Supporting Information

Effects of Sb Deviation from Its Stoichiometric Ratio on the Micro- and Electronic Structures and Thermoelectric Properties of $Cu_{12}Sb_4S_{13}$

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1. The detailed Rietveld refinements result of $Cu_{12}Sb_{4+\delta}S_{13}$ (δ=-0.2, -0.1, 0, 0.1, 0.2, 0.3) samples

Table S1 The detailed Rietveld refinements result of $Cu_{12}Sb_{3.8}S_{13}$.

Atoms	Site	x	y	z	SOF	Uiso
Cu1	12d	0.25	0.5	0	0.97(8)	0.023(1)
Cu2	12e	0.209(9)	0	0	0.85(9)	0.035(9)
Sb	8c	0.268(4)	0.268(4)	0.268(4)	0.94(5)	0.022(7)
S1	2a	0	0	0	0.98(5)	0.025(1)
S2	24g	-0.111(3)	-0.111(3)	0.361(4)	0.94(2)	0.040(9)

Table S2 The detailed Rietveld refinements result of $Cu_{12}Sb_{3.9}S_{13}$.

Atoms	Site	x	y	z	SOF	Uiso
Cu1	12d	0.25	0.5	0	0.99(9)	0.017(5)
Cu2	12e	0.212(5)	0	0	0.91(4)	0.055(6)
Sb	8c	0.267(8)	0.267(8)	0.267(8)	0.96(4)	0.018(2)
S1	2a	0	0	0	0.99(8)	0.016(5)
S2	24g	-0.112(8)	-0.112(8)	0.364(3)	0.96(5)	0.025(1)

Table S3 The detailed Rietveld refinements result of $Cu_{12}Sb_{4.0}S_{13}$.

Atoms	Site	x	y	z	SOF	Uiso
Cu1	12d	0.25	0.5	0	1.01(5)	0.023(4)
Cu2	12e	0.214(6)	0	0	0.93(3)	0.004(0)
Sb	8c	0.268(7)	0.268(7)	0.268(7)	0.99(5)	0.017(9)
S1	2a	0	0	0	1	0.025(1)
S2	24g	-0.115(1)	-0.115(1)	0.363(8)	0.97(1)	0.016(2)

Table S4 The detailed Rietveld refinements result of $Cu_{12}Sb_{4.1}S_{13}$.

Atoms	Site	x	y	z	SOF	Uiso
Cu1	12d	0.25	0.5	0	1.00(4)	0.061(9)
Cu2	12e	0.223(9)	0	0	0.98(4)	0.024(4)
Sb	8c	0.268(3)	0.268(3)	0.268(3)	1	0.017(4)
S1	2a	0	0	0	1	0.025(1)
S2	24g	-0.112(7)	-0.112(7)	0.366(6)	0.99 (0)	0.017(1)

Table S5 The detailed Rietveld refinements result of $Cu_{12}Sb_{4.2}S_{13}$.

Atoms	Site	x	y	z	SOF	Uiso
Cu1	12d	0.25	0.5	0	1	0.061(3)
Cu2	12e	0.214(1)	0	0	0.98(1)	0.024(2)
Sb	8c	0.268(7)	0.268(7)	0.268(7)	1	0.017(2)
S1	2a	0	0	0	1	0.047(3)
S2	24g	-0.115(3)	-0.115(3)	0.369(7)	0.98(6)	0.021(8)

Table S6 The detailed Rietveld refinements result of $Cu_{12}Sb_{4.3}S_{13}$.

Atoms	Site	x	y	z	SOF	Uiso
Cu1	12d	0.25	0.5	0	1	0.063(3)
Cu2	12e	0.215(1)	0	0	0.97(1)	0.069(3)
Sb	8c	0.268(7)	0.268(7)	0.268(7)	1	0.060(9)
S1	2a	0	0	0	1	0.000(1)
S2	24g	-0.116(9)	-0.116 (9)	0.369(7)	0.98(5)	0.038(1)

2. The ratio of $g(E)_{\delta}/g(E)_{\delta=0}$

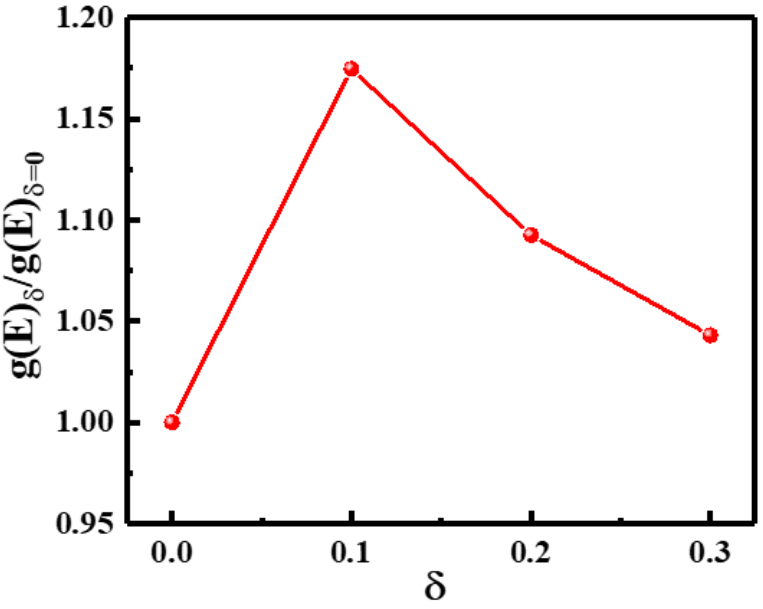

Figure S1 The ratio of $g(E)_{\delta}/g(E)_{\delta=0}$ for $Cu_{12}Sb_{4+\delta}S_{13}$ (δ=0, 0.1, 0.2 and 0.3) samples, which is obtained by fitting of measured susceptibility χ to formula (4) at T>90K.

3.**The UPS spectra data**

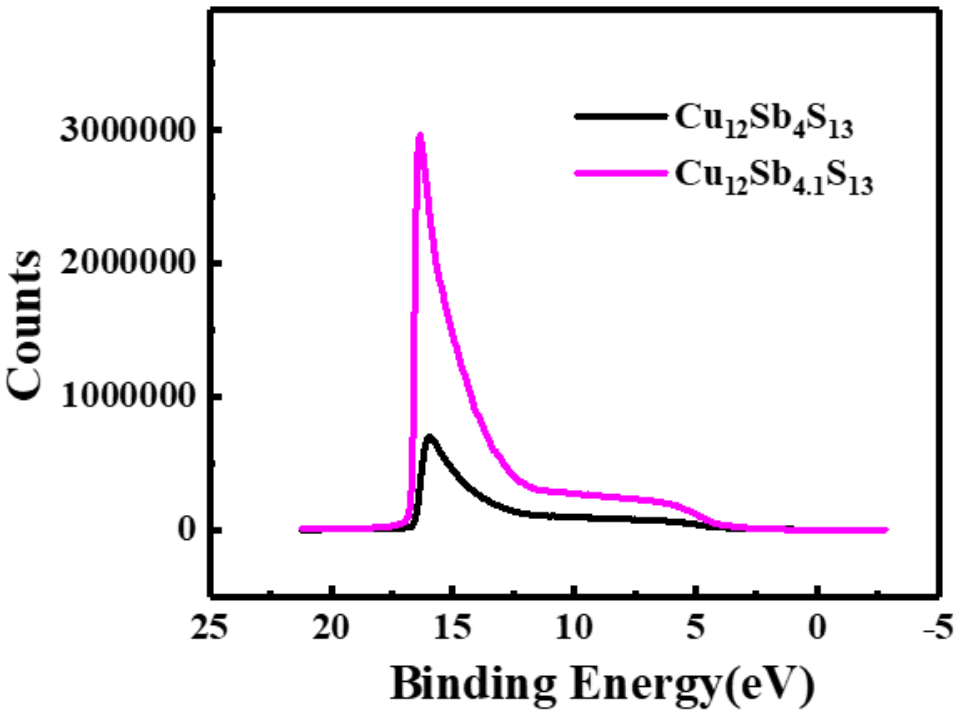

Figure S2. The UPS spectra of $Cu_{12}Sb_4S_{13}$ and $Cu_{12}Sb_{4.1}S_{13}$ samples.

4. The structure of $Cu_{12}Sb_{4.175}S_{13.045}$

As we mentioned in the text, different vacancy positions will lead to different ground-state energies. There are two kinds of Cu ions in $Cu_{12}Sb_4S_{13}$, one can link one S ions with other 5 Cu ions to form a Cu octahedron, one cannot. Meanwhile, there are also two kinds of S ions in $Cu_{12}Sb_4S_{13}$, one can link 6 Cu ions to form a Cu octahedron; one cannot. Figure S3 (a), (b) present their position in the system. Thus, there are eight possible formations in the missing of one Cu ion and S ion considering whether these Cu and S ions are linked. To calculate the lattice constants, firstly, we get volume per atom by using total volume divided by the number (56) of ions of the defected unit cell. Then multiply the number (58) of ions in the original not defected unit cell. Finally, open cube from this revised total volume to get the lattice constants. The detailed of ground-state energies and lattice constants are listed in Table S1. The selected structure is also depicted in Figure S3 (c).

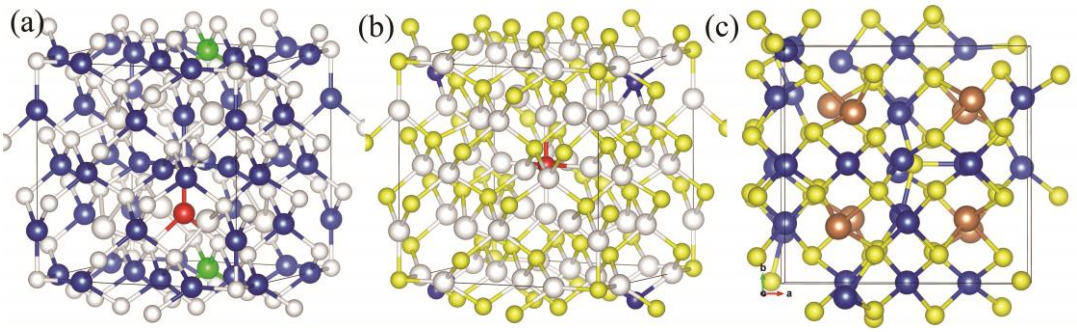

Figure S3 (a) Schematic diagram of two kind of Cu ions positions in $Cu_{12}Sb_4S_{13}$, red ball denotes one of **Cu1** type ion, and green ball denotes one of **Cu2** type ion; (b) schematic diagram of two kind of S ions positions in $Cu_{12}Sb_4S_{13}$, red ball denotes one of **S1** type ion, and blue ball denotes one of **S2** type ion; (c) selected $Cu_{12}Sb_{4.174}S_{13.044}$ structure, blue balls denote Cu ions, earth yellow balls denote Sb ions, and bright yellow balls denote S ions.

Table S7: Ground-state energies of possible formations in the missing of one Cu ion and S, lattice constants are also listed in the subsequent brackets. * means selected structure in our calculations.

Vacancies positions	**Energy (Lattice constants) eV (Å)**	**Vacancies positions**	**Energy (Lattice constants) eV (Å)**
*Cu*1and *S*1 not linked	-251.023(10.257)	*Cu*1 and *S*1 linked	-250.316(10.263)
*Cu*1 and *S*2 not linked	-251.035(10.359)	***Cu*1 and *S*2 linked***	**-251.594(10.361)**
*Cu*2 and *S*1 not linked	-250.272(10.231)	*Cu*2 and *S*1 linked	impossible
*Cu*2 and *S*2 not linked	-250.489(10.352)	*Cu*2 and *S*2 linked	-250.877(10.361)