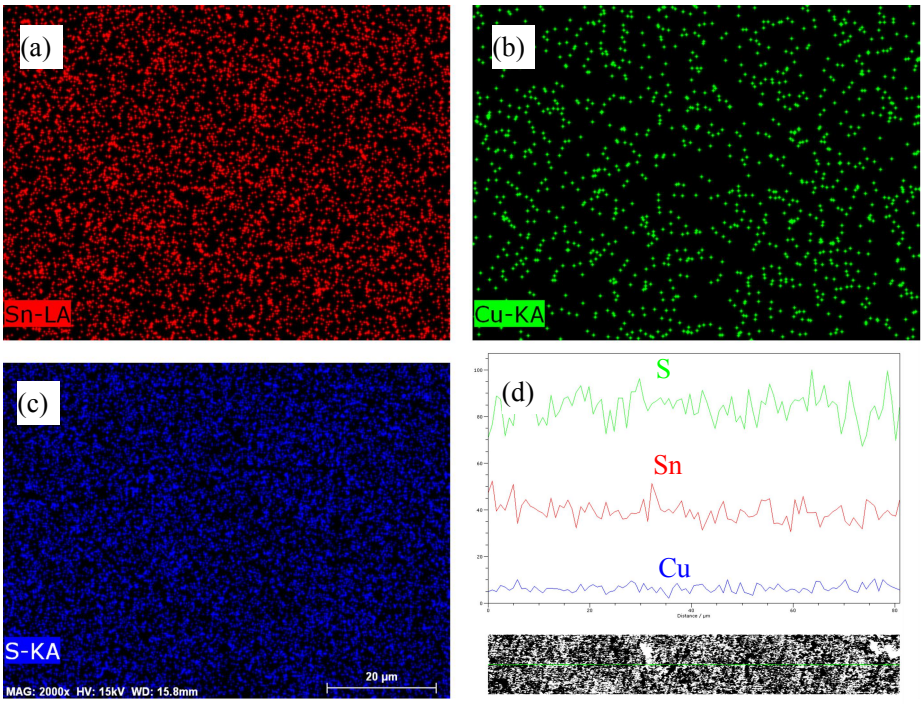

Fig.S2 EPMA mapping of three elements on polished $Cu_4Sn_{7.5}S_{16}$ surface (a) Sn, (b) Cu, (c) S and (d) line scanning analysis of the chemical compositions.

Table S2 Binding energies from the Cu2$p_{3/2}$, Cu2$p_{1/2}$, Sn3$d_{5/2}$, Sn3$d_{3/2}$ and S2$p_{3/2}$, S2$p_{1/2}$ core-level photoelectron spectra for the $Cu_4Sn_{7+x}S_{16}$ (x=0, 0.5) compounds.

Compound	Cu2$p_{3/2}$, Cu2$p_{1/2}$（eV）	Sn3$d_{5/2}$, Sn3$d_{3/2}$（eV）	S2$p_{3/2}$, S2$p_{1/2}$（eV）
$Cu_4Sn_7S_{16}$	932.20, 952.22	486.35, 494.60	161.45, 162.65
$Cu_4Sn_{7.5}S_{16}$	932.30, 952.22	486.50, 494.85	161.65, 162.85

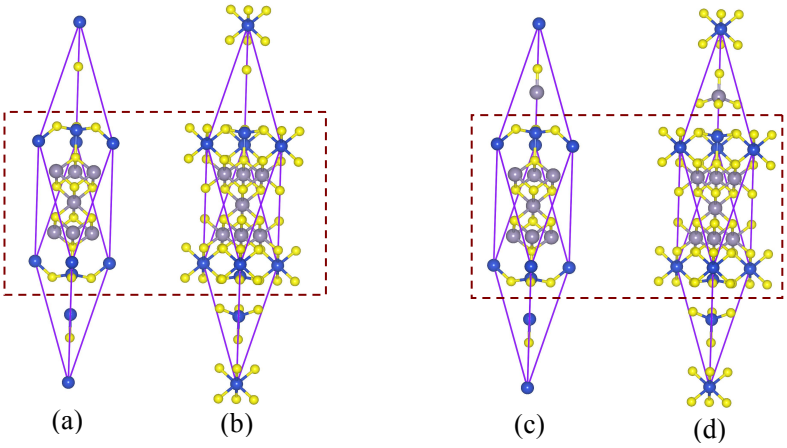

Fig. S3 Calculated rhombohedral Representations of $Cu_4Sn_{7+x}S_{16}$ encircled by dotted lines. (a) Unit cell of $Cu_4Sn_7S_{16}$; (b) Unit cell of $Cu_4Sn_7S_{16}$ with outer side atoms; (c) Unit cell of $Cu_4Sn_8S_{16}$; (d) Unit cell of $Cu_4Sn_8S_{16}$ with outer side atoms.

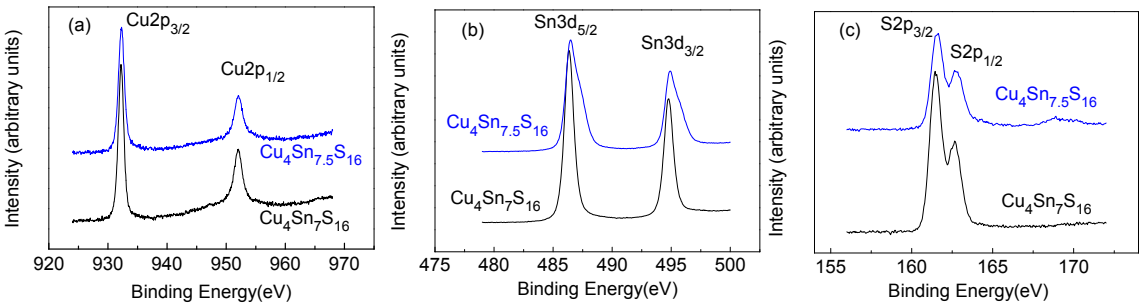

Fig.S4 X-ray photoelectron spectroscopy spectra of (a) Cu2$p_{3/2}$, Cu2$p_{1/2}$, (b) Sn3$d_{5/2}$, Sn3$d_{3/2}$, (c) S2$p_{3/2}$, S2$p_{1/2}$ for $Cu_4Sn_{7+x}S_{16}$ (x=0, 0.5).

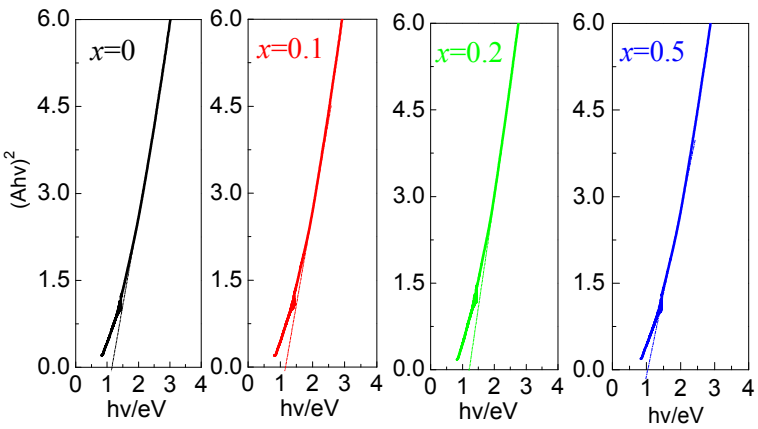

Fig. S5 Measured bandgap (E_g) determined by using the $(Ahv)^2$~(hv) relation.