1. Supporting information

S1. Superstructure Models

Table S1 Crystallographic Information for the superstructure models.

Annealing temperature (K)	473	573	673	723	823
Crystal data					
Chemical formula	Cu_3Sn	Cu_3Sn	Cu_3Sn	Cu_3Sn	Cu_3Sn
M_r	309.3	309.3	309.3	309.3	309.3
Crystal system, space group			Orthorhombic, *Cmcm*		
Temperature (K)	293	293	293	293	293
a, *b*, *c* (Å)	5.5210 (2), 47.781 (3), 4.3340 (2)	5.5185 (3), 47.768 (2), 4.3320 (2)	5.5196 (1), 38.2386 (12), 4.3321 (1)	5.5184 (2), 38.2337 (15), 4.3326 (2)	5.5199 (1), 47.7904 (9), 4.3326 (1)
V (Å^3)	1143.30 (10)	1141.95 (9)	914.34 (4)	914.13 (6)	1142.93 (4)
Z	20	20	16	16	20
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α
μ (mm^{-1})	37.87	37.92	37.89	37.89	37.89
Crystal size (mm)	0.06 × 0.02 × 0.02	0.09 × 0.05 × 0.03	0.14 × 0.05 × 0.02	0.10 × 0.07 × 0.04	0.08 × 0.06 × 0.04
Data collection					
Diffractometer	Xcalibur, Eos diffractometer				
Absorption correction	Analytical *CrysAlis PRO*, Agilent Technologies, Version 1.171.36.32 (release 02-08-2013 CrysAlis171 .NET) (compiled Aug 2 2013,16:46:58) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C.				

	Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897)				
T_{min}, T_{max}	0.372, 0.7	0.227, 0.551	0.095, 0.529	0.199, 0.434	0.15, 0.281
No. of measured, independent and observed [$I > 3\sigma(I)$] reflections	5911, 851, 332	8193, 840, 382	7324, 689, 389	5405, 673, 384	8648, 855, 447
R_{int}	0.032	0.031	0.034	0.026	0.020
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.669	0.662	0.669	0.667	0.669
Refinement					
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.172, 1.17	0.029, 0.107, 1.62	0.026, 0.097, 1.96	0.022, 0.063, 1.26	0.023, 0.088, 1.71
No. of reflections	851	840	689	673	855
No. of parameters	72	72	58	58	72
No. of restraints	0	0	0	0	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.22, −2.36	1.75, −1.84	1.34, −1.25	1.55, −1.60	1.35, −1.20

S2. Modulated Models

Table S2 Crystallographic Information for the modulated models.

Annealing	473	573	673	723	823
Temperature (K)					
Crystal data					
Chemical formula	$Cu_{3.048}Sn_{0.952}$	$Cu_{3.027}Sn_{0.973}$	$Cu_{3.031}Sn_{0.969}$	$Cu_{3.022}Sn_{0.978}$	$Cu_{3.013}Sn_{0.987}$
M_r	306.7	307.9	307.6	308.1	308.6
Crystal system, space group	Orthorhombic, *Xmcm*(0β0)000†				
Temperature (K)	293	293	293	293	293
Wave vectors	**q** = 0.0949(2)**b***	**q** = 0.1014(3)**b***	**q** = 0.12155(9)**b***	**q** = 0.12434(17)**b***	**q** = 0.10015(7)**b***
a, *b*, *c* (Å)	5.528 (2), 4.783 (4), 4.3391 (18)	5.525 (2), 4.781 (3), 4.3385 (17)	5.529 (2), 4.787 (3), 4.3381 (17)	5.523 (3), 4.783 (3), 4.336 (2)	5.529 (2), 4.788 (2), 4.3411 (19)
V (Å^3)	114.73 (11)	114.60 (9)	114.82 (9)	114.54 (11)	114.92 (8)
Z	2	2	2	2	2
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α	Mo Kα
μ (mm^{-1})	37.66	37.74	37.66	37.77	37.66
Crystal size (mm)	0.24 × 0.05 × 0.03	0.09 × 0.05 × 0.02	0.14 × 0.05 × 0.02	0.12 × 0.06 × 0.04	0.08 × 0.06 × 0.04
Data collection					
Diffractometer	Xcalibur, Eos diffractometer				
Absorption correction	Analytical *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.33 (release 27-03-2014 CrysAlis171 .NET) (compiled Mar 27 2014,17:12:48) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R.				

	C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.				
T_{min}, T_{max}	0.148, 0.474	0.15, 0.51	0.091, 0.495	0.107, 0.368	0.152, 0.283
No. of measured, independent and observed [$I > 3\sigma(I)$] reflections	4102, 591, 276	9022, 919, 406	6406, 598, 384	4697, 583, 357	9463, 932, 463
R_{int}	0.029	0.029	0.034	0.026	0.021
$(\sin\theta/\lambda)_{max}$ ($Å^{-1}$)	0.668	0.662	0.668	0.666	0.667
Refinement					
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.103, 1.34	0.038, 0.112, 1.52	0.040, 0.135, 2.90	0.056, 0.129, 2.34	0.048, 0.133, 2.08
No. of reflections	591	919	598	583	932
No. of parameters	24	32	24	24	32
No. of restraints	0	0	0	0	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	2.84, −3.75	3.07, −3.48	4.38, −5.80	6.12, −6.61	4.46, −5.61

† Symmetry operations: (1) x_1, x_2, x_3, x_4; (2) $-x_1$, x_2, x_3, x_4; (3) x_1, x_2, $-x_3$, x_4; (4) $-x_1$, $-x_2+2/3$, $-x_3+1/2$, $-x_4$; (5) $-x_1$, x_2, $-x_3$, x_4; (6) x_1, $-x_2+2/3$, $-x_3+1/2$, $-x_4$; (7) $-x_1$, $-x_2+2/3$, $x_3+1/2$, $-x_4$; (8) x_1, $-x_2+2/3$, $x_3+1/2$, $-x_4$; (9) $x_1+1/2$, x_2, x_3, $x_4+1/2$; (10) $-x_1+1/2$, x_2, x_3, $x_4+1/2$; (11) $x_1+1/2$, x_2, $-x_3$, $x_4+1/2$; (12) $-x_1+1/2$, $-x_2+2/3$, $-x_3+1/2$, $-x_4+1/2$; (13) $-x_1+1/2$, x_2, $-x_3$, $x_4+1/2$; (14) $x_1+1/2$, $-x_2+2/3$, $-x_3+1/2$, $-x_4+1/2$; (15) $-x_1+1/2$, $-x_2+2/3$, $x_3+1/2$, $-x_4+1/2$; (16) $x_1+1/2$, $-x_2+2/3$, $x_3+1/2$, $-x_4+1/2$.

Computer programs: *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.33 (release 27-03-2014 CrysAlis171 .NET) (compiled Mar 27 2014,17:12:48).

S3. Lift Information for the Structure Family

Table S3 References for Figure 3.

structure type	3*d* space group	3+1*d* space group	t_0	references
AuCd	*Pmcm* (No. 51)	*Cmcm*(α00)0*s*0	0	(Chang, 1951)
		$\alpha = 1$		
Au_4Zr	*Pnma* (No. 62)	*Cmcm*(α00)0*s*0	0	(Stolz & Schubert, 1962)
		$\alpha = 1$		
Cu_3Sb	*Pmnm* (No. 59)	*Xmcm*(0β0)000ǂ	0.25	(Günzel & Schubert, 1958)
		$\beta = 1$		
		Cmcm(α00)0*s*0	0	
		$\alpha \approx 0.5$		
$Cu_{11}Sb_3$	*Amm*2 (No. 38)	*Cmcm*(α00)0*s*0	1/28	(Jandali *et al.*, 1982)
		$\alpha \approx 0.57$		
$Cu_{3+x}Sn_{1-y}Sb_y$	*Cmcm* (No. 63)	*Xmcm*(0β0)000	-	Own data
		$\beta \approx 0.25$		
$Cu_{3+x}Sn$	*Cmcm* (No. 63)	*Xmcm*(0β0)000	-	This work
		$\beta \approx 0.125, 0.1$		
$Cu_{3-x}Ni_xSn$	*Cmcm* (No. 63)*	*Xmcm*(0β0)000	0	(Van Sande *et al.*, 1978)
		$\beta \approx$ 0.167, 0.125, 0.1		
$Cu_{3-x}Zn_xSn$	*Cmcm* (No. 63)*	*Xmcm*(0β0)000	0	(Van Sande *et al.*, 1978)
		$\beta \approx 0.25, 0.167, 0.125, 0.1$		
Cu_2Ti	*Cmcm* (No. 63)	*Cmcm*(α00)0*s*0	0	(Schubert, 1965)
		$\alpha \approx 0.2$		
$LiZn_{4-x}$	none	*Cmcm*(α00)0*s*0	-	(Pavlyuk *et al.*, 2014)
		$\alpha \approx 0.57$		
Rh_5V_3	*Cmcm* (No. 63)	*Xmcm*(0β0)000	0	(Waterstrat & Dickens, 1973)
		$\beta = 0.5$		

* TEM study without structure solution

S4. Commensurate Refinements of the modulated model

A range of test refinements has been performed using the 573 K dataset to understand whether Cu_3Sn is truly incommensurate or not. For this purpose, a general model of a 1x10x1 superstructure in the general space group *Cm*2*m* was used in combination with different t_0 values. All of these refinements suffer from significant parameter correlations for the refineable harmonic terms of the displacive modulation. Further, the compositions were not refineable without severe stability problems. For t_0 values around 0.065 (or multiples of it), all harmonic displacement parameters were negative, and thus indicating that these models with very high Cu:Sn ratios are not a correct choice. (Figure S1) In general, the refinements were worse than the presented incommensurate modulated model (MM). (Figure S2)

Figure S1 Atomic arrangements of the tested commensurate modulated model refinements (573K sample) in the orthorhombic space group *Cm*2*m*.

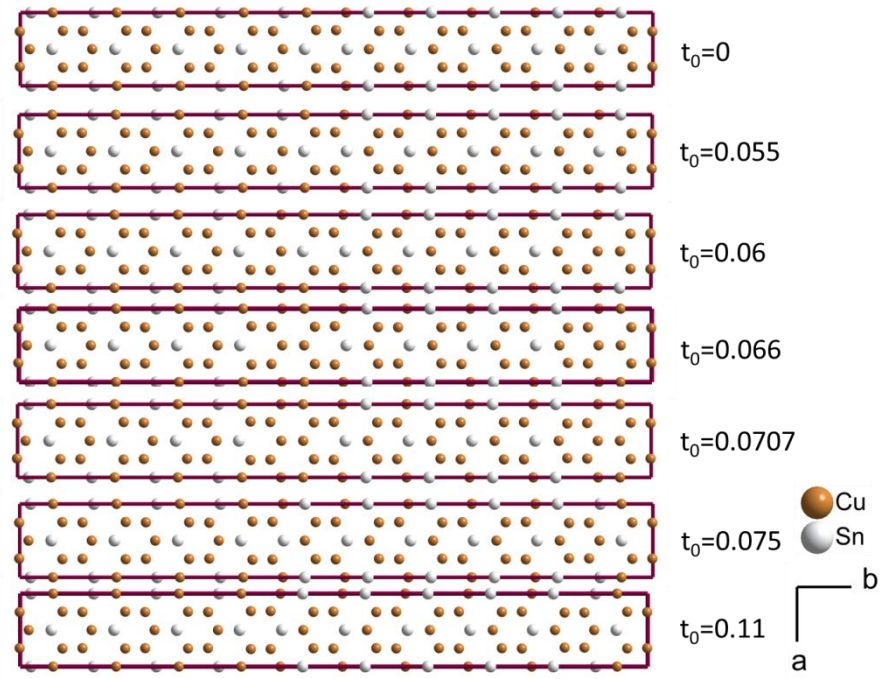

Figure S2 R-factors vs. t_0 for commensurate refinements of the modulated model (Blue) in comparison with the incommensurate refinement of the 573K sample (Red).