$La_{1-x}Bi_{1+x}S_3$ (x~0.08): An *n*-Type Semiconductor

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Supporting Information

Table S1. Single Crystal Data and Structure Refinement for $La_{0.92}Bi_{1.08}S_3$ Collected at Room Temperature.

Empirical formula	$La_{0.92}Bi_{1.08}S_3$
Formula weight	449.97
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/m
Unit cell dimensions	a = 28.0447(19) Å, α = 90.00° b = 4.0722(2) Å, β = 118.493(5)° c = 14.7350(9) Å, γ = 90.00°
Volume	1478.96(15) $Å^3$
Z	12
Density (calculated)	6.063 g/cm^3
Absorption coefficient	47.553 mm^{-1}
F(000)	2282
θ range for data collection	4.19 to 34.78°
Index ranges	-44<=h<=44, -6<=k<=6, -23<=l<=23
Reflections collected	19673
Independent reflections	3487 [R_{int} = 0.0778]
Completeness to θ = 24.97°	97.3%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3487 / 0 / 100
Goodness-of-fit	0.926
Final R indices [>2σ(I)]	R_{obs} = 0.0319, wR_{obs} = 0.0546
R indices [all data]	R_{all} = 0.0523, wR_{all} = 0.0586
Largest diff. peak and hole	2.936 and -2.998 e·$Å^{-3}$

$R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR=\{\Sigma[w(|F_o|^2-|F_c|^2)^2]/\Sigma[w(|F_o|^4)]\}^{1/2}$ and $w=1/[\sigma^2(F_o^2)+(0.0257P)^2+0.0000P]$ where $P=(F_o^2+2F_c^2)/3$

Table S2. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for $La_{0.92}Bi_{1.08}S_3$ at Room Temperature.

Label	x	y	z	Occupancy	U_{eq}*
Bi(1)	1279(1)	0	2852(1)	1	16(1)
Bi(2)	1327(1)	0	7640(1)	1	14(1)
Bi(3)	2164(1)	0	816(1)	1	16(1)
La(1)	2955(1)	0	4088(2)	0.747(7)	11(1)
Bi(4)	2876(2)	0	4372(3)	0.253(7)	21(1)
La(2)	4444(1)	0	593(1)	1	10(1)
La(3)	5282(1)	0	3959(1)	1	11(1)
S(1)	368(1)	0	7727(2)	1	11(1)
S(2)	1218(1)	0	4616(2)	1	11(1)
S(3)	1276(1)	0	864(2)	1	13(1)
S(4)	2342(1)	0	7634(2)	1	17(1)
S(5)	2861(1)	0	6035(2)	1	16(1)
S(6)	3323(1)	0	665(2)	1	17(1)
S(7)	3946(2)	0	3654(2)	1	23(1)
S(8)	5590(1)	0	2291(2)	1	14(1)
S(9)	0	0	5000	1	17(1)
S(10)	0	0	0	1	15(1)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for $La_{0.92}Bi_{1.08}S_3$ at Room Temperature.

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi(1)	18(1)	16(1)	18(1)	0	11(1)	0
Bi(2)	16(1)	13(1)	15(1)	0	9(1)	0
Bi(3)	16(1)	16(1)	17(1)	0	10(1)	0
La(1)	13(1)	10(1)	10(1)	0	6(1)	0
Bi(4)	24(1)	17(1)	22(2)	0	11(1)	0
La(2)	11(1)	8(1)	11(1)	0	6(1)	0
La(3)	17(1)	7(1)	10(1)	0	8(1)	0
S(1)	12(1)	10(1)	11(1)	0	5(1)	0
S(2)	12(1)	11(1)	11(1)	0	6(1)	0
S(3)	14(1)	14(1)	11(1)	0	5(1)	0
S(4)	16(1)	22(1)	15(1)	0	7(1)	0
S(5)	14(1)	14(1)	20(1)	0	9(1)	0
S(6)	19(1)	19(1)	15(1)	0	9(1)	0
S(7)	34(2)	16(1)	10(1)	0	4(1)	0
S(8)	11(1)	18(1)	12(1)	0	4(1)	0
S(9)	25(2)	10(2)	24(2)	0	19(2)	0
S(10)	19(2)	10(2)	22(2)	0	16(2)	0

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ...+ 2hka^*b^*U_{12}]$.

Table S4. Bond Lengths [Å] for $La_{0.92}Bi_{1.08}S_3$ at Room Temperature.

Label	Distances
Bi(1)-S(8) ×2	2.6514(13)
Bi(1)-S(2)	2.685(2)
Bi(1)-S(3)	2.926(2)
Bi(1)-S(5) ×2	2.9805(17)
Bi(2)-S(7) ×2	2.6410(15)
Bi(2)-S(1)	2.755(2)
Bi(2)-S(4)	2.850(2)
Bi(2)-S(6) ×2	3.0019(17)
Bi(3)-S(3)	2.524(2)
Bi(3)-S(6) ×2	2.8159(16)
Bi(3)-S(4) ×2	2.8739(17)
Bi(3)-S(6)	3.3635(32)
La(1)-S(2) ×2	2.9906(16)
La(1)-S(5)	3.003(3)
La(1)-S(5) ×2	3.004(2)
La(1)-S(4) ×2	3.044(2)
La(1)-S(7)	3.136(4)
Bi(4)-S(5)	2.470(6)
Bi(4)-S(5) ×2	2.755(3)
Bi(4)-S(2) ×2	3.036(2)
Bi(4)-S(4)	3.3968(42)
La(2)-S(10) ×2	2.9391(3)
La(2)-S(3) ×2	2.9498(16)
La(2)-S(8)	2.986(2)
La(2)-S(1) ×2	3.0498(16)
La(2)-S(6)	3.196(2)
La(3)-S(9) ×2	2.8770(3)
La(3)-S(8)	2.971(2)
La(3)-S(1) ×2	3.0528(16)
La(3)-S(2) ×2	3.0903(16)
La(3)-S(7)	3.129(2)

The powder XRD pattern and Rietveld fit for the smashed and powdered crystals are shown in Figure S1. The data are well fitted with the *C2/m* structure solved by single-crystal X-ray diffraction. The Rietveld quality factors R_p and wR_p are 0.0292 and 0.0383 respectively, which indicates good agreements between the experimental and simulated data. The phase purity of the sample is confirmed by the refinement result, which makes the property characterizations like thermopower reliable.

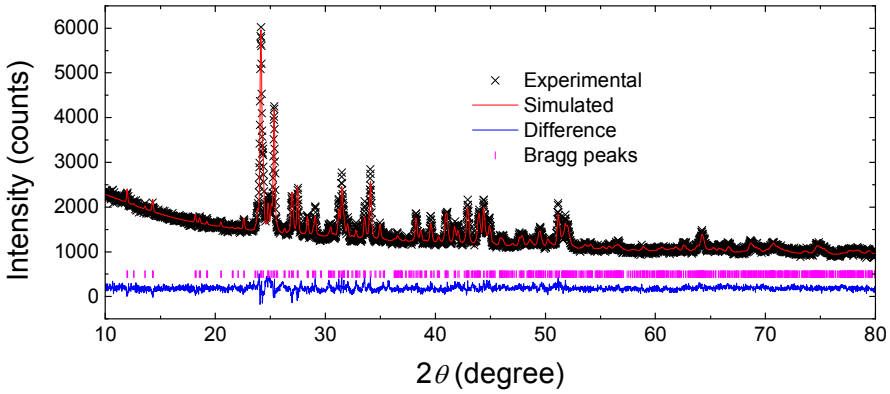

Figure S1. Powder x-ray diffraction (XRD) pattern and Rietveld fit for the smashed and powdered $La_{0.92}Bi_{1.08}S_3$ crystals.