Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
This journal is © The Royal Society of Chemistry 2021

Supplementary Information

Synthesis and Characterization of a New Family of Layered $Pb_xSn_{4-x}As_3$ Alloys

Karl G. Koster,[a] Yaxian Wang,[b] Michael R. Scudder,[a] Curtis E. Moore,[a] Wolfgang Windl,[b] Joshua E. Goldberger[a]

[a]Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH 43210, USA

[b]Department of Materials Science and Engineering, The Ohio State University, Columbus, OH 43210, USA

Email: goldberger@chemistry.ohio-state.edu

Table S1. Structure refinement data of a single crystal of $Pb_{0.68}Sn_{3.32}As_3$.

Empirical formula	As3 Pb0.676(10) Sn3.324(10)	
Molecular formula	As3 Pb0.676(10) Sn3.324(10)	
Formula weight	759.40	
Temperature	300.0 K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	R -3 m	
Unit cell dimensions	a = 4.0967(3) Å	α= 90°.
	b = 4.0967(3) Å	β= 90°.
	c = 36.401(4) Å	γ = 120°.
Volume	529.07(9) $Å^3$	
Z	3	
Density (calculated)	7.150 Mg/m^3	
Absorption coefficient	41.573 mm^{-1}	
F(000)	962	
Crystal size	0.059 x 0.056 x 0.048 mm^3	
Crystal color, habit	Metallic Silver Block	
Theta range for data collection	1.678 to 30.553°.	
Index ranges	-5<=h<=5, -5<=k<=5, -51<=l<=51	
Reflections collected	7396	
Independent reflections	257 [R(int) = 0.0495, R(sigma) = 0.0146]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.0326 and 0.0053	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	257 / 0 / 14	
Goodness-of-fit on F^2	1.084	
Final R indices [I>2sigma(I)]	R1 = 0.0272, wR2 = 0.0697	
R indices (all data)	R1 = 0.0374, wR2 = 0.0732	
Extinction coefficient	0.00045(13)	
Largest diff. peak and hole	1.205 and -1.630 e.$Å^{-3}$	

Table S2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $Pb_{0.68}Sn_{3.32}As_3$, from single-crystal diffraction measurements. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
As(1)	0	0	-0.0685(1)	0.031(1)
As(2)	0	0	0.5000	0.033(1)
Sn(1)	0	0	0.6362(1)	0.031(1)
Sn(2)	0	0	0.2114(1)	0.033(1)
Pb(2)	0	0	0.2114(1)	0.033(1)

Table S3. Anisotropic displacement parameters (Å^2) for $Pb_{0.68}Sn_{3.32}As_3$ from single-crystal diffraction measurements. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
As(1)	0.028(1)	0.028(1)	0.036(1)	0	0	0.014(1)
As(2)	0.031(1)	0.031(1)	0.035(1)	0	0	0.016(1)
Sn(1)	0.031(1)	0.031(1)	0.031(1)	0	0	0.015(1)
Sn(2)	0.032(1)	0.032(1)	0.034(1)	0	0	0.016(1)
Pb(2)	0.032(1)	0.032(1)	0.034(1)	0	0	0.016(1)

X-ray Fluorescence Analysis

Mixtures of Sn powder and $PbCl_2$ powder were analyzed with X-ray fluorescence spectroscopy and the ratio between the X-ray peak at 12.5 keV (attributed to Pb) and the X-ray peak at 25keV (attributed to Sn) was plotted as a function of molar ratio to create a calibration curve. Then, crystalline samples of $Pb_xSn_{4-x}As_3$ were also analyzed with X-ray fluorescence spectroscopy and their Pb:Sn peak ratios were used to calculate the Pb:Sn molar ratio in each crystal, which allowed the precise chemical formula of each $Pb_xSn_{4-x}As_3$ crystal to be determined. Several crystals were measured using this technique, and these values were averaged together, resulting in an average value for each $Pb_xSn_{4-x}As_3$ value. Error bars on each point represent one standard deviation from the average.

This analysis determined that Sn_4As_3, $Pb_{0.25}Sn_{3.75}As_3$, $Pb_{0.59}Sn_{3.41}As_3$, $Pb_{0.76}Sn_{3.24}As_3$, and $Pb_{1.06}Sn_{2.94}As_3$ are the 5 compounds in the $Pb_xSn_{4-x}As_3$ alloy series.

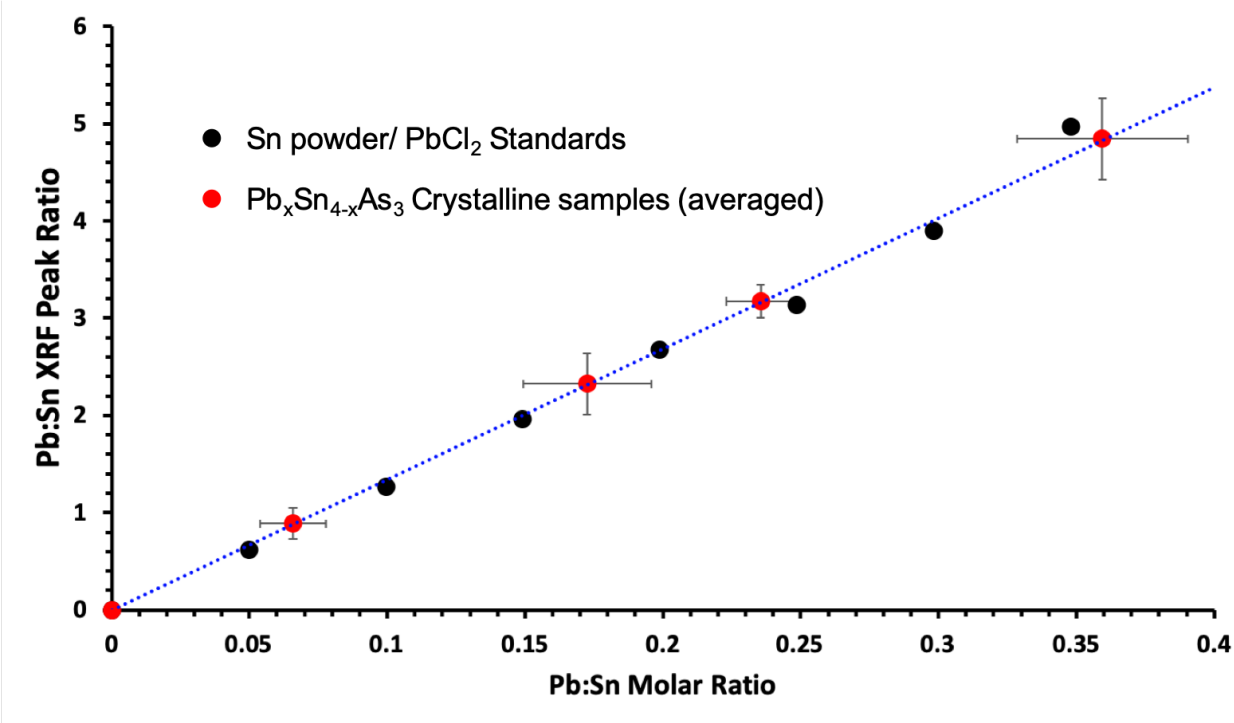

Figure S1: XRF calibration curve of Sn/$PbCl_2$ mixtures used to quantify Pb:Sn ratio in $Pb_xSn_{4-x}As_3$.

SEM/EDX

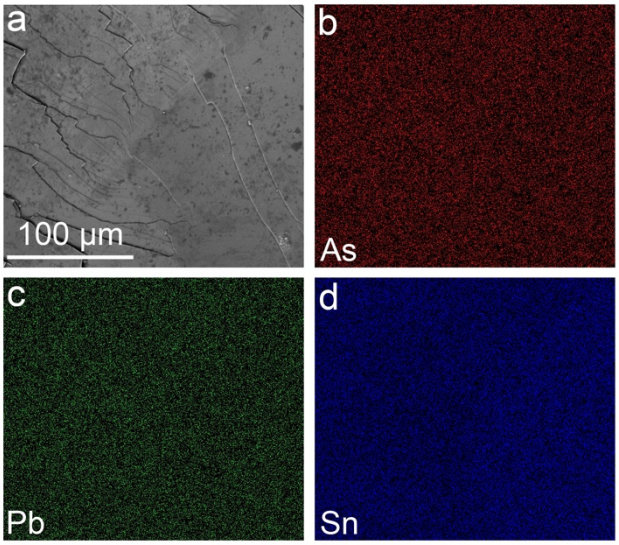

Figure S2: (a) SEM image of a $Pb_{0.59}Sn_{3.41}As_3$ single crystal. Elemental mapping of (b) As, (c) Pb, and (d) Sn show a uniform dispersion of the component elements throughout the sample.

Rietveld Refinements of Powder X-ray Diffraction Data

Rietveld refinements were performed on powder X-ray diffraction patterns of Sn_4As_3, $Pb_{0.25}Sn_{3.75}As_3$, $Pb_{0.59}Sn_{3.41}As_3$, $Pb_{0.76}Sn_{3.24}As_3$, and $Pb_{1.06}Sn_{2.94}As_3$ in order to fully characterize these crystalline phases. Previous analysis of single-crystal X-ray diffraction (Tables S1-S3) concluded that the Pb occupies only Sn site 2, with an insignificant amount of Pb on Sn site 1. Thus, in the Rietveld refinement of the powder X-ray diffraction patterns, the Pb/Sn occupancy on Site 2 was fixed to the value determined via XRF. Additionally, Sn_4As_3 was treated as *R3m* while $Pb_xSn_{4-x}As_3$ alloys were treated as *R-3m*, as determined via single-crystal X-ray diffraction.

Sn_4As_3

Table S4. Crystal data and refinement results for Sn_4As_3.

Empirical Formula	Sn_4As_3
Fw (g/mol)	699.60
Space group	R3m
a (Å)	4.0865(1)
c (Å)	36.0468(4)
V (Å^3)	521.33(1)
Z	3
T (K)	295
Lambda (Å)	1.5406
Pattern Range (2θ, degrees)	20-85
wR	8.42
wRmin	3.84
GOF	2.20

Table S5. Fractional atomic coordinates, site occupancies, and isotropic displacement parameters based on the refined Sn_4As_3 structure.

Site	X	Y	Z	Atom	Occupancy	U11	U33
Sn (1)	0	0	0.2901(6)	Sn	1	0.045(2)	0.027(1)
Sn (2)	0	0	0.7125(6)	Sn	1	0.045(2)	0.027(1)
Sn (3)	0	0	0.1373(3)	Sn	1	0.045(2)	0.027(1)
Sn (4)	0	0	0.8656(2)	Sn	1	0.045(2)	0.027(1)
As (1)	0	0	0.5714(9)	As	1	0.031(4)	0.026(1)
As (2)	0	0	0.0028(6)	As	1	0.031(4)	0.026(1)
As (3)	0	0	0.4314(7)	As	1	0.031(4)	0.026(1)

$Pb_{0.25}Sn_{3.75}As_3$

Table S6. Crystal data and refinement results for $Pb_{0.25}Sn_{3.75}As_3$.

Empirical Formula	$Pb_{0.25}Sn_{3.75}As_3$
Fw (g/mol)	721.73
Space group	R-3m
a (Å)	4.0972(1)
c (Å)	36.2185(4)
V ($Å^3$)	526.55(2)
Z	3
T (K)	295
Lambda (Å)	1.5406
Pattern Range (2θ, degree)	20-85
wR	8.75
wRmin	3.52
GOF	2.50

Table S7. Fractional atomic coordinates, site occupancies, and isotropic displacement parameters based on the refined $Pb_{0.25}Sn_{3.75}As_3$ structure. Pb occupancy on site Sn (2) was fixed to the value determined with XRF.

Site	X	Y	Z	Atom	Occupancy	U11	U33
Sn (1)	0	0	0.6361(1)	Sn	1	0.044(7)	0.015(3)
Sn (2)	0	0	0.2106(1)	Sn	0.875	0.044(7)	0.015(3)
				Pb	0.125	0.044(7)	0.015(3)
As (1)	0	0	-0.0690(1)	As	1	0.049(14)	0.028(1)
As (2)	0	0	0.5000	As	1	0.049(14)	0.028(1)

$Pb_{0.59}Sn_{3.41}As_3$

Table S8. Crystal data and refinement results for $Pb_{0.59}Sn_{3.41}As_3$.

Empirical Formula	$Pb_{0.59}Sn_{3.41}As_3$
Fw (g/mol)	751.81
Space group	R-3m
a (Å)	4.0985(1)
c (Å)	36.3182(5)
V ($Å^3$)	528.32(2)
Z	3
T (K)	295
Lambda (Å)	1.5406
Pattern Range (2θ, degree)	20-85
wR	7.75
wRmin	3.55
GOF	2.19

Table S9. Fractional atomic coordinates, site occupancies, and isotropic displacement parameters based on the refined $Pb_{0.59}Sn_{3.41}As_3$structure. Pb occupancy on site Sn (2) was fixed to the value determined with XRF.

Site	X	Y	Z	Atom	Occupancy	U11	U33
Sn (1)	0	0	0.6362(1)	Sn	1	0.028(2)	0.023(1)
Sn (2)	0	0	0.2104(1)	Sn	0.705	0.028(2)	0.023(1)
				Pb	0.295	0.028(2)	0.023(1)
As (1)	0	0	-0.0690(1)	As	1	0.030(7)	0.017(1)
As (2)	0	0	0.5000	As	1	0.030(7)	0.017(1)

$Pb_{0.76}Sn_{3.24}As_3$

Table S10. Crystal data and refinement results for $Pb_{0.76}Sn_{3.24}As_3$.

Empirical Formula	$Pb_{0.76}Sn_{3.24}As_3$
Fw (g/mol)	766.86
Space group	R-3m
a (Å)	4.1060(1)
c (Å)	36.4600(4)
V ($Å^3$)	532.32(2)
Z	3
T (K)	295
Lambda (Å)	1.5406
Pattern Range (2θ, degree)	20-85
wR	7.78
wRmin	3.50
GOF	2.23

Table S11. Fractional atomic coordinates, site occupancies, and isotropic displacement parameters from the refined $Pb_{0.76}Sn_{3.24}As_3$ structure. Pb occupancy on site Sn (2) was fixed to the value determined with XRF.

Site	X	Y	Z	Atom	Occupancy	U11	U33
Sn (1)	0	0	0.6365(1)	Sn	1	0.027(1)	0.036(1)
Sn (2)	0	0	0.3031(1)	Sn	0.620	0.027(1)	0.036(1)
				Pb	0.380	0.027(1)	0.036(1)
As (1)	0	0	-0.0691(1)	As	1	0.042(7)	0.018(1)
As (2)	0	0	0.5000	As	1	0.042(7)	0.018(1)

$Pb_{1.06}Sn_{2.94}As_3$

Table S12. Crystal data and refinement results for $Pb_{1.06}Sn_{2.94}As_3$.

Empirical Formula	$Pb_{1.06}Sn_{2.94}As_3$
Fw (g/mol)	793.40
Space group	R-3m
a (Å)	4.1017(3)
c (Å)	36.5268(15)
V ($Å^3$)	532.19(3)
Z	3
T (K)	295
Lambda (Å)	1.5406
Pattern Range (2θ, degree)	5-90
wR	6.87
wRmin	3.40
GOF	2.03

Table S13. Fractional atomic coordinates, site occupancies, and isotropic displacement parameters based on the refined $Pb_{1.06}Sn_{2.94}As_3$ structure. Pb occupancy on site Sn (2) was fixed to the value determined with XRF.

Site	X	Y	Z	Atom	Occupancy	U11	U33
Sn (1)	0	0	0.6370(2)	Sn	1	0.029(2)	0.029(1)
Sn (2)	0	0	0.2116(2)	Sn	0.470	0.029(2)	0.029(1)
				Pb	0.530	0.029(2)	0.029(1)
As (1)	0	0	-0.0658(2)	As	1	0.024(7)	0.010(2)
As (2)	0	0	0.5000	As	1	0.024(7)	0.010(2)

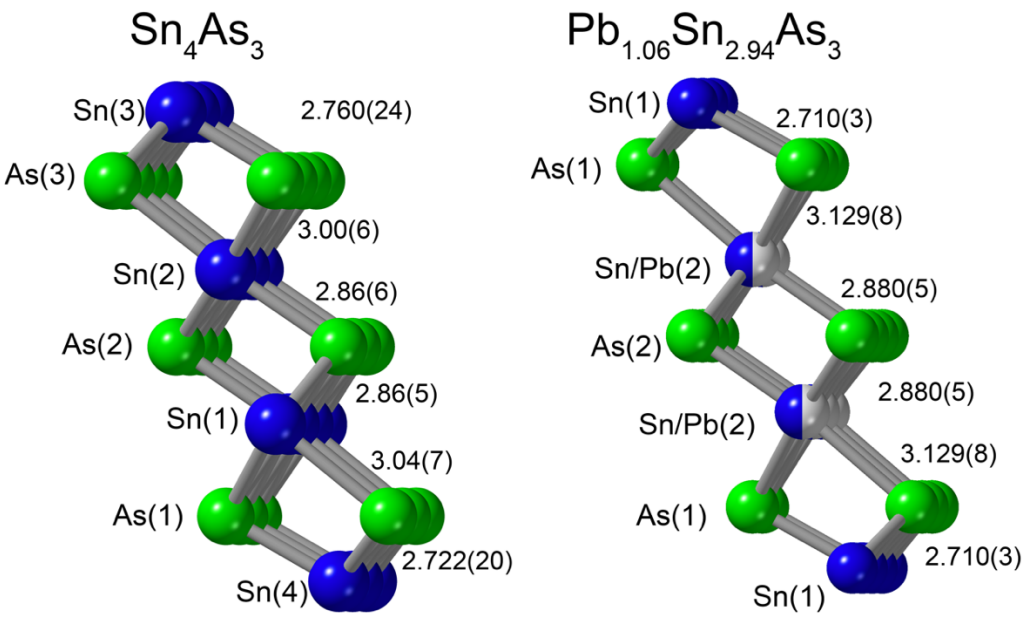

Figure S3: Pictorial representation of refined Sn-As bond length changes between *R3m* Sn_4As_3 and *R-3m* $Pb_{1.06}Sn_{2.94}As_3$. The lone pair distortions at the interior Sn sites are prevalent both with and without Pb substitution.

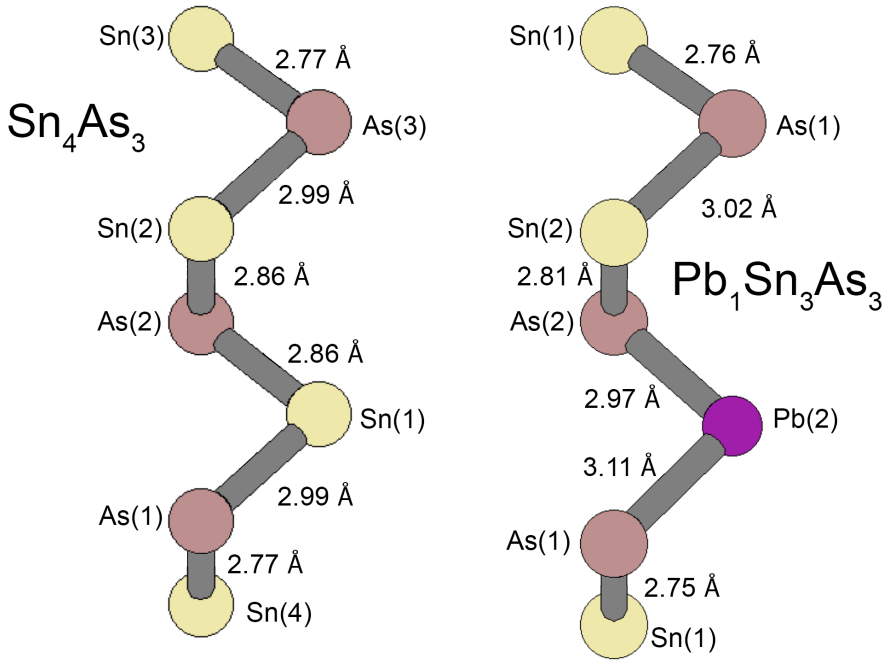

Figure S4: Pictorial representation of DFT-calculated bond lengths for Sn_4As_3 (left) and $Pb_1Sn_3As_3$ (right), in which Pb occupies one of the two Sn(2) sites in a single 7-layer packet. The structure was not constrained to any symmetry in these energy minimization calculations. Still, the atomic sites were labelled assuming Sn_4As_3 had *R3m* symmetry, and $Pb_1Sn_3As_3$ had *R-3m* symmetry.