Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Cation vacancy related crystal structure and bandgap and theirs effects on the thermoelectric performance of Cu-ternaries $Cu_{3+\delta}In_5Te_9$ (δ=0-0.175)

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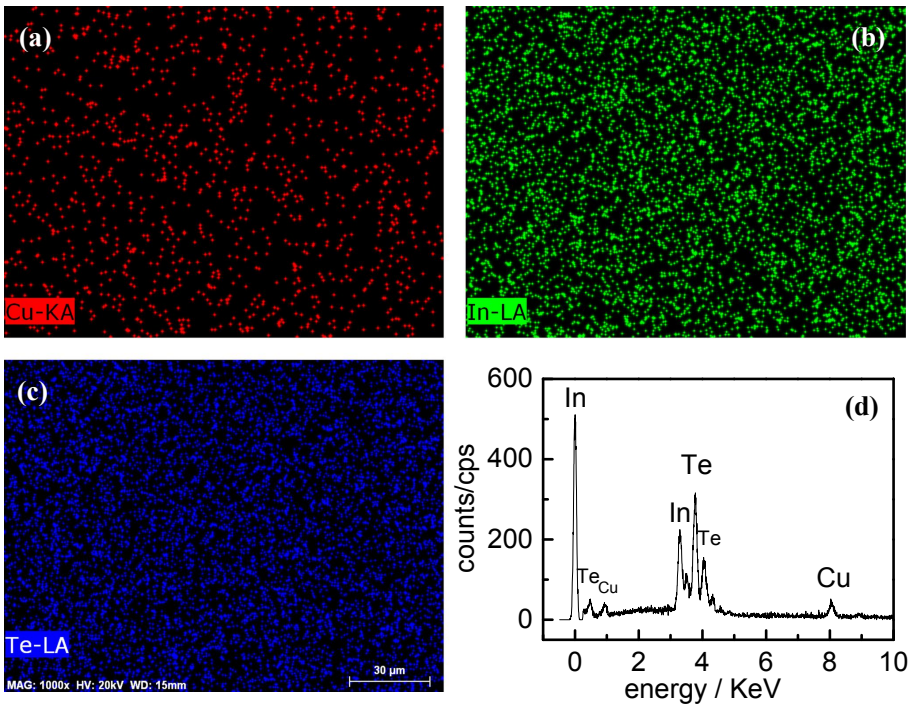

Fig.S1 EPMA mappings of three elements on polished sample $Cu_{3.1}In_5Te_9$ surface (a) Cu, (b) In, (c) Te, (d) an EDAX pattern.

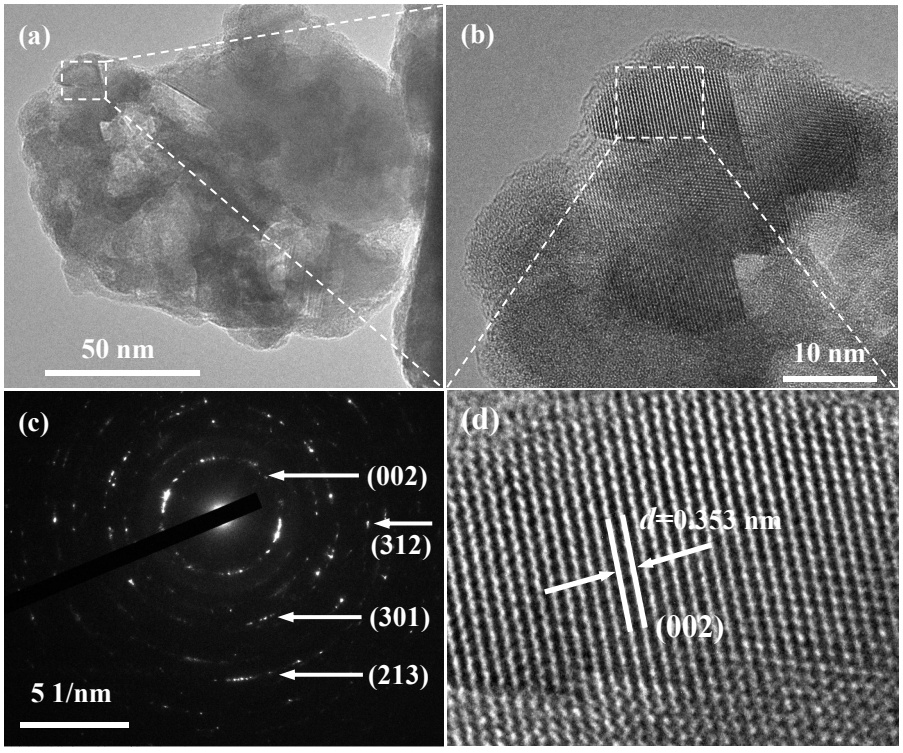

Fig. S2 Microstructures of the $Cu_{3+\delta}In_5Te_9$ (δ=0.1) powder sample. (a) TEM image; (b) Zoomed view in (a); (c) Corresponding selected area electron diffraction (SAED) pattern; (d) Magnified image of (b), the *d* spacing between (002) planes is 0.353 nm.

Table S1 Average molars of three elements identified in ($Cu_{3+\delta}In_5Te_9$) (δ=0, 0.1) (taken from three different areas).

Compounds	Cu	In	Te
δ= 0	2.86±0.02	5.06±0.03	9.03±0.03
δ= 0.1	3.06±0.02	5.03±0.01	9.0±0.03

Table S2 Experimental Parameters of Powder X-ray Diffraction, and Refined Crystallographic $Cu_{3+\delta}In_5Te_9$ (δ=0)

Chemical Formula	$Cu_3In_5Te_9$
Space group	P4*mm*
Z	1
a (Å)	8.7385(4)
b (Å)	8.7385(4)
c (Å)	7.1298(2)
V (Å^3)	544.44(10)
Number of structure parameters	11
Number of profile parameters	15
R_B (%)	4.29
R_p (%)	4.24
R_{wp} (%)	5.44
S	1.29

Table S3 Wyckoff Positions, Atomic Coordinates, and Occupancies of $Cu_{3+\delta}In_5Te_9$ (δ=0).

Atom	Site	*x*	*y*	*z*	U_{iso}	Occupancy
In1	2a	0	0	0	0.0029(2)	0.9696(3)
In4	8a	0	0	0	0.0029(2)	0.0304(6)
Cu1	2b	0	0	0.5	0.4937(9)	1
Cu2	4d	0	0.5	0.25	0.0149(1)	1
Te9	18i	0.2477(7)	0.2477(7)	0.3993(3)	0.0390(5)	1

Table S4 Experimental Parameters of Powder X-ray Diffraction, and Refined Crystallographic $Cu_{3+\delta}In_5Te_9$ (δ=0.05).

Chemical Formula	$Cu_{3.05}In_5Te_9$
Space group	P4*mm*
Z	1
a (Å)	8.7405(3)
b (Å)	8.7405(3)
c (Å)	7.1446(6)
V (Å^3)	V=545.82(5)
Number of structure parameters	11
Number of profile parameters	26
R_B (%)	4.43
R_p (%)	4.46
R_{wp} (%)	5.57
S	1.25

Table S5 Wyckoff Positions, Atomic Coordinates, and Occupancies of $Cu_{3+\delta}In_5Te_9$ (δ=0.05).

Atom	Site	*x*	*y*	*z*	U_{iso}	Occupancy
In1	2a	0	0	0	0.0026(2)	0.9634(3)
In4	8a	0	0	0	0.0026(2)	0.0341(6)
Cu1	2b	0	0	0.5	0.4821(9)	1
Cu2	4d	0	0.5	0.25	0.0049(1)	1
Te9	18i	0.2479(6)	0.2479(6)	0.3994(8)	0.0159(9)	1

Table S6 Experimental Parameters of Powder X-ray Diffraction, and Refined Crystallographic $Cu_{3+\delta}In_5Te_9$ (δ=0.075).

Chemical Formula	$Cu_{3.075}In_5Te_9$
Space group	P4*mm*
Z	1
a (Å)	8.7429(9)
b (Å)	8.7429(9)
c (Å)	7.1460(7)
V (Å^3)	V=546.22(5)
Number of structure parameters	13
Number of profile parameters	29
R_B (%)	4.71
R_p (%)	4.88
R_{wp} (%)	6.08
S	1.23

Table S7 Wyckoff Positions, Atomic Coordinates, and Occupancies of $Cu_{3+\delta}In_5Te_9$ (δ=0.075).

Atom	Site	*x*	*y*	*z*	U_{iso}	Occupancy
In1	2a	0	0	0	0.0038(2)	0.9619(3)
In4	8a	0	0	0	0.0038(2)	0.0353(6)
Cu1	2b	0	0	0.5	0.4729(9)	1
Cu2	4d	0	0.5	0.25	0.0425(1)	1
Te9	18i	0.2476(7)	0.2476(7)	0.3996(3)	0.0314(5)	1

Table S8 Experimental Parameters of Powder X-ray Diffraction, and Refined Crystallographic $Cu_{3+\delta}In_5Te_9$ (δ=0.1).

Chemical Formula	$Cu_{3.1}In_5Te_9$
Space group	P4*mm*
Z	1
a (Å)	8.7453(6)
b (Å)	8.7453(6)
c (Å)	7.1491(3)
V (Å^3)	546.76(15)
Number of structure parameters	12
Number of profile parameters	28
R_B (%)	4.38
R_p (%)	4.22
R_{wp} (%)	5.69
S	1.33

Table S9 Wyckoff Positions, Atomic Coordinates, and Occupancies of $Cu_{3+\delta}In_5Te_9$ (δ=0.1).

Atom	Site	*x*	*y*	*z*	U_{iso}	Occupancy
In1	2a	0	0	0	0.0059(2)	0.9603(3)
In4	8a	0	0	0	0.0059(2)	0.0364(6)
Cu1	2b	0	0	0.5	0.2594(9)	1
Cu2	4d	0	0.5	0.25	0.0069(1)	1
Te9	18i	0.2487(6)	0.2487(6)	0.4003(8)	0.0458(9)	1

Table S10 Experimental Parameters of Powder X-ray Diffraction, and Refined Crystallographic $Cu_{3+\delta}In_5Te_9$ (δ=0.15).

Chemical Formula	$Cu_{3.15}In_5Te_9$
Space group	P4*mm*
Z	1
a (Å)	8.7465(5)
b (Å)	8.7465(5)
c (Å)	7.1513(3)
V (Å^3)	V=547.08(5)
Number of structure parameters	11
Number of profile parameters	26
R_B (%)	4.34
R_p (%)	4.42
R_{wp} (%)	5.32
S	1.22

Table S11 Wyckoff Positions, Atomic Coordinates, and Occupancies of $Cu_{3+\delta}In_5Te_9$ (δ=0.15).

Atom	Site	*x*	*y*	*z*	U_{iso}	Occupancy
In1	2a	0	0	0	0.0026(2)	0.9594(3)
In4	8a	0	0	0	0.0026(2)	0.0334(6)
Cu1	2b	0	0	0.5	0.4821(9)	1
Cu2	4d	0	0.5	0.25	0.0044(1)	1
Te9	18i	0.2490(6)	0.2490(6)	0.3998(8)	0.0151(9)	1

Table S12 Experimental Parameters of Powder X-ray Diffraction, and Refined Crystallographic $Cu_{3+\delta}In_5Te_9$ (δ=0.175).

Chemical Formula	$Cu_{3.175}In_5Te_9$
Space group	P4*mm*
Z	1
a (Å)	8.7478(4)
b (Å)	8.7478(4)
c (Å)	7.1546(6)
V (Å^3)	547.49(10)
Number of structure parameters	11
Number of profile parameters	15
R_B (%)	4.31
R_p (%)	4.22
R_{wp} (%)	5.41
S	1.25

Table S13 Wyckoff Positions, Atomic Coordinates, and Occupancies of $Cu_{3+\delta}In_5Te_9$ (δ=0.175).

Atom	Site	*x*	*y*	*z*	U_{iso}	Occupancy
In1	2a	0	0	0	0.0031(2)	0.9498(3)
In4	8a	0	0	0	0.0031(2)	0.0321(6)
Cu1	2b	0	0	0.5	0.4867(9)	1
Cu2	4d	0	0.5	0.25	0.0159(1)	1
Te9	18i	0.2491(7)	0.2491(7)	0.4009(3)	0.0392(5)	1