Composition- and Band-Gap-Tunable Synthesis of Wurtzite-Derived $Cu_2ZnSn(S_{1-x}Se_x)_4$ Nanocrystals: Theoretical and Experimental Insights

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Table S1. Space Groups and Atomic Positions of the Wurtzite-Kesterite and Kesterite CZTSSe.

structure	wurtzite-kesterite CZTSSe	structure	kesterite CZTSSe
space group	*P1*	space group	*I -4*
(0, 0, 0)	Cu	(0,0,0)	Cu
(1/2, 0, 0)	Zn	(1/2, 1/2, 0)	Zn
(1/4, 1/2, 0)	Cu	(0, 1/2, 1/4)	Cu
(3/4, 1/2, 0)	Sn	（1/2, 0, 1/4）	Sn
(0, 1/3, 1/2)	Zn	（0, 0, 1/2）	Zn
(1/2, 1/3, 1/2)	Cu	（1/2, 1/2, 1/2）	Cu
(1/4, 5/6, 1/2)	Sn	(0, 1/2, 3/4)	Sn
(3/4, 5/6, 1/2)	Cu	(1/2, 0, 3/4)	Cu
(0,0,3/8)	S/Se	(1/4, 1/4, 1/8)	S/Se
(1/4, 1/2, 3/8)	S/Se	(3/4, 3/4, 1/8)	S/Se
(1/2, 0, 3/8)	S/Se	(1/4, 3/4, 3/8)	S/Se
(3/4, 1/2, 3/8)	S/Se	(3/4, 1/4, 3/8)	S/Se
(0, 1/3, 7/8)	S/Se	(1/4, 1/4, 5/8)	S/Se
(1/2, 1/3, 7/8)	S/Se	(3/4, 3/4, 5/8)	S/Se
(1/4, 5/6, 7/8)	S/Se	(1/4, 3/4, 7/8)	S/Se
(3/4, 5/6, 7/8)	S/Se	(3/4, 1/4, 7/8)	S/Se

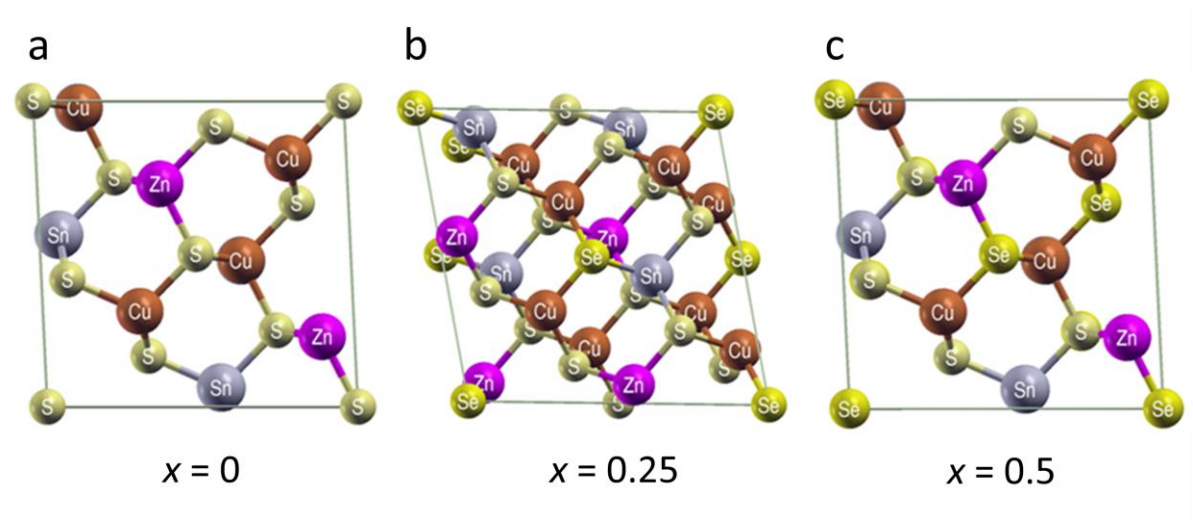

Figure S1. The plot of the special quasi-random structures of wurtzite-derived CZTSSe with (a) $x = 0$, (b) $x = 0.25$ and (c) $x = 0.50$, in which S and Se occupy the anion sublattice and the Cu, Zn and Sn are ordered as in the wurtzite-kesterite structure.

Table S2. The Basis Vectors ***a***, ***b***, ***c*** and the Atomic Coordinates (Relative to Basis Vectors) of the Special Quasi-Random Structures (SQS) for Wurtzite-Derived CZTSSe Alloys with x = 0.25 and x = 0.50. The SQS with x = 0.75 can be Derived from that with x = 0.25. The Same Supercell as the SQS with x = 0.50 Is Used for the Calculations of Pure CZTS and CZTSe.

x = 0.5				x = 0.25			
a (Å)	0.00	-6.85	-6.51		7.81	0.00	-6.44
b (Å)	0.00	6.85	-6.51		-7.81	0.00	-6.44
c (Å)	7.92	0.00	0.00		0.00	6.75	0.00
	relative atomic coordinates				relative atomic coordinates		
Cu	0.81250	0.81250	-0.00000	Cu	0.81250	0.81250	-0.00000
Cu	0.31250	0.31250	-0.00000	Cu	0.31250	0.31250	-0.00000
Cu	0.56250	1.06250	0.25000	Cu	0.93750	0.68750	0.50000
Cu	0.06250	0.56250	0.25000	Cu	0.43750	0.18750	0.50000
Cu	0.39583	0.72917	0.50000	Cu	0.31250	0.81250	0.33333
Cu	-0.10417	0.22917	0.50000	Cu	0.81250	0.31250	0.33333
Cu	0.14583	0.97917	0.75000	Cu	0.43750	0.68750	0.83333
Cu	-0.35417	0.47917	0.75000	Cu	0.93750	0.18750	0.83333
Zn	0.81250	0.81250	0.50000	Zn	0.06250	0.56250	-0.00000
Zn	0.31250	0.31250	0.50000	Zn	0.56250	0.06250	-0.00000
Zn	0.39583	0.72917	-0.00000	Zn	0.56250	0.56250	0.33333
Zn	-0.10417	0.22917	-0.00000	Zn	0.06250	0.06250	0.33333
Sn	0.56250	1.06250	0.75000	Sn	0.68750	0.93750	0.50000
Sn	0.06250	0.56250	0.75000	Sn	0.18750	0.43750	0.50000
Sn	0.14583	0.97917	0.25000	Sn	0.18750	0.93750	0.83333
Sn	-0.35417	0.47917	0.25000	Sn	0.68750	0.43750	0.83333
S	0.58333	0.91667	0.50000	S	0.62500	0.37500	0.50000
S	0.33333	1.16667	0.75000	S	0.50000	1.00000	0.33333
S	0.58333	0.91667	0.00000	S	0.62500	0.87500	0.83333
S	0.08333	0.41667	0.00000	S	0.12500	0.37500	0.83333
S	0.75000	1.25000	0.75000	S	0.25000	0.75000	0.00000
S	0.25000	0.75000	0.75000	S	0.75000	0.25000	0.00000
S	0.33333	1.16667	0.25000	S	0.75000	0.75000	0.33333
S	-0.16667	0.66667	0.25000	S	0.25000	0.25000	0.33333
Se	1.00000	1.00000	0.00000	S	0.37500	0.62500	0.50000
Se	0.50000	0.50000	0.00000	S	0.87500	0.12500	0.50000
Se	0.75000	1.25000	0.25000	S	0.87500	0.62500	0.83333
Se	0.25000	0.75000	0.25000	S	0.37500	0.12500	0.83333
Se	0.08333	0.41667	0.50000	Se	0.00000	1.00000	0.00000
Se	-0.16667	0.66667	0.75000	Se	0.50000	0.50000	0.00000
Se	1.00000	1.00000	0.50000	Se	0.12500	0.87500	0.50000
Se	0.50000	0.50000	0.50000	Se	-0.00000	0.50000	0.33333

Table S3. Amounts of CuI, $Zn(CH_3COO)_2 \cdot 2H_2O$, $SnCl_2 \cdot 2H_2O$, 1-Dodecanethiol and Diphenyl Disenenide Used for Synthesizing the CZTSSe Nanocrsytals with Different Composition *x*. Since the Zn Source Shows Lower Reactivity than the Cu and Sn Sources, the Reagent Contains More Zn Salt Than the Stoichiometric Amount for the Expected Cation Ratio of Nanocrystals. Different Amounts of 1-Dodecanethiol and Diphenyl Diselenide Were Added as Anion Sources to Adjust the Composition *x*.

sample	CuI *(mmol)*	$Zn(CH_3COO)_2 \cdot 2H_2O$ *(mmol)*	$SnCl_2 \cdot 2H_2O$ *(mmol)*	1-dodecanethiol	diphenyl disenenide *(mmol)*
1#	0.28	0.39	0.14	0.60	0
2#	0.28	0.40	0.14	0.60	0.07
3#	0.28	0.42	0.21	0.60	0.14
4#	0.28	0.35	0.14	0.60	0.28
5#	0.28	0.35	0.14	0.08	1.12

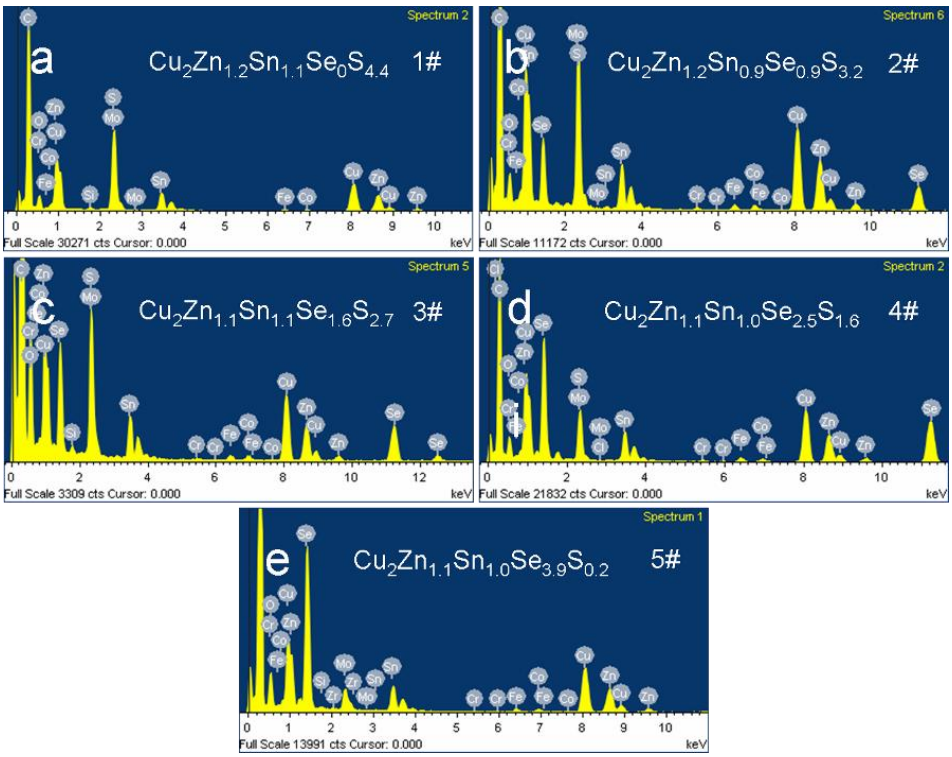

Figure S2. EDS spectra of all samples 1-5. Fe, Co, and Cr signal originates from the sample holder. The cation molar ratio of Cu:Zn:Sn is close to 2:1:1, and the composition parameter *x* varies from 0 to 0.95.

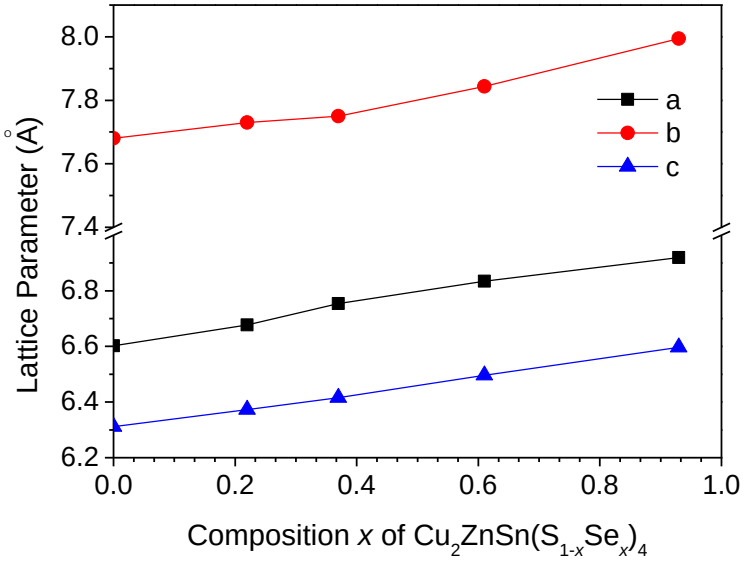

Figure S3. The dependences of the lattice parameters ***a, b*** and ***c*** on the compositions of the samples 1-5.

Table S4. Lattice Parameters and Phase Purities of Samples 1-5 Determined by the Rietveld Fits

sample	lattice parameters (Å)			phase purity	*Rp*	*Rwp*	*Rexp*	χ^2
	a	***b***	***c***					
1#, *x* = 0	6.60192 (0.00079)	7.68051 (0.00103)	6.31169 (0.00041)	92.00 (0.40)%	2.64%	3.43%	1.61%	4.54%
2#, *x* = 0.22	6.67739 (0.00270)	7.72959 (0.00322)	6.37260 (0.00048)	95.70(0.47)%	2.10%	2.75%	1.38%	3.98%
3#, *x* = 0.37	6.75382 (0.00213)	7.75007 (0.00237)	6.41599 (0.00131)	67.42(0.62)%	2.40%	3.25%	1.60%	4.12%
4#, *x* = 0.61	6.83456 (0.00159)	7.84340 (0.00188)	6.49599 (0.00097)	95.67(0.42)%	1.83%	2.33%	1.30%	3.23%
5#, *x* = 0.93	6.91918 (0.00175)	7.99415 (0.00205)	6.59656 (0.00062)	88.73(0.70)%	4.54%	6.11%	1.61%	14.4%