

Supporting information

Copper Hyper-stoichiometry, the Key for the Optimization of Thermoelectric Properties in Stannoidite $\text{Cu}_{8+x}\text{Fe}_{3-x}\text{Sn}_2\text{S}_{12}$.

Ventrapati Pavan Kumar,[†] Tristan Barbier,[†] Vincent Caignaert,[†] Bernard Raveau,[†] Ramzy Daou,[†] Bernard Malaman,[‡] Gérard Le Caër,[#] Pierric Lemoine,[§] and Emmanuel Guilmeau^{,†}*

[†] Laboratoire CRISMAT, UMR 6508 CNRS/ENSICAEN, 6 bd du Marechal Juin, 14050 Caen Cedex 4, France

[‡] Institut Jean Lamour, UMR 7198, CNRS, Université de Lorraine, Faculté des Sciences et Technologie, B.P. 70239, 54506 Vandœuvre-lès-Nancy Cedex, France

[#] Institut de Physique de Rennes, UMR UR1-CNRS 6251, Université de Rennes I, Campus de Beaulieu, Bâtiment 11A, F-35042 Rennes Cedex, France

[§] Institut des Sciences Chimiques de Rennes (ISCR) - UMR CNRS 6226, Université de Rennes I, Campus de Beaulieu, Bâtiment 10A, 35042 Rennes Cedex, France

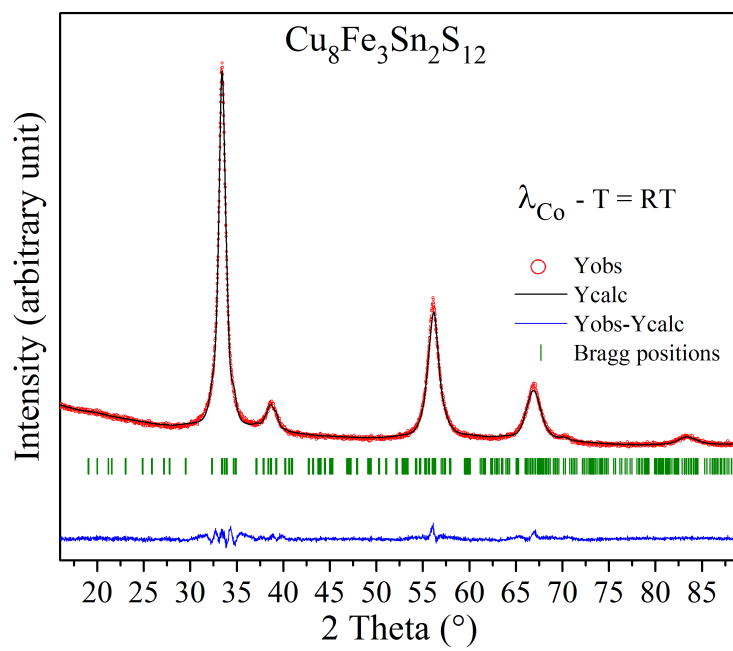


Figure S1 : Pattern matching of PXRD pattern of as ball-milled $\text{Cu}_8\text{Fe}_3\text{Sn}_2\text{S}_{12}$ powder.

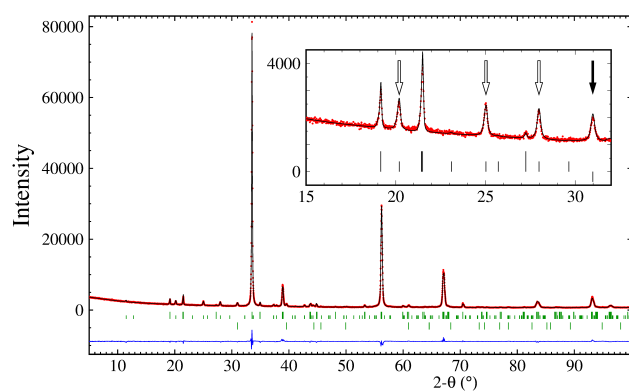


Figure S2: Rietveld refinement of $\text{Cu}_{8.3}\text{Fe}_{2.7}\text{Sn}_2\text{S}_{12}$: Red dots, black and blue curves represent the observed, calculated and difference plots respectively. The green vertical lines represent the position of the Bragg reflections. Top lines are reflections of the stannoidite: short lines are $h,k,l=3n+1$ and $h,k,l=3n+2$ reflections while large lines are $h,k,l=3n$ reflections. Bottom lines are reflections of the SnO_2 impurity. The inset shows the broadening of the h,k,l reflections with $l=3n+1$ and $l=3n+2$ (white arrows) and the main reflection of the SnO_2 impurity (<1% wt., black arrow).

Table S1: Crystallographic data for $\text{Cu}_{8+x}\text{Fe}_{3-x}\text{Sn}_2\text{S}_{12}$.

	$x = 0$	$x = 0.3$
Space group	I 222	I 222
Cell parameters:	a = 10.758(1) Å b = 5.3971(2) Å c = 16.135(2) Å	a = 10.747(1) Å b = 5.3808(2) Å c = 16.082(2) Å
Cell volume:	936.79(6) Å ³	929.97(6) Å ³
χ^2	3.71	3.28
R _{Bragg}	3.41%	4.36%

Table S2: Atomic coordinates for $\text{Cu}_{8+x}\text{Fe}_{3-x}\text{Sn}_2\text{S}_{12}$ (First line for $x = 0$, second line for $x = 0.3$)

Site	Wyckoff	x	y	z
Fe1	2a	0	0	0
Cu1	2b	1/2	0	0
Cu2	2c	0	0	1/2
Cu3	4f	0.247(4) 0.249(3)	0	1/2
Fe2	4i	0	0	0.333(3) 0.332(1)
Sn1	4j	0	1/2	0.169(2) 0.168(1)
Cu4	8k	0.250(3)	-0.001(27) 0.001(11)	0.168(2) 0.169(1)
S1	8k	0.123(7) 0.116(3)	0.255(14) 0.252(5)	0.083(7) 0.084(3)
S2	8k	0.367(8) 0.360(3)	0.760(14) 0.767(5)	0.085(8) 0.083(3)
S3	8k	0.130(12) 0.130(5)	0.753(16) 0.742(7)	0.259(4) 0.260(2)