Supporting Information

Co-regulation of the copper vacancy concentration and point defects leading to the enhanced thermoelectric performance of $Cu_3In_5Te_9$-based chalcogenides

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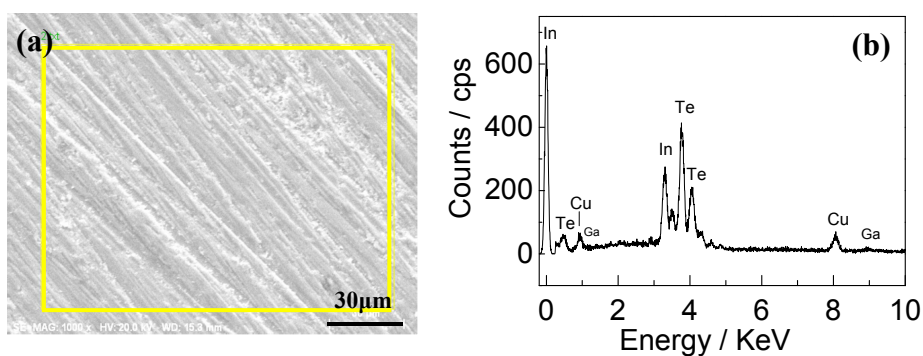

Figure S1 (a) The fracture surface of $(Cu_{3+x}In_{5-x}Ga_xTe_9)$ (x=0.3); (d) An EDAX pattern.

Table S1 Average molars of four elements identified in $(Cu_{3+x}In_{5-x}Ga_xTe_9)$ (x=0, 0.3) (taken from three different areas). The error of the compositions are about 5%.

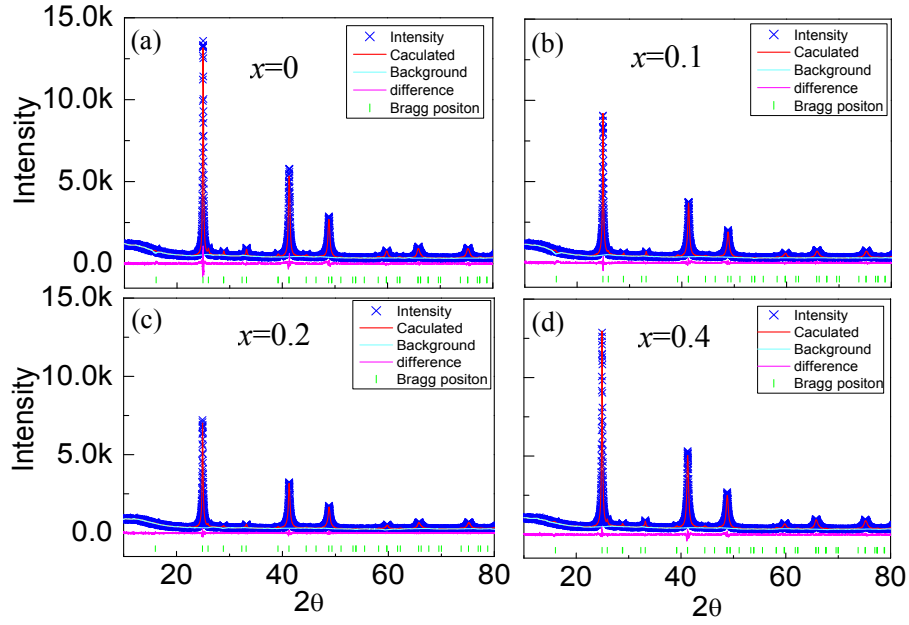| Compounds	Cu	In	Te	Ga
x= 0	2.86	5.08	9.04	----
x= 0.1	2.94	5.04	9.02	0.08
x= 0.3	3.23	4.65	9.11	0.29

Figure S2　Rietveld refinements using the X-ray diffraction data to the samples $Cu_{3+x}In_{5-x}Ga_xTe_9$ ($x=0$, 0.1, 0.2, 0.4).

Table S2 Experimental Parameters of Powder X-ray Diffraction, and Refined Crystallographic Data of $Cu_{3+x}In_{5-x}Ga_xTe_9$ ($x=0$).

Chemical Formula	$Cu_3In_5Te_9$
Space group	P4(75)
a (Å)	8.73854(7)
b (Å)	8.73854(7)
c (Å)	7.12986(9)
V (Å^3)	544.45(10)
Number of structure parameters	11
Number of profile parameters	13
[a] R_B (%)	4.29
[b] R_p (%)	4.24
[c] R_{wp} (%)	5.44
[d] S	1.28

$$^aR_B = \sum\left|I_{O,h} - I_{C,h}\right| / \sum\left|I_{O,h}\right| \quad ^bR_P = \sum\left|y_i - y_{C,i}\right| / \sum y_i \quad ^cR_{wp} = \left[\sum w_i\left|y_i - Y_{C,i}\right|^2 / \sum w_i y_i^2\right]^{\frac{1}{2}} \quad ^dS = R_{wp} / R_{exp}$$

Table S3 Experimental Parameters of Powder X-ray Diffraction, and Refined Crystallographic Data of $Cu_{3+x}In_{5-x}Ga_xTe_9$ (x=0.1).

Chemical Formula	$Cu_{3.1}In_{4.9}Ga_{0.1}Te_9$
Space group	P4(75)
a (Å)	8.73052(8)
b (Å)	8.73052(8)
c (Å)	7.10306(7)
V (Å^3)	541.41(5)
Number of structure parameters	12
Number of profile parameters	19
[a] R_B (%)	4.43
[b] R_p (%)	4.46
[c] R_{wp} (%)	5.57
[d] S	1.25

Table S4 Experimental Parameters of Powder X-ray Diffraction, and Refined Crystallographic Data of $Cu_{3+x}In_{5-x}Ga_xTe_9$ (x=0.2).

Chemical Formula	$Cu_{3.2}In_{4.8}Ga_{0.2}Te_9$
Space group	P4(75)
a (Å)	8.71896(5)
b (Å)	8.71896(5)
c (Å)	7.09668(7)
V (Å^3)	539.49(9)
Number of structure parameters	13
Number of profile parameters	29
[a] R_B (%)	4.69
[b] R_p (%)	4.90
[c] R_{wp} (%)	6.00
[d] S	1.23

Table S5 Experimental Parameters of Powder X-ray Diffraction, and Refined Crystallographic Data of $Cu_{3+x}In_{5-x}Ga_xTe_9$ (x=0.4).

Chemical Formula	$Cu_{3.4}In_{4.6}Ga_{0.4}Te_9$
Space group	P4(75)
a (Å)	8.690(6)
b (Å)	8.690(6)
c (Å)	7.05(3)
V (Å^3)	532.38(15)
Number of structure parameters	13
Number of profile parameters	29
[a] R_B (%)	4.37
[b] R_p (%)	4.20
[c] R_{wp} (%)	5.53
[d] S	1.31

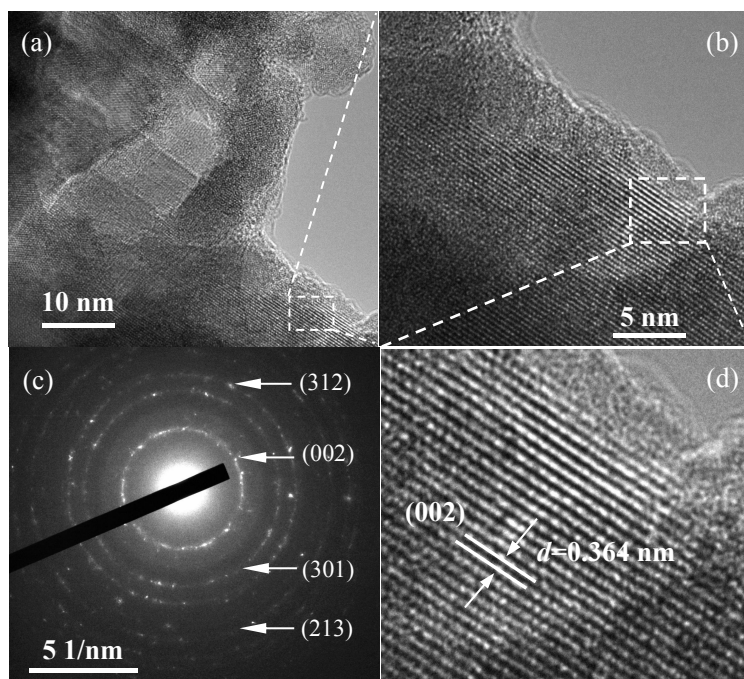Figure S3 Microstructures of the intrinsic $Cu_3In_5Te_9$ powder sample (V_c=0.11, x=0). (a) TEM image; (b) Zoomed view in (a); (c) Corresponding selected area electron diffraction (SAED) pattern; (d) Magnified image of (b).
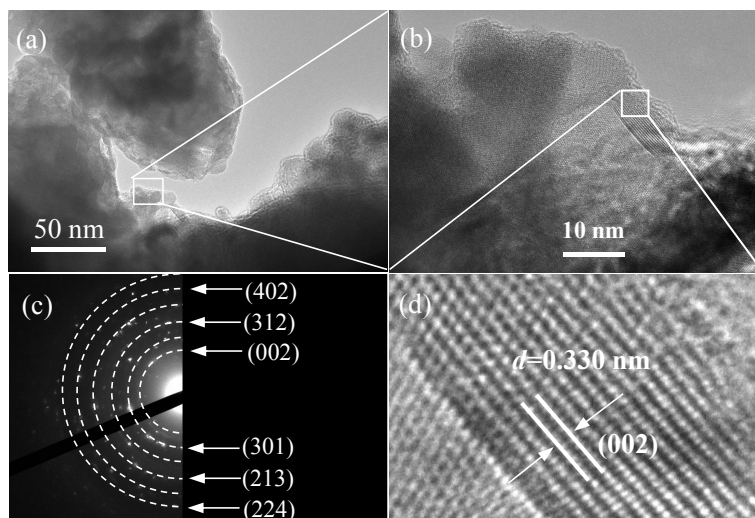
Figure S4 Microstructures of the $Cu_{3+x}In_{5+x}Ga_xTe_9$ powder sample (V_c=0.078, x=0.3). (a) TEM image; (b) Zoomed view in (a); (c) Corresponding selected area electron diffraction (SAED) pattern; (d) Magnified image of (b).
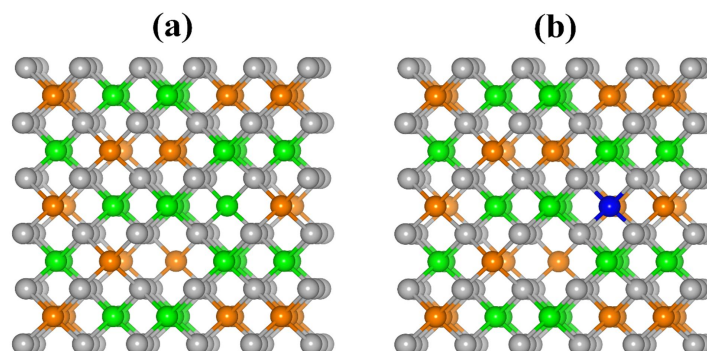

Figure S5 Crystal structures of (a) $Cu_{10}In_{17}Te_{32}$ and (b) $Cu_{11}In_{16}GaTe_{32}$. Cu, In, Te, and Ga are in yellow, green, grey, and blue, respectively.
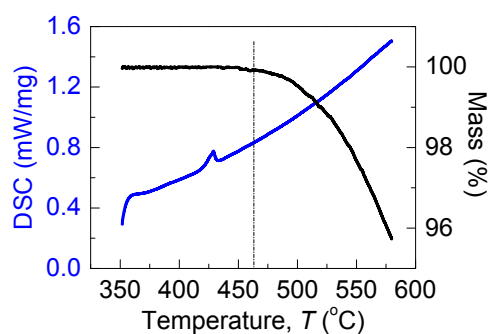

Figure S6 TGA/DSC data for $Cu_3In_5Te_9$, with exothermic effect at ~ 427 ºC, at which an order-disorder transition might occur.