Supporting Information

Substitution of Au or Hg into $BaTl_2$ and $BaIn_2$. New Ternary Examples of Smaller $CeCu_2$-Type Intermetallic Phases

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Table S1. Details of crystal data and structure refinement for $BaAu_{0.40(2)}Tl_{1.60(7)}$ (**1**)

Empirical formula	$BaAu_{0.40(2)}Tl_{1.60(7)}$
Color and Habit	Silvery, irregular block
Crystal Size (mm)	0.176×0.119×0.087
Crystal system	Orthorhombic
Space group, *Z*	*Imma* (No 74), 4
Unit cell dimensions	
a, *b*, *c* (Å); *V* (Å^3)	5.140(1), 8.317(2), 8.809(2); 376.6(1)
Formula weight	543.12
Density(calc.) (Mg/m^3)	9.580
Absorption coefficient (mm^{-1})	93.909
F(000)	869
Diffractometer	Bruker Smart APEX CCD
Radiation	Mo–$K\alpha$ (λ = 0.71073 Å)
T, °K	293(2)
θ_{range} (deg)	3.37 – 28.12
Reflections measured	1114
Index ranges of measured data	-6<=h<=6, -4<=k<=10, -11<=l<=10
Independent reflections	266 (R_{int} = 0.0475)
Observed Reflections	246 (>2 σ (I))
Absorption Correction	SADABS
System Used	Bruker SHELXTL PLUS (PC Version)
Structure Solution, Refinement	SHELXS-97 (Sheldrick, 1997)
Refinement Method	Full-matrix least-squares on F^2
Parameter/Restraints/Data (obs.)	11 / 0 / 246
Completeness to theta = 28.12	97.8 %
Final R indices (obs.)[a]	R1 = 0.0367, wR2 = 0.0992
R indices (all)	R1 = 0.0390, wR2 = 0.1007
Weighting Scheme[b]	*a* = 0.0635, *b* = 47.8107
Goodness-of-fit	1.004
Largest difference peak (e.A^{-3})	4.37, -5.57

[a] $R1=\sum(||F_o|-|F_c||)/\sum|F_o|$, $wR2=\{\sum w[(F_o^2-F_c^2)^2]/\sum w[(F_o^2)^2]\}^{1/2}$; [b] $w=1/[\sigma^2(F_o^2)+(aP)^2+bP]$, in which $P=(F_o^2+2F_c^2)/3$].

Table S2. Atomic coordinates and displacement parameters ($Å^2$) for $BaAu_{0.40(2)}Tl_{1.60(7)}$ (**1**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

atom	Wyck	*x*	*y*	*z*	U(eq)
Ba	4e	0	1/4	0.9604(2)	0.017(1)
Tl/Au	8h	0	0.5514(1)	0.6645(1)	0.015(1)

Table S3 Anisotropic displacement parameters ($Å^2$) for $BaAu_{0.40(2)}Tl_{1.60(7)}$ (**1**)

atom	U11	U22	U33	U23	U13	U12
Ba	0.022(1)	0.009(1)	0.020(1)	0	0	0
Tl/Au	0.008(1)	0.030(1)	0.009(1)	-0.001(1)	0	0

Table S4. Bond lengths [Å] for $BaAu_{0.40(2)}Tl_{1.60(7)}$ (**1**)

Tl-Tl#1	2.9793(9)
Tl-Tl#2	2.9793(9)
Tl-Tl#3	3.021(2)
Tl-Tl#4	3.303(2)
Tl-Ba#5	3.544(1)
Tl-Ba#6	3.544(1)
Tl-Ba	3.617(2)
Tl-Ba#7	3.694(2)
Tl-Ba#8	3.755(1)
Tl-Ba#9	3.755(1)
Ba-Tl#10	3.544(1)
Ba-Tl#11	3.544(1)
Ba-Tl#12	3.544(1)
Ba-Tl#13	3.544(1)
Ba-Tl#14	3.617(2)
Ba-Tl#7	3.694(2)
Ba-Tl#15	3.694(2)
Ba-Tl#8	3.755(1)
Ba-Tl#1	3.755(1)
Ba-Tl#9	3.755(1)
Ba-Tl#2	3.755(1)

Symmetry transformations used to generate equivalent atoms:
#1 x+1/2,y,-z+1/2 #2 x-1/2,y,-z+1/2
#3 -x,-y+1,-z #4 -x,-y+3/2,z #5 x-1/2,y+1/2,z-1/2
#6 x+1/2,y+1/2,z-1/2 #7 -x,-y+1,-z+1
#8 -x-1/2,-y+1/2,-z+1/2 #9 -x+1/2,-y+1/2,-z+1/2
#10 -x+1/2,-y+1,z+1/2 #11 x+1/2,y-1/2,z+1/2
#12 x-1/2,y-1/2,z+1/2 #13 -x-1/2,-y+1,z+1/2
#14 -x,-y+1/2,z #15 x,y-1/2,-z+1

Table S5. Details of crystal data collections and structure refinement for $BaAu_{0.36(4)}In_{1.64(4)}$ (**2**)

Empirical formula	$BaAu_{0.36(4)}In_{1.64(4)}$
Color and Habit	Silvery luster, irregular block
Crystal Size (mm)	0.077×0.075×0.061
Crystal system	Orthorhombic
Space group, *Z*	*Imma* (No 74), 4
Unit cell dimensions	
a, *b*, *c* (Å); *V* (Å^3)	5.104(1), 8.461(2), 8.580(2); 370.5(1)
Formula weight	396.55
Density(calc.) (Mg/m^3)	7.098
Absorption coefficient (mm^{-1})	34.321
F(000)	658
Diffractometer	Bruker Smart APEX CCD
Radiation	Mo–$K\alpha$ (λ = 0.71073 Å)
T, °K	293(2)
θ_{range} (deg)	3.38 – 28.20
Reflections measured	1119
Index ranges of measured data	-10<=h<=10, -6<=k<=3, -10<=l<=10
Independent reflections	257 (R_{int} = 0.0242)
Observed Reflections	247 (>2 σ (I))
Absorption Correction	SADABS
System Used	Brukeer SHELXTL PLUS (PC Version)
Structure Solution, Refinement	SHELXS-97 (Sheldrick, 1997)
Refinement Method	Full-matrix least-squares on F^2
Data (obs.)/ restraints/parameters	247 / 0 / 13
Completeness to theta = 28.20	94.5 %
Final R indices (obs.)[a]	R1 = 0.0394, wR2 = 0.0979
R indices (all)	R1 = 0.0407, wR2 = 0.0983
Weighting Scheme[b]	*a* = 0.0406, *b* = 67.768
Extinction coefficient	0.0011(4)
Goodness-of-fit	1.005
Largest difference peak (e.A^{-3})	3.54, -5.64

[a] $R1=\sum(||F_o|-|F_c||)/\sum|F_o|$, $wR2=\{\sum w[(F_o^2-F_c^2)^2]/\sum w[(F_o^2)^2]\}^{1/2}$; [b] $w=1/[\sigma^2(F_o^2)+(aP)^2+bP]$, in which $P=(F_o^2+2F_c^2)/3]$.

Table S6. Atomic coordinates and isotropic displacement parameters (Å^2) for $BaAu_{0.36(4)}In_{1.64(4)}$ (**2**)

atom	Wyck	*x*	*y*	*z*	U(eq)	Occupancy
Ba	4e	0	1/4	0.9515(2)	0.020(1)	
Au/In	8h	0	0.5582(2)	0.6635(1)	0.024(1)	0.18/0.82(2)

Table S7. Anisotropic displacement parameters (Å^2) for $BaAu_{0.36(4)}In_{1.64(4)}$ (**2**)

atom	U11	U22	U33	U23	U13	U12
Ba	0.025(1)	0.014(1)	0.022(1)	0	0	0
Au/In	0.015(1)	0.040(1)	0.017(1)	-0.005(1)	0	0

Table S8. Bond lengths [Å] for $BaAu_{0.36(4)}In_{1.64(4)}$ (**2**)

Ba-Au#1	3.529(1)
Ba-In#1	3.529(1)
Ba-Au#2	3.529(1)
Ba-In#2	3.529(1)
Ba-Au#3	3.529(1)
Ba-In#3	3.529(1)
Ba-Au#4	3.529(1)
Ba-In#4	3.529(1)
Ba-Au#5	3.593(2)
Ba-In#5	3.593(2)
Ba-In	3.593(2)
In-Au#6	2.953(1)
In-In#6	2.953(1)
In-Au#7	2.953(1)
In-In#7	2.953(1)
In-Au#8	2.972(2)
In-In#8	2.972(2)
In-Au#9	3.246(3)
In-In#9	3.246(3)
In-Ba#10	3.529(1)
In-Ba#11	3.529(1)
In-Ba#12	3.681(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,-y+1,z+1/2 #2 x+1/2,y-1/2,z+1/2
#3 x-1/2,y-1/2,z+1/2 #4 -x-1/2,-y+1,z+1/2
#5 -x,-y+1/2,z #6 x+1/2,y,-z+3/2
#7 x-1/2,y,-z+3/2 #8 -x,-y+1,-z+1
#9 -x,-y+3/2,z #10 x-1/2,y+1/2,z-1/2
#11 x+1/2,y+1/2,z-1/2 #12 -x,-y+1,-z+2

Table S9. Details of crystal data and structure refinement for $BaHg_{0.92(2)}In_{1.08(2)}$ (**3**)

Empirical formula	$BaHg_{0.92(2)}In_{1.08(2)}$
Color and Habit	Silvery luster, irregular block
Crystal Size (mm)	0.101×0.092×0.082
Crystal system	Orthorhombic
Space group, *Z*	*Imma* (No 74), 4
Unit cell dimensions	
a, *b*, *c* (Å); *V* (Å^3)	5.145(1), 8.373(2), 8.715(2); 375.4(1)
Formula weight	445.67
Density(calc.) (Mg/m^3)	7.885
Absorption coefficient (mm^{-1})	54.117
F(000)	730
Diffractometer	Bruker Smart APEX CCD
Radiation	Mo–$K\alpha$ (λ = 0.71073 Å)
T, °K	293(2)
θ_{range} (deg)	3.37 – 27.85
Reflections measured	2272
Index ranges of measured data	-4<=h<=6, -9<=k<=10, -8<=l<=11
Independent reflections	265 (R_{int} = 0.0370)
Observed Reflections	260 (>2 σ (I))
Absorption Correction	SADABS
System Used	Bruker SHELXTL PLUS (PC Version)
Structure Solution, Refinement	SHELXS-97 (Sheldrick, 1997)
Refinement Method	Full-matrix least-squares on F^2
Data (obs.)/ restraints/parameters	260 / 0 / 13
Completeness to theta = 27.85	99.3 %
Final R indices (obs.)[a]	R1 = 0.0258, wR2 = 0.1094
R indices (all)	R1 = 0.0263, wR2 = 0.1105
Weighting Scheme[b]	*a* = 0.0958, *b* = 7.4626
Extinction coefficient	0.0017(5)
Goodness-of-fit	1.001
Largest difference peak (e.A^{-3})	2.68, -1.65

[a] $R1=\sum(||F_o|-|F_c||)/\sum|F_o|$, $wR2=\{\sum w[(F_o^2-F_c^2)^2]/\sum w[(F_o^2)^2]\}^{1/2}$; [b] $w=1/[\sigma^2(F_o^2)+(aP)^2+bP]$, in which $P=(F_o^2+2F_c^2)/3$].

Table S10. Atomic coordinates and isotropic displacement parameters ($Å^2$) for $BaHg_{0.92(2)}In_{1.08(2)}$ (**3**)

atom	Wyck	*x*	*y*	*z*	U(eq)	Occupancy
Ba	4e	0	1/4	0.9583(1)	0.015(1)	
Hg/In	8h	0	0.5533(1)	0.6649(1)	0.018(1)	0.46/0.54(1)

Table S11. Anisotropic displacement parameters ($Å^2$) for $BaHg_{0.92(2)}In_{1.08(2)}$ (**3**)

atom	U11	U22	U33	U23	U13	U12
Ba	0.017(1)	0.014(1)	0.015(1)	0	0	0
Hg/In	0.013(1)	0.030(1)	0.012(1)	-0.001(1)	0	0

Table S12. Bond lengths [Å] for $BaHg_{0.92(2)}In_{1.08(2)}$ (**3**)

Ba-In#1	3.5456(9)
Ba-Hg#1	3.5456(9)
Ba-In#2	3.5456(9)
Ba-Hg#2	3.5456(9)
Ba-In#3	3.546(1)
Ba-Hg#3	3.546(1)
Ba-In#4	3.5456(9)
Ba-Hg#4	3.5456(9)
Ba-In#5	3.604(1)
Ba-Hg#5	3.604(1)
Ba-Hg	3.604(1)
Hg-In#6	2.9699(8)
Hg-Hg#6	2.9699(8)
Hg-In#7	2.9699(8)
Hg-Hg#7	2.9699(8)
Hg-In#8	3.009(2)
Hg-Hg#8	3.009(2)
Hg-In#9	3.294(2)
Hg-Hg#9	3.294(2)
Hg-Ba#10	3.5456(9)
Hg-Ba#11	3.546(1)
Hg-Ba#12	3.674(1)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,-y+1,z+1/2 #2 x+1/2,y-1/2,z+1/2
#3 x-1/2,y-1/2,z+1/2 #4 -x-1/2,-y+1,z+1/2
#5 -x,-y+1/2,z #6 x+1/2,y,-z+3/2
#7 x-1/2,y,-z+3/2 #8 -x,-y+1,-z+1
#9 -x,-y+3/2,z #10 x-1/2,y+1/2,z-1/2
#11 x+1/2,y+1/2,z-1/2 #12 -x,-y+1,-z+2

Table S13. Crystal data and structure refinement for $SrAg_{0.8(2)}In_{1.2(2)}$

Empirical formula	$SrAg_{0.8(2)}In_{1.2(2)}$
Crystal Size (mm)	0.15×0.10×0.10
Crystal system	Orthorhombic
Space group, *Z*	*Imma* (No 74), 4
Unit cell dimensions	
a, *b*, *c* (Å); *V* (Å^3)	4.977(1), 8.579(2), 7.975(2); 340.5(1)
Formula weight	311.53
Density(calc.) (Mg/m^3)	6.078
Absorption coefficient (mm^{-1})	27.894
F(000)	537
Diffractometer	Bruker Smart APEX CCD
Radiation	Mo–*Kα*(*λ*=0.71073 Å)
T, °K	293(2)
θ_{range} (deg)	3.49 – 30.15
Reflections measured	988
Index ranges of measured data	-6<=h<=10, -6<=k<=5, -9<=l<=11
Independent reflections	243 (R_{int} = 0.0335)
Observed Reflections	235 (>2 σ (I))
Absorption Correction	SADABS
System Used	Bruker SHELXTL PLUS (PC Version)
Structure Solution, Refinement	SHELXS-97 (Sheldrick, 1997)
Refinement Method	Full-matrix least-squares on F^2
Data (obs.)/ restraints/parameters	235/0/12
Completeness to theta = 30.15	82.9 %
Final R indices (obs.)[a]	R1 = 0.0217, wR2 = 0.0656
R indices (all)	R1 = 0.0227, wR2 = 0.0660
Weighting Scheme[b]	*a* = 0.0508, *b* = 1.8373
Goodness-of-fit	1.003
Largest difference peak (e.A^{-3})	1.43 and -1.17

[a] $R1=\sum(||F_o|-|F_c||)/\sum|F_o|$, $wR2=\{\sum w[(F_o^2-F_c^2)^2]/\sum w[(F_o^2)^2]\}^{1/2}$; [b] $w=1/[\sigma^2(F_o^2)+(aP)^2+bP]$ in which $P=(F_o^2+2F_c^2)/3$].

Table S14. Atomic coordinates and isotropic displacement parameters ($Å^2$) for $SrAg_{0.8(2)}In_{1.2(2)}$

atom	Wyck	*x*	*y*	*z*	U(eq)	Occupancy
Sr	4e	0	1/4	0.9554(1)	0.015(1)	
Ag/In	8h	0	0.5532(1)	0.6640(1)	0.017(1)	0.4/0.6(1)

Table S15. Anisotropic displacement parameters ($Å^2$) for $SrAg_{0.8(2)}In_{1.2(2)}$

atom	U11	U22	U33	U23	U13	U12
Sr	0.018(1)	0.014(1)	0.013(1)	0	0	0
Ag/In	0.028(1)	0.011(1)	0.011(1)	0	-0.001(1)	0

Table S16. Bond lengths [Å] for $SrAg_{0.8(2)}In_{1.2(2)}$

In(1)-Ag(2)#1	2.771(1)
In(1)-In(1)#1	2.771(1)
In(1)-Ag(2)#2	2.8410(6)
In(1)-In(1)#2	2.8410(6)
In(1)-In(1)#3	2.8410(6)
In(1)-Ag(2)#3	2.8410(6)
In(1)-In(1)#4	3.376(1)
In(1)-Ag(2)#4	3.376(1)
In(1)-Sr(3)#5	3.4363(7)
In(1)-Sr(3)#6	3.4363(7)
In(1)-Sr(3)#7	3.473(1)
In(1)-Sr(3)#1	3.4882(9)
Sr(3)-Ag(2)#5	3.4363(7)
Sr(3)-In(1)#5	3.4363(7)
Sr(3)-Ag(2)#8	3.4363(7)
Sr(3)-Ag(2)#9	3.4363(7)
Sr(3)-Ag(2)#6	3.4363(7)
Sr(3)-In(1)#6	3.4363(7)
Sr(3)-In(1)#8	3.4363(7)
Sr(3)-In(1)#9	3.4363(7)
Sr(3)-Ag(2)#10	3.473(1)
Sr(3)-In(1)#10	3.473(1)
Sr(3)-In(1)#11	3.473(1)
Sr(3)-Ag(2)#11	3.473(1)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,-y+1/2,-z+3/2 #2 x,y+1/2,-z+2
#3 x,y-1/2,-z+2 #4 -x,-y+1/2,z #5 -x,-y,-z+1
#6 -x,-y+1,-z+1 #7 x,y,z+1 #8 x,y+1/2,-z+1
#9 x,y-1/2,-z+1 #10 -x,-y+1/2,z-1
#11 x,y,z-1

Table S17. Unit cell comparisons for a series of $CeCu_2$-type phases (*Imma*)

Compd.	*a* (Å)	*b*(Å)	*c*(Å)	*c/a*	*V*(Å^3)
$BaIn_2$[a]	5.220(2)	8.504(3)	8.520(3)	1.631	378.2(4)
$BaAu_{0.1}In_{1.9}$[b]	5.1991(1)	8.4965(5)	8.5393(1)	1.642	377.22(2)
$BaAu_{0.2}In_{1.8}$[b]	5.1544(1)	8.4791(2)	8.5603(2)	1.661	374.13(2)
$BaAu_{0.36(4)}In_{1.64(4)}$ (**2**)[c]	5.104(1)	8.461(2)	8.580(2)	1.681	370.5(1)
$BaAu_{0.4}In_{1.6}$[b]	5.0868(1)	8.4371(2)	8.5632(2)	1.684	367.51(1)

[a] Wendorff, M.; Röhr, C. *Z. Anorg. Allg. Chem.* **2005**, *631*, 338; [b] loaded composition, cell parameters from powder refinement; [c] refined composition and cell parameters from single crystal study.

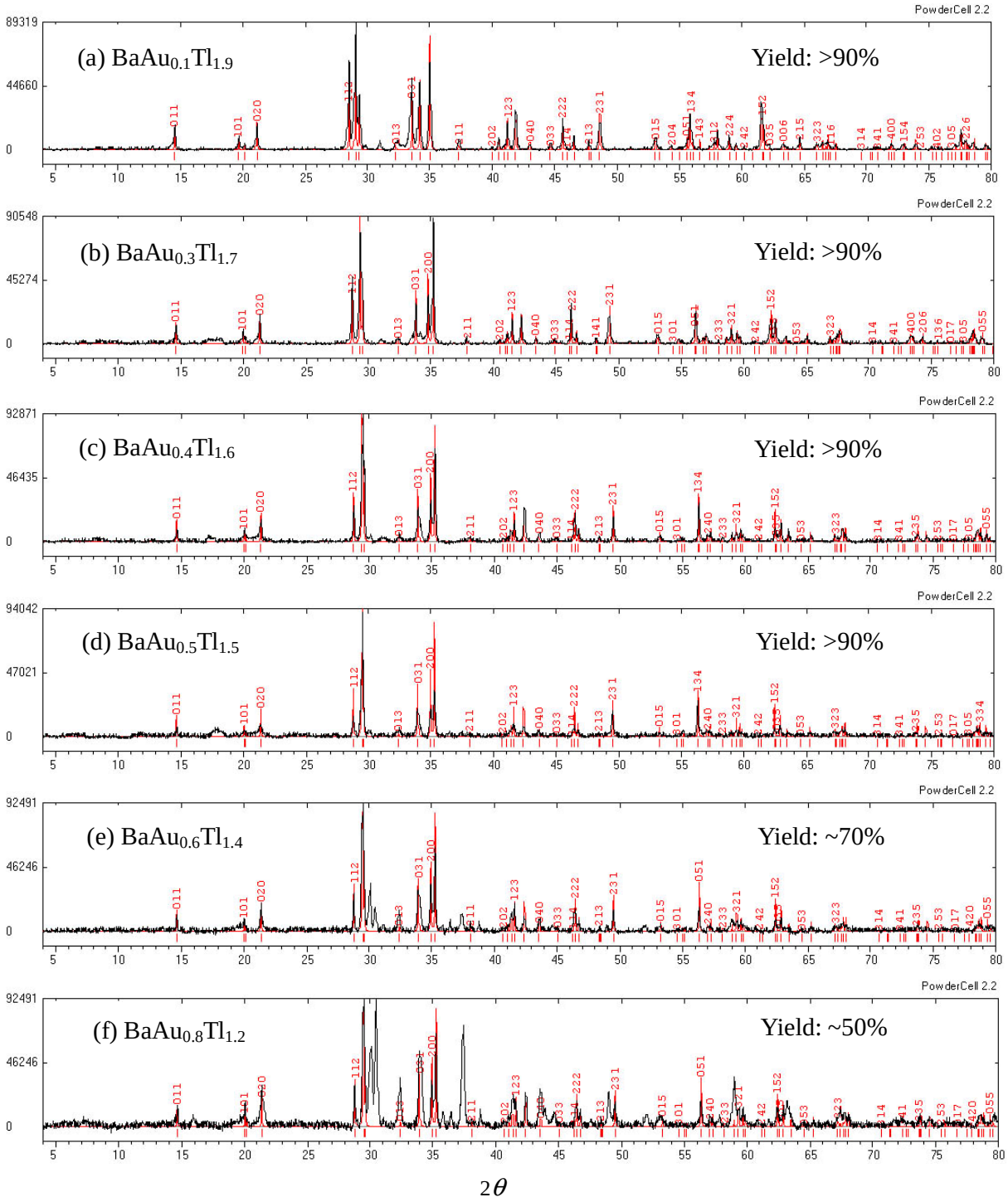

Figure S1. Powder patterns showing the high yield (>90%) products of $CeCu_2$ type for a series of loaded $BaAu_xTl_{2-x}$ compositions for x =: (a) 0.1, (b) 0.3, (c) 0.4, (d) 0.5, (e) 0.6 and (f) 0.8. The red and black represent the calculated ($CeCu_2$ type) and experimental patterns, respectively. The homogeneity region is judged to be x = 0.1 – 0.5.

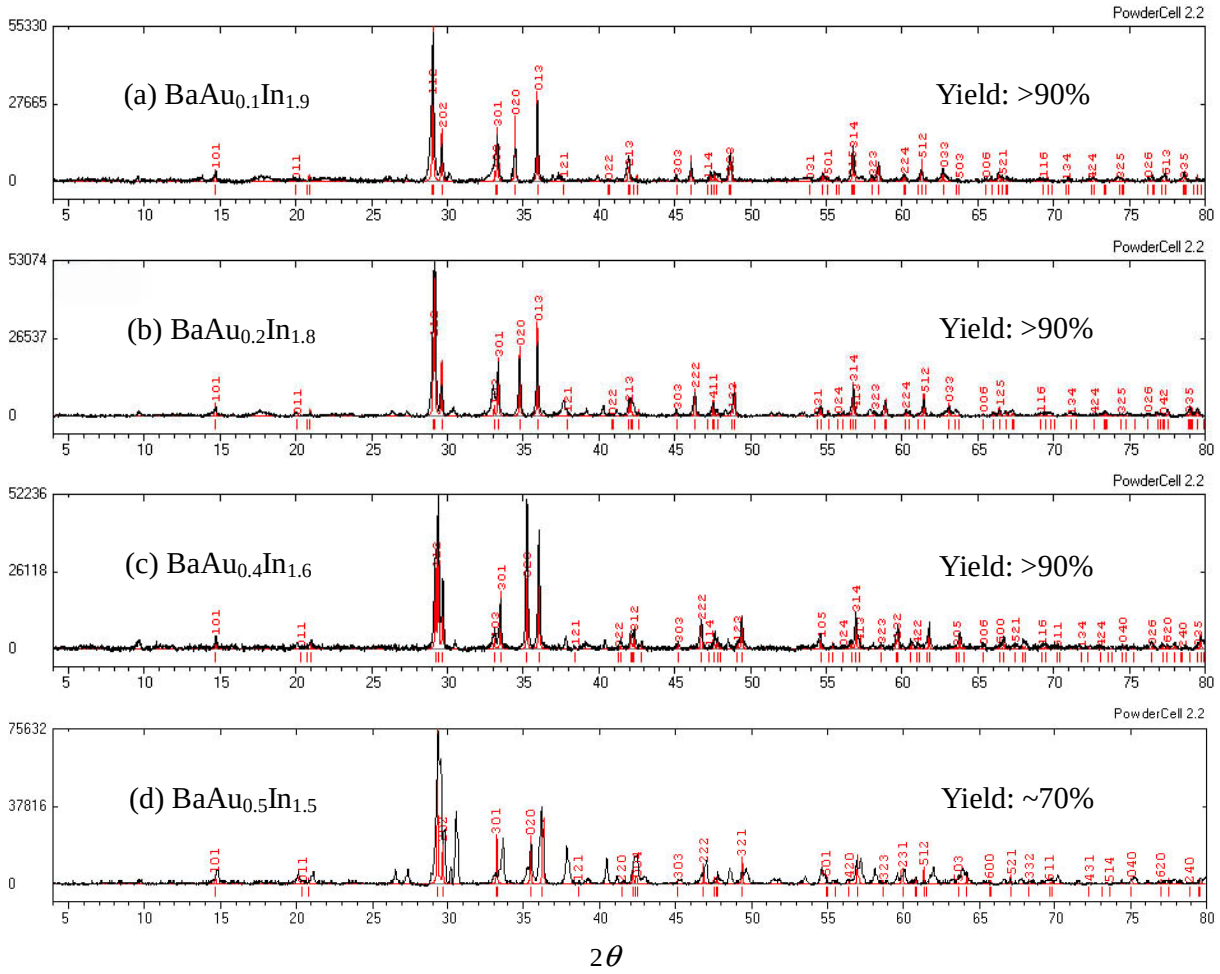

Figure S2. Powder patterns showing the high yield (>90%) of $CeCu_2$ type products for a series of loading $BaAu_xIn_{2-x}$ compositions for x =: (a) 0.1, (b) 0.2, (c) 0.4 and (d) 0.5. The red and black are the calculated ($CeCu_2$ type) and experimental patterns, respectively. The homogeneity region is judged to be x = 0.1 – 0.4.

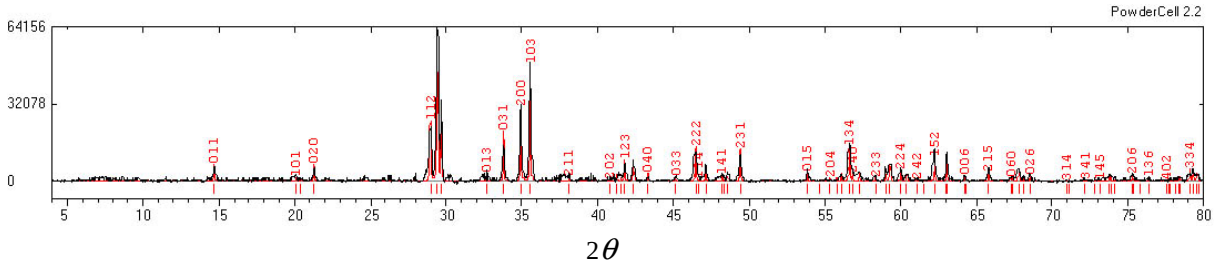

Figure S3. Powder pattern of high quality (> 90%) **3** obtained from a loaded BaHgIn composition. Red and black refer to the calculated ($CeCu_2$ type phase) and experimental patterns, respectively.

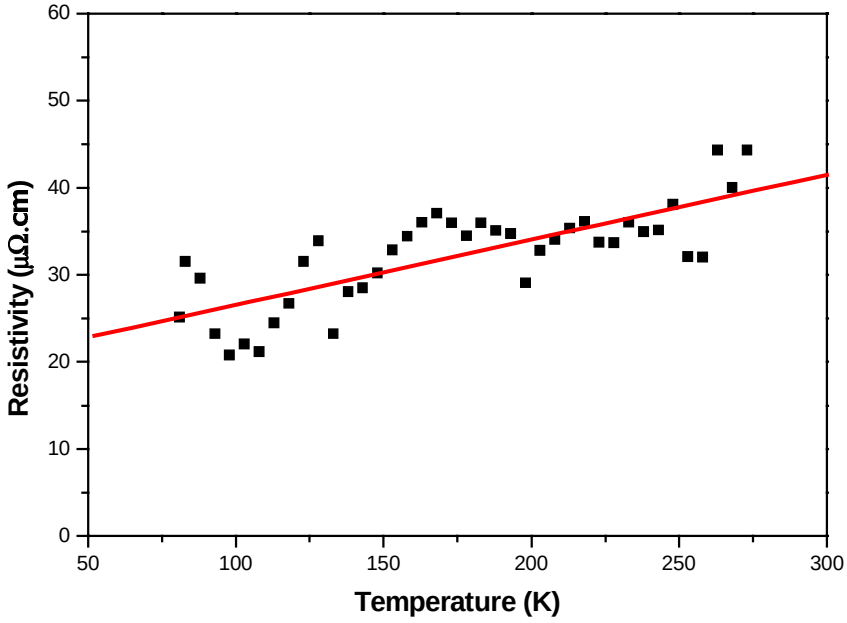

Figure S4. Temperature-dependent electrical resistivities (μΩ·cm) of $BaAu_{0.40(2)}Tl_{1.60(7)}$.

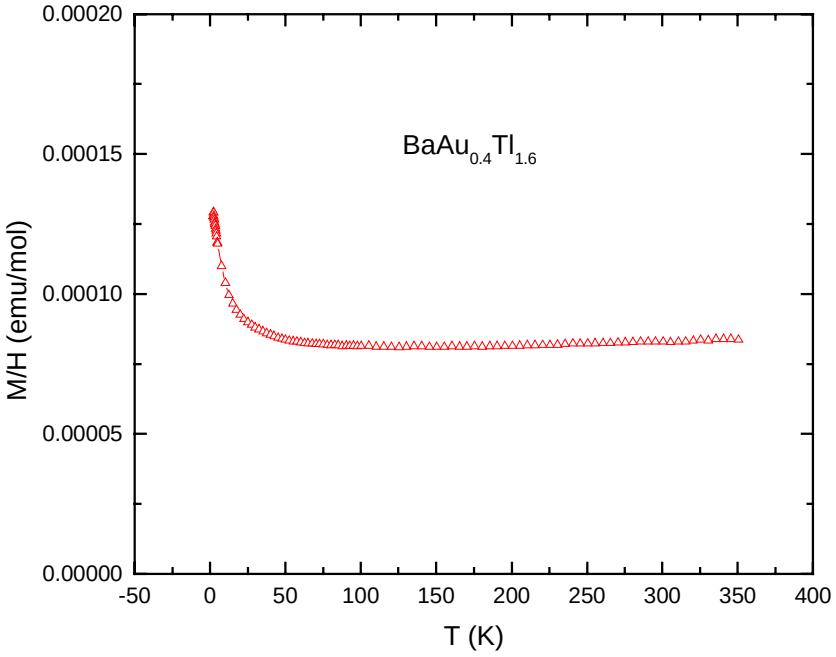

Figure S5. Molar magnetic susceptibilities (emu·mol^{-1}) of $BaAu_{0.40(2)}Tl_{1.60(7)}$, measured at a magnetic flux density of 3Tesla.