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

Supporting materials for

Unveiling the atomic defects and electronic structure in $Cu_{2.2}Zn_{0.8}SnSe_{4-x}Te_x$ (x=0 to 0.04) by X-ray absorption Fine structure spectroscopy

1. EXAFS spectra and XANES spectra; Figure.S1-S6

2. EXAFS fitting results: Table.S1-S6

3. XANES calculation generated electronic occupation: Table.S7-S11

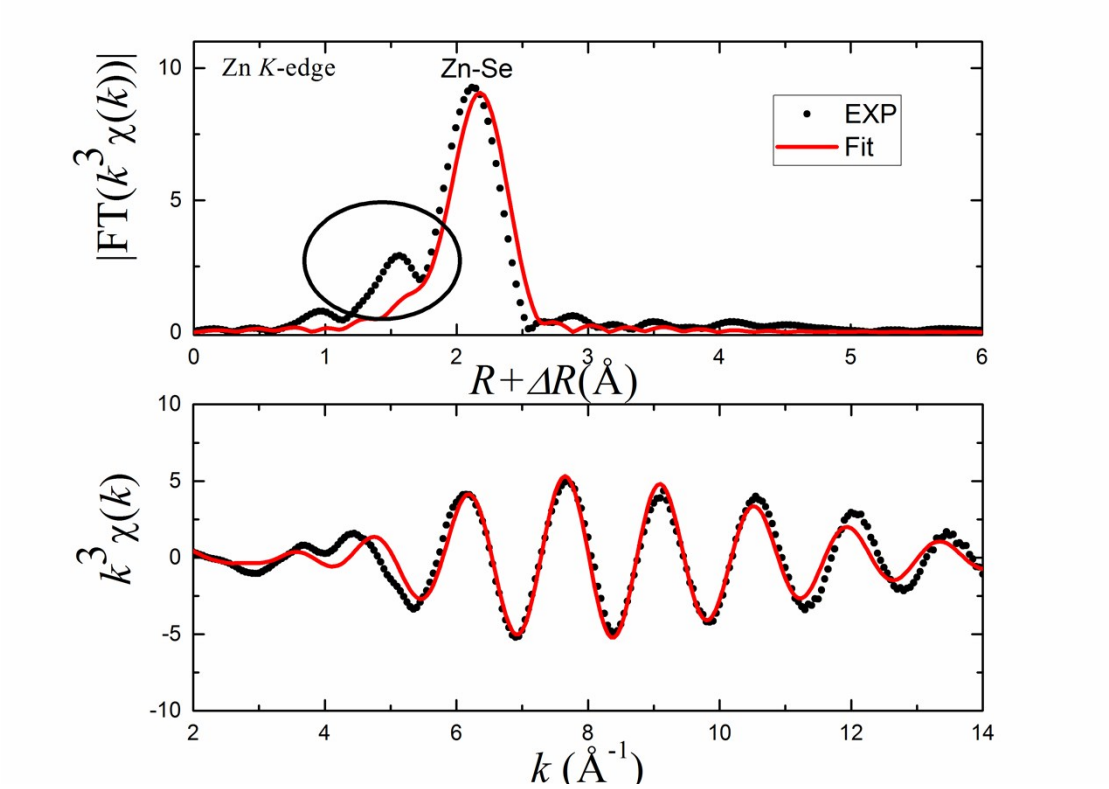

Figure.S1. The Zn *K*-edge EXAFS spectrum cannot be fitted well with CZTSe model; the black ellipse highlights the unidentified peak

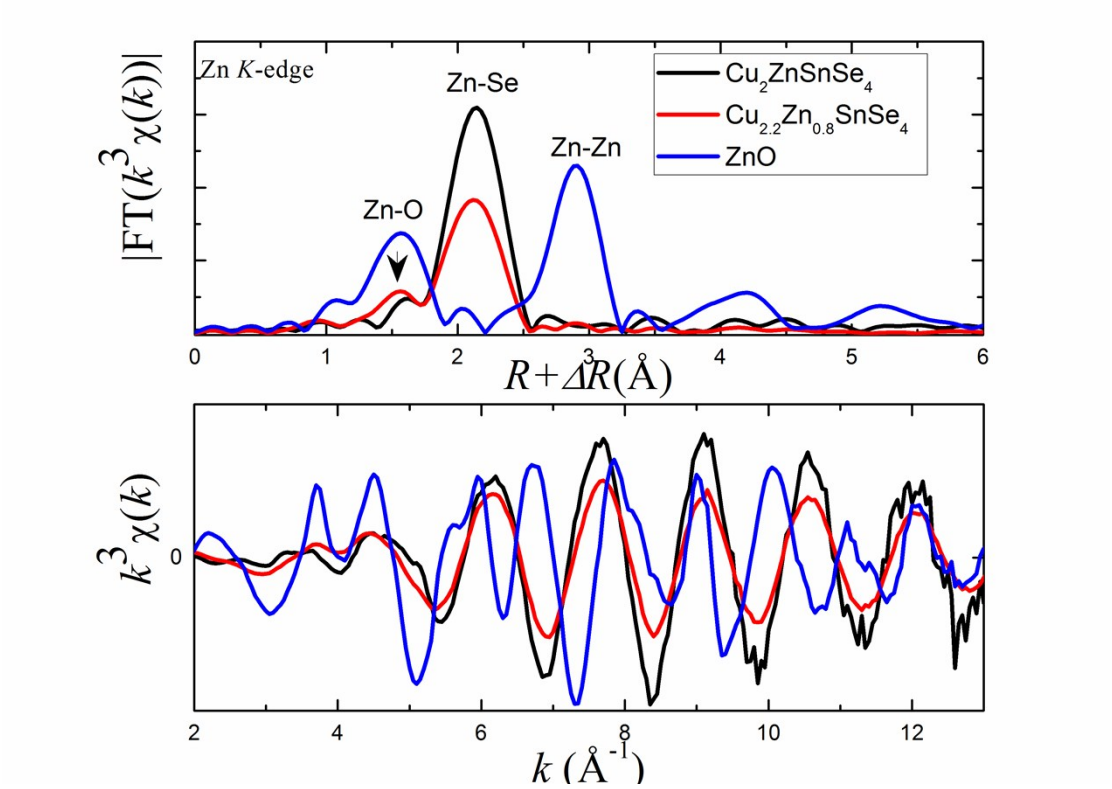

Figure.S2 Comparison of Zn K-edge EXAFS spectra for the oxygen-free $Cu_2ZnSnSe_4$, $Cu_{2.2}Zn_{0.8}SnSe_4$ in this work and reference ZnO; the pronounced peak was identified as Zn-O bond.

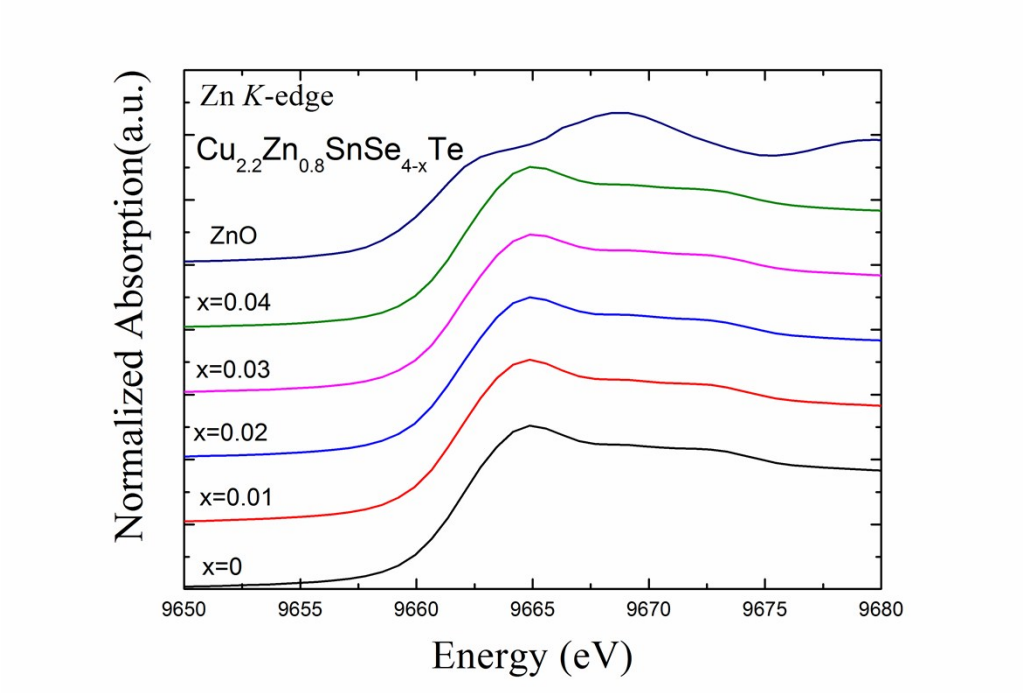

Figure.S3 Comparison of XANES at Zn *K*-edge for $Cu_{2.2}Zn_{0.8}SnSe_{4-x}Te_x$ (x=0-0.04) and ZnO

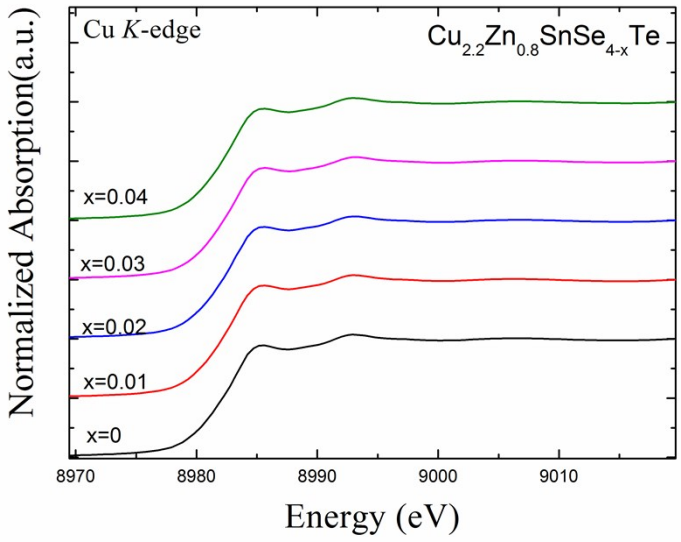

Figure.S4 Comparison of XANES at Cu *K*-edge for $Cu_{2.2}Zn_{0.8}SnSe_{4-x}Te_x$ (x=0-0.04)

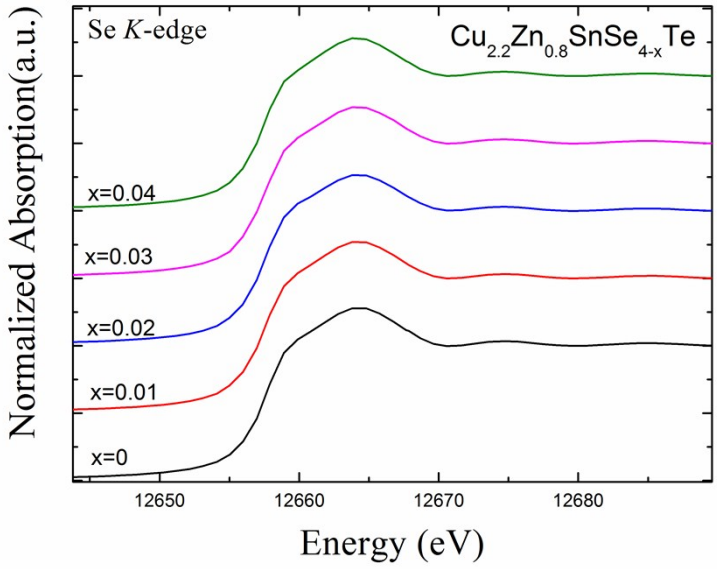

Figure.S5 Comparison of XANES at Se *K*-edge for $Cu_{2.2}Zn_{0.8}SnSe_{4-x}Te_x$ (x=0-0.04)

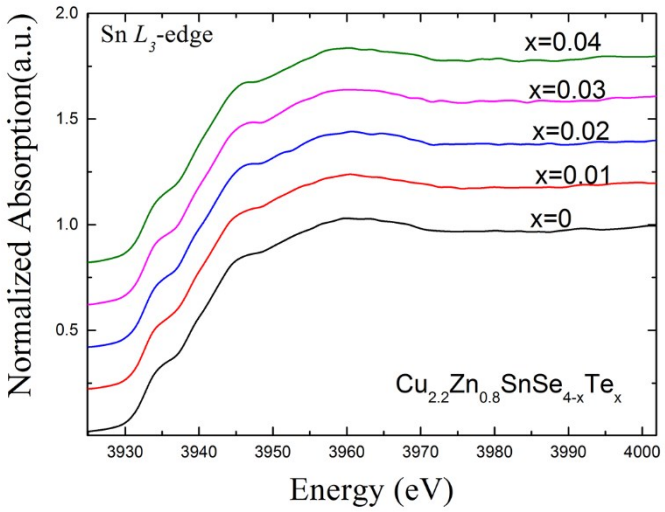

Figure.S6 Comparison of XANES at Sn L_3-edge for $Cu_{2.2}Zn_{0.8}SnSe_{4-x}Te_x$ (x=0-0.04)

Table.S1 Local coordination environment for Keisterite and stannite phase $Cu_2ZnSnSe_4$

Phase	**Keisterite**		**Stannite**	
Central atom	First shell	Bond-distance(Å)	First shell	Bond-distance(Å)
Zn	Zn-4Se	2.4873	Zn-4Se	2.5050
Cu	Cu_{2a}-4Se	2.4424	Cu-4Se	2.4287
	Cu_{2c}-4Se	2.4415		
Se	Se-Cu_{2c}	2.4415	Se-2Cu	2.4287
	Se-Cu_{2a}	2.4423		
	Se-1Zn	2.4873	Se-1Zn	2.5050
	Se-1Sn	2.6152	Se-1Sn	2.6222
Sn	Sn-4Se	2.6152	Sn-4Se	2.6222

Table.S2. EXAFS Fitting parameters at Zn, Cu and Se *K*-edge for $Cu_{2.2}Zn_{0.8}SnSe_{4-x}Te_x$ (x=0-0.04)

	***k* range[Å^{-1}]**	***R* range[Å]**	**S_0^2**	**k weight**	**Independent point N_{idp}**
Zn K-edge	2-13	1-3	0.97	3	11
Cu K-edge	2-13	1-3	0.9	3	11
Se K-edge	2-13	1-3	0.9	3	11

Table.S3. EXAFS Fitting results of pristine $Cu_{2.2}Zn_{0.8}SnSe_4$ at Zn, Cu and Se *K*-edge using Keisterite (I-4, SG82) and Stannite phase (I-42m, SG121), respectively; CN: coordination number, R: bond distance, σ^2: means square relative displacement, ΔE: energy shift; R-factor: fitting quality

Zn *K*-edge, SG121	Path	CN	R(Å)	σ^2 ($\times 10^{-3}$) (Å^2)	ΔE(eV)	R-factor
$Cu_{2.2}Zn_{0.8}SnSe_4$	Zn-Se	2.7±0.6	2.44±0.004	7.3±0.5	0.882	0.007
	Zn-O	0.9±0.1	1.95±0.012			
Zn *K*-edge, SG82						
$Cu_{2.2}Zn_{0.8}SnSe_4$	Zn-Se	2.7±0.2	2.44±0.004	7.3±0.6	0.871±0.06	0.007
	Zn-O	0.9±0.1	1.95±0.012		0.871±0.06	
Cu *K*-edge, SG121						
$Cu_{2.2}Zn_{0.8}SnSe_4$	Cu-Se	3.2±0.3	2.40±0.004	8.2±0.7	1±0.812	0.006
Cu K-edge SG82						
$Cu_{2.2}Zn_{0.8}SnSe_4$	Cu-Se	3.2±0.2	2.40±0.004	8.2±0.6	0.992±0.812	0.003
Se *K*-edge, SG121						
$Cu_{2.2}Zn_{0.8}SnSe_4$	Se-Cu	1.7±0.3	2.40±0.004	4.49±1.4	1.37±1.24	0.02
	Se-Zn	0.1±0.1	2.44±0.004			
	Se-Sn	1.0±0.2	2.56±0.020			
Se *K*-edge, SG82						
$Cu_{2.2}Zn_{0.8}SnSe_4$	Se-Cu	1.7±0.3	2.40±0.004	4.43±1.42	1.43±1.24	0.02
	Se-Zn	0.1±0.1	2.44±0.004			
	Se-Sn	0.6±0.2	2.56±0.020			

Table.S4 Zn *K*-edge EXAFS fitting results for $Cu_{2.2}Zn_{0.8}SnSe_{4-x}Te_x$ (x=0-0.04) CN: coordination number, R: bond distance, σ^2: means square relative displacement, ΔE: energy shift; R-factor: fitting quality

Samples	Path	CN	R(Å)	σ^2 ($\times 10^{-3}$) (Å^2)	ΔE(eV)	R-factor
$Cu_{2.2}Zn_{0.8}SnSe_4$	Zn-Se	2.7±0.2	2.44±0.004	7.3±0.6	0.871±0.06	0.007
	Zn-O	0.9±0.1	1.95±0.012			
$Cu_{2.2}Zn_{0.8}SnSe_{3.99}Te_{0.01}$	Zn-Se	2.7±0.2	2.45±0.005	7.4±0.6	0.846±0.377	0.008
	Zn-O	0.9±0.1	1.95±0.011			
$Cu_{2.2}Zn_{0.8}SnSe_{3.98}Te_{0.02}$	Zn-Se	2.6±0.3	2.44±0.005	7.6±0.7	1.028±0.215	0.013
	Zn-O	1.0±0.1	1.94±0.013			
$Cu_{2.2}Zn_{0.8}SnSe_{3.97}Te_{0.03}$	Zn-Se	2.5±0.2	2.44±0.004	7.3±0.6	0.821±0.624	0.007
	Zn-O	0.9±0.1	1.95±0.013			
$Cu_{2.2}Zn_{0.8}SnSe_{3.96}Te_{0.04}$	Zn-Se	2.6±0.2	2.45±0.004	7.3±0.5	1.127±0.668	0.005
	Zn-O	1.0±0.1	1.95±0.009			

Table.S5 Cu *K*-edge EXAFS fitting results for $Cu_{2.2}Zn_{0.8}SnSe_{4-x}Te_x$ (x=0-0.04) CN: coordination number, R: bond distance, σ^2: means square relative displacement, ΔE: energy shift; R-factor:

fitting quality

Samples	Path	CN	R(Å)	σ^2 ($\times10^{-3}$) (Å^2)	ΔE(eV)	R-factor
$Cu_{2.2}Zn_{0.8}SnSe_4$	Cu-Se	3.2±0.2	2.40±0.004	8.2±0.6	0.992±0.812	0.003
$Cu_{2.2}Zn_{0.8}SnSe_{3.99}Te_{0.01}$	Cu-Se	3.2±0.3	2.40±0.004	8.4±0.8	0.957±0.982	0.009
$Cu_{2.2}Zn_{0.8}SnSe_{3.98}Te_{0.02}$	Cu-Se	3.0±0.2	2.40±0.004	8.0±0.6	0.804±0.693	0.006
$Cu_{2.2}Zn_{0.8}SnSe_{3.97}Te_{0.03}$	Cu-Se	3.1±0.3	2.40±0.006	8.3±0.9	1.699±1.093	0.012
$Cu_{2.2}Zn_{0.8}SnSe_{3.96}Te_{0.04}$	Cu-Se	3.1±0.3	2.40±0.006	8.3±0.9	1.519±1.038	0.010

Table.S6 Se *K*-edge EXAFS fitting results for $Cu_{2.2}Zn_{0.8}SnSe_{4-x}Te_x$ (x=0-0.04) CN: coordination number, R: bond distance, σ^2: means square relative displacement, ΔE: energy shift; R-factor: fitting quality

Samples	Path	CN	R(Å)	σ^2 ($\times10^{-3}$) (Å^2)	ΔE(eV)	R-factor
$Cu_{2.2}Zn_{0.8}SnSe_4$	Se-Cu	1.7±0.3	2.40±0.004	4.49±1.4	1.37±1.24	0.02
	Se-Zn	0.1±0.1	2.44±0.004			
	Se-Sn	1.0±0.2	2.56±0.020			
$Cu_{2.2}Zn_{0.8}SnSe_{3.99}Te_{0.01}$	Se-Cu	1.7±0.3	2.40±0.004	4.68±1.4	1.38±1.24	0.028
	Se-Zn	0.1±0.1	2.45±0.005			
	Se-Sn	0.6±0.2	2.56±0.018			
$Cu_{2.2}Zn_{0.8}SnSe_{3.99}Te_{0.02}$	Se-Cu	1.7±0.3	2.40±0.004	4.68±1.5	1.31±1.24	0.027
	Se-Zn	0.1±0.1	2.44±0.005			
	Se-Sn	0.6±0.2	2.56±0.02			
$Cu_{2.2}Zn_{0.8}SnSe_{3.99}Te_{0.03}$	Se-Cu	1.7±0.3	2.40±0.006	4.62±1.4	1.38±1.22	0.026
	Se-Zn	0.1±0.1	2.44±0.004			
	Se-Sn	0.7±0.2	2.56±0.019			
$Cu_{2.2}Zn_{0.8}SnSe_{3.99}Te_{0.04}$	Se-Cu	1.6±0.3	2.40±0.006	4.56±1.4	1.24±1.24	0.027
	Se-Zn	0.1±0.1	2.45±0.004			
	Se-Sn	0.7±0.2	2.56±0.018			

Table.S7 Electron occupation of $Cu_{2.2}Zn_{0.8}SnSe_{4-x}Te_x$ calculated with Te(@Se) as the cluster center

Atoms	*s*	*p*	*d*	Charge Transfer	Electron configuration	Valence
Te-exc	1.903	4.292	0.398	0.409	$[Kr]4d^{10}5s^25p^4$	-2, 4, 6
Se	1.907	3.907	0.299	-0.112	$[Ar]3d^{10}4s^24p^4$	-2, 4, 6
Cu	0.597	0.664	9.579	0.159	$[Ar]3d^{10}4s^1$	2,1
Sn	0.516	1.731	10.396	0.358	$[Kr]4d^{10}5s^25p^2$	4, 2
Zn	0.962	1.099	10.168	-0.230	$[Ar]3d^{10}4s^2$	2

Table.S8 Electron occupation of $Cu_{2.2}Zn_{0.8}SnSe_{4-x}Te_x$ calculated with Se as the cluster center

Te L_3-edge	*s*	*p*	*d*	Charge Transfer	Electron configuration	Valence
Se-exc	1.966	4.576	0.260	0.198	$[Kr]4d^{10}5s^25p^4$	-2, 4, 6
Se	1.895	3.930	0.268	-0.093	$[Ar]3d^{10}4s^24p^4$	-2, 4, 6
Cu	0.594	0.660	9.614	0.131	$[Ar]3d^{10}4s^1$	2,1
Sn	1.558	1.705	10.397	0.340	$[Kr]4d^{10}5s^25p^2$	4, 2

Zn	0.963	1.078	10.190	-0.231	[Ar]$3d^{10}4s^2$	2

Table.S9 Electron occupation of $Cu_{2.2}Zn_{0.8}SnSe_{4-x}Te_x$ by Cu *K*-edge XANES calculations

Cu *K*-edge	*s*	*p*	*d*	Charge Transfer	Electron configuration	Valence
Cu-exc	0.948	1.139	10.198	-0.285	[Ar]$3d^{10}4s^1$	2,1
Se	1.900	3.927	0.251	-0.078	[Ar]$3d^{10}4s^24p^4$	-2, 4, 6
Cu	0.600	0.678	9.598	0.125	[Ar]$3d^{10}4s^1$	2,1
Sn	1.528	1.749	10.400	0.323	[Kr]$4d^{10}5s^25p^2$	4, 2
Zn	0.964	1.109	10.185	-0.259	[Ar]$3d^{10}4s^2$	2

Table.S10 Electron occupation of $Cu_{2.2}Zn_{0.8}SnSe_{4-x}Te_x$ by Sn *K*-edge XANES calculations

Sn *K*-edge	*s*	*p*	*d*	Charge Transfer	Electron configuration	Valence
Sn-exc	1.759	2.346	10.460	0.435	[Kr]$4d^{10}5s^25p^2$	4, 2
Se	1.898	3.877	0.282	-0.057	[Ar]$3d^{10}4s^24p^4$	-2, 4, 6
Cu	0.613	0.684	9.598	0.105	[Ar]$3d^{10}4s^1$	2,1
Sn	1.530	1.766	10.401	0.303	[Kr]$4d^{10}5s^25p^2$	4, 2
Zn	0.977	1.122	10.186	-0.285	[Ar]$3d^{10}4s^2$	2

Table.S11 Electron occupation of $Cu_{2.2}Zn_{0.8}SnSe_{4-x}Te_x$ by Zn *K*-edge XANES calculations

Zn *K*-edge	*s*	*p*	*d*	Charge Transfer	Electron configuration	Valence
Zn-exc	1.232	1.421	10.328	0.019	[Ar]$3d^{10}4s^2$	2
Se	1.896	3.864	0.271	-0.031	[Ar]$3d^{10}4s^24p^4$	-2, 4, 6
Cu	0.617	0.694	9.606	0.082	[Ar]$3d^{10}4s^1$	2,1
Sn	1.534	1.790	10.406	0.270	[Kr]$4d^{10}5s^25p^2$	4, 2
Zn	0.988	1.133	10.190	-0.311	[Ar]$3d^{10}4s^2$	2