Supporting Information

Ultralow Thermal Conductivity through the interplay of composition and disorder between thick and thin layers of Makovickyite structure

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Table S1. Table showing the similar fit with the same number of refined parameters indicating reasonable support for split positions Bi3/Pb1 and no additional benefit for the anharmonic refinements.

	R(obs)	wR2(obs)	R(all)	wR2(all)	GOF(all)	N(ref)	N(par)	ρ(max)	ρ(min)
Split-model	0.0394	0.1154	0.0446	0.1194	1.42	1064	71	2.61	-2.66
Anharm-3	0.0401	0.1160	0.0453	0.1196	1.43	1064	71	2.13	-2.81
Anharm-4	0.0346	0.1037	0.0393	0.1070	1.28	1064	80	1.75	-1.73

Table S2. Final atomic coordinates and equivalent isotropic displacement parameters of the atoms for compounds **I**. $U_{(eq)}$ = 1/3 of the trace of the orthogonalized U_{eq} tensor.

Atom	Wyckoff	S.O.F	x	Y	z	U(eq)
$Ag_{0.72}Bi_{5.48}Cu_{0.88}S_9$, **I**						
Bi(1)	4i	0.74	0.3498(1)	0	0.4347(1)	0.0020(1)
Ag(1)	4i	0.26	0.3498(1)	0	0.4347(1)	0.0020(1)
Bi(2)	4i	1	0.0530(1)	0	0.3076(1)	0.0022(1)
Bi(3)	4i	1	0.7480(1)	0	0.1232(1)	0.0026(1)
Ag(2)	2a	0.20	0	0	0	0.0077(5)
Cu(1)	4g	0.35	0	0.1963(16)	0	0.0037(2)
Cu(2)	4i	0.07	0.0224(17)	0.5	0.0531(17)	0.0030(6)
Cu(3)	4i	0.02	0.0410(60)	0.5	0.0040(60)	0.0029(6)
S(1)	2c	1	0	0	0.5	0.0017(1)
S(2)	4i	1	0.4100(2)	0	0.2707(2)	0.0020(1)
S(3)	4i	1	0.3576(2)	0	0.0426(2)	0.0014(1)
S(4)	4i	1	0.2928(2)	0	0.6249(3)	0.0026(1)
S(5)	4i	1	0.1010(2)	0	0.1383(2)	0.0019(1)

Table S3. Final atomic coordinates and equivalent isotropic displacement parameters of the atoms for compounds **II**. $U_{(eq)}$ = 1/3 of the trace of the orthogonalized U_{eq} tensor.

Atom	Wyckoff	S.O.F	x	y	z	U(eq)
$Ag_{0.70}Bi_{5.30}Cu_{1.3}S_9$, **II**						
Bi(1)	4i	0.72	0.3494(1)	0	0.4347(1)	0.0021(1)
Ag(1)	4i	0.28	0.3494(1)	0	0.4347(1)	0.0021(1)
Bi(2)	4i	0.93	0.0524(1)	0	0.3086(1)	0.0020(1)
Ag(2)	4i	0.07	0.0524(1)		0.3086(1)	0.0020(1)
Bi(3)	4i	1	0.7482(1)	0	0.1237(1)	0.0026(1)
Cu(1)	4g	0.34	0	0.2025(19)	0	0.0042(2)
Cu(2)	4i	0.09	0.0216(12)	0.5	0.0513(13)	0.0033(4)
Cu(3)	4i	0.1	0.270(20)	0	-0.0231(16)	0.0038(8)
Cu(4)	2a	0.24	0	0	0	0.0040(5)
S(1)	2c	1	0	0	0.5	0.0017(1)
S(2)	4i	1	0.4097(2)	0	0.2706(2)	0.0020(1)
S(3)	4i	1	0.3572(2)	0	0.0424(2)	0.0016(1)
S(4)	4i	1	0.2934(2)	0	0.6239(3)	0.0026(1)
S(5)	4i	1	0.1017(2)	0	0.1394(2)	0.0021(1)

Table S4. Final atomic coordinates and equivalent isotropic displacement parameters of the atoms for compounds **III**. $U_{(eq)}$ = 1/3 of the trace of the orthogonalized U_{eq} tensor.

Atom	Wyckoff	S.O.F	x	y	z	U(eq)
$Ag_{0.34}Bi_{4.54}Cu_{1.98}PbS_9$, **III**						
Bi(1)	4i	0.83	0.3493(1)	0	0.4336(1)	0.0020(1)
Ag(1)	4i	0.17	0.3493(1)	0	0.4336(1)	0.0020(1)
Bi(2)	4i	0.94	0.0520(1)	0	0.3092(1)	0.0020(1)
Cu(3)	4i	0.06	-0.002(30)		0.2570(30)	0.0045(7)
Bi(3)	4i	0.5	0.7547(3)	0	0.1166(2)	0.0027(1)
Pb(1)	4i	0.5	0.7437(4)	0	0.1387(2)	0.0049(1)
Cu(1)	4i	0.4	-0.0210(4)	0.5	-0.0762(7)	0.0059(3)
Cu(2)	4i	0.33	0.0487(5)	0	-0.0444(8)	0.0046(2)
Cu(2A)	4g	0.2	0	1780(40)	0	0.0064(5)
S(1)	2c	1	0	0	0.5	0.0019(1)
S(2)	4i	1	0.4094(2)	0	0.2707(2)	0.0020(1)
S(3)	4i	1	0.3575(2)	0	0.0406(2)	0.0018(1)
S(4)	4i	1	0.2933(4)	0	0.6258(2)	0.0026(1)
S(5)	4i	1	0.0980(2)	0	0.1417(2)	0.0020(1)

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **I**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

Atoms	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
			$Ag_{0.72}Bi_{5.48}Cu_{0.88}S_9$, **I**			
Bi(1)	18(1)	18(1)	24(1)	0	4(1)	0
Ag(1)	18(1)	18(1)	24(1)	0	4(1)	0
Bi(2)	24(1)	22(1)	20(1)	0	4(1)	0
Bi(3)	29(1)	29(1)	18(1)	0	-2(1)	0
Ag(2)	91(9)	59(6)	59(6)	0	-57(6)	0
Cu(1)	20(2)	61(4)	30(3)	0	1(2)	0
Cu(2)	20(9)	58(8)	11(8)	0	3(8)	0
Cu(3)	18(14)	59(8)	7(11)	0	-4(11)	0
S(1)	17(2)	20(2)	14(2)	0	3(2)	0
S(2)	21(2)	18(2)	20(2)	0	1(1)	0
S(3)	18(1)	15(1)	11(1)	0	4(1)	0
S(4)	19(2)	18(2)	37(2)	0	0(1)	0

Table S6. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **II**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

Atoms	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
			$Ag_{0.70}Bi_{5.30}Cu_{1.3}S_9$, **II**			
Bi(1)	20(1)	20(1)	21(1)	0	3(1)	0
Ag(1)	20(1)	20(1)	21(1)	0	3(1)	0
Bi(2)	24(1)	21(1)	16(1)	0	3(1)	0
Ag(2)	24(1)	21(1)	16(1)	0	3(1)	0
Bi(3)	31(1)	28(1)	16(1)	0	-3(1)	0
Cu(1)	21(3)	78(5)	27(3)	0	1(2)	0
Cu(2)	13(7)	64(7)	26(7)	0	14(6)	0
Cu(3)	29(12)	65(8)	17(5)	0	-2(7)	0
Cu(4)	24(10)	70(7)	23(6)	0	-3(6)	0
S(1)	18(2)	19(2)	14(2)	0	2(2)	0
S(2)	21(1)	21(2)	16(1)	0	0(1)	0
S(3)	19(1)	19(1)	10(1)	0	1(1)	0
S(4)	20(2)	19(2)	38(2)	0	-2(1)	0

Table S7. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **III**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

Atoms	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
$Ag_{0.34}Bi_{4.54}Cu_{1.98}PbS_9$, **III**						
Bi(1)	16(1)	19(1)	24(1)	0	2(1)	0
Ag(1)	16(1)	19(1)	24(1)	0	2(1)	0
Bi(2)	19(1)	20(1)	19(1)	0	1(1)	0
Cu(3)	59(15)	26(13)	51(15)	0	13(14)	0
Bi(3)	31(1)	27(1)	15(1)	0	-14(1)	0
Pb(1)	50(1)	24(1)	70(3)	0	6(2)	0
Cu(1)	32(3)	41(3)	94(5)	0	-14(3)	0
Cu(2)	31(3)	24(3)	74(5)	0	-17(3)	0
Cu(2A)	23(5)	110(10)	56(7)	0	-4(5)	0
S(1)	20(2)	15(2)	22(2)	0	2(2)	0
S(2)	17(2)	22(2)	20(2)	0	1(1)	0
S(3)	17(1)	18(1)	17(2)	0	0(1)	0
S(4)	15(2)	19(2)	41(2)	0	-5(1)	0

Table S8. Refined lattice constants and final Rietveld refinement parameters for compounds, **I** – **III**.

	I	**II**	**III**
Formula	$Ag_{0.72}Bi_{5.48}Cu_{0.88}S_9$	$Ag_{0.70}Bi_{5.30}Cu_{1.3}S_9$	$Ag_{0.34}Bi_{4.54}Cu_{1.98}PbS_9$
Unit cell	a = 13.1832(7)	a = 13.1887(8)	a = 13.3373(20)
	b = 4.04828(15)	b = 4.04196(16)	b = 4.0391(3)
	c = 14.6292(9)	c = 14.6176(10)	c = 14.7888(24)
	β = 99.401(3)	β = 99.501(4)	β = 99.822(9)
Volume	770.26(4)	768.54(4)	785.00(8)
Rw	6.819	6.744	7.301
RF^2	9.526	8.494	10.866

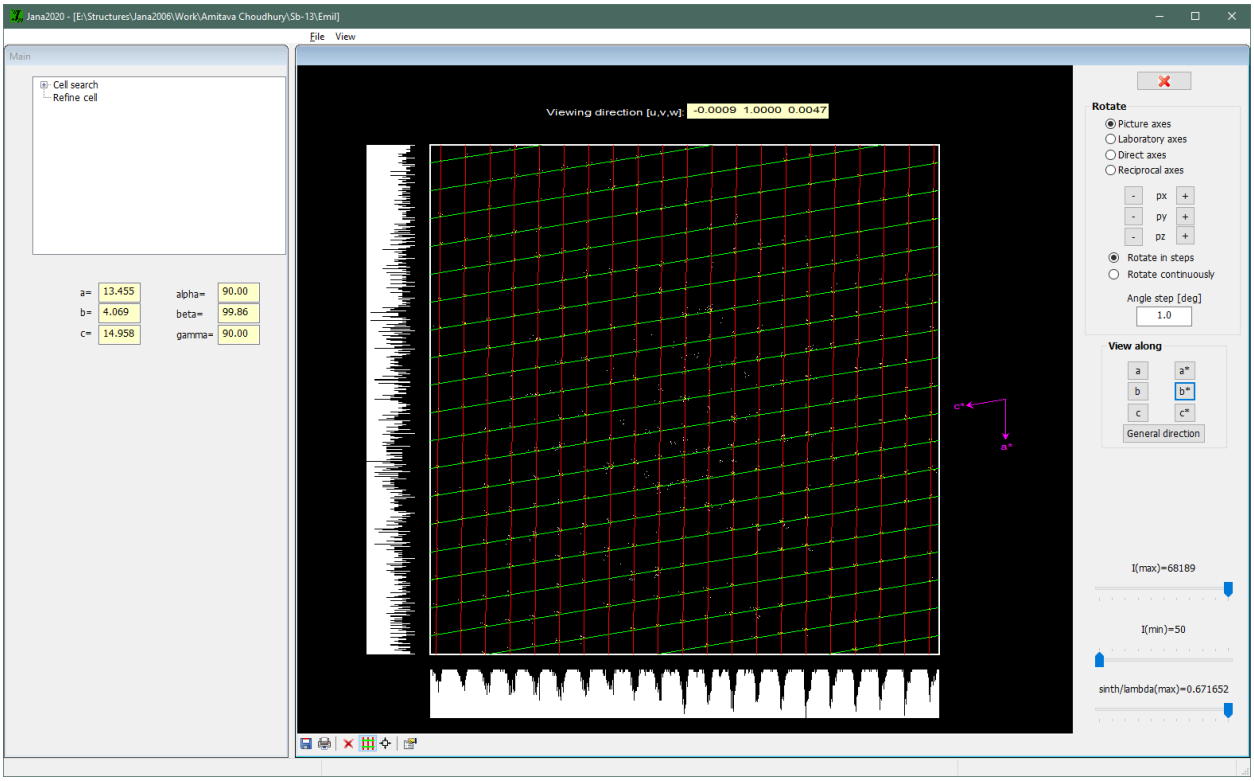

Figure S1. Diffraction pattern from the raw data frames projected on reciprocal lattice. The used cell, a = 13.45, b = 4.069, and c = 14.958, β = 99.86. It can be seen from the above figure that there are only a few additional spots. However, there are no systematic unaccounted spots that would call for a cell doubling along c-axis.

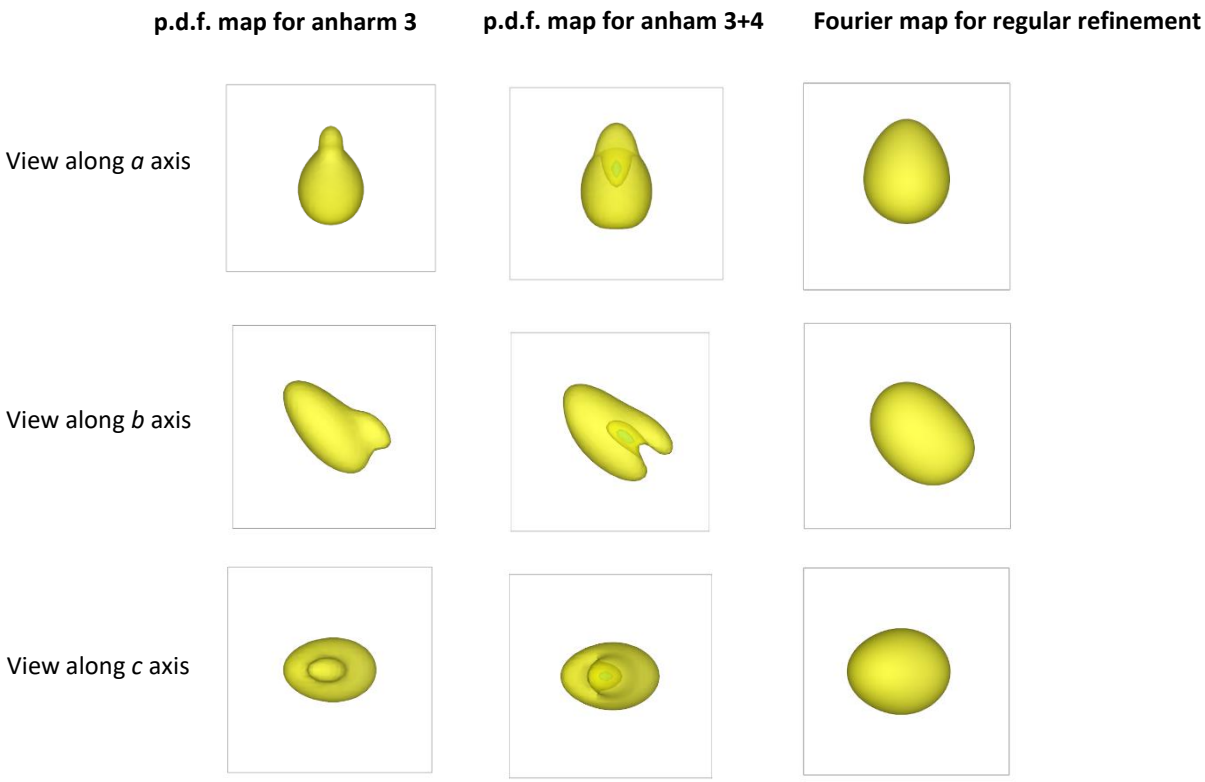

Figure S2. The probability density function p.d.f. is calculated from the refined anharmonic ADPs in the direct space (from a, b, and c-directions). This means that there are no termination effects in such maps. Introduction of 4th order tensor leads to an unrealistic distribution of atoms in the Bi3/Pd1 site. On the other hand, the shape of the p.d.f with using only 3rd term seems to indicate split atom positions as we have used in the regular model.

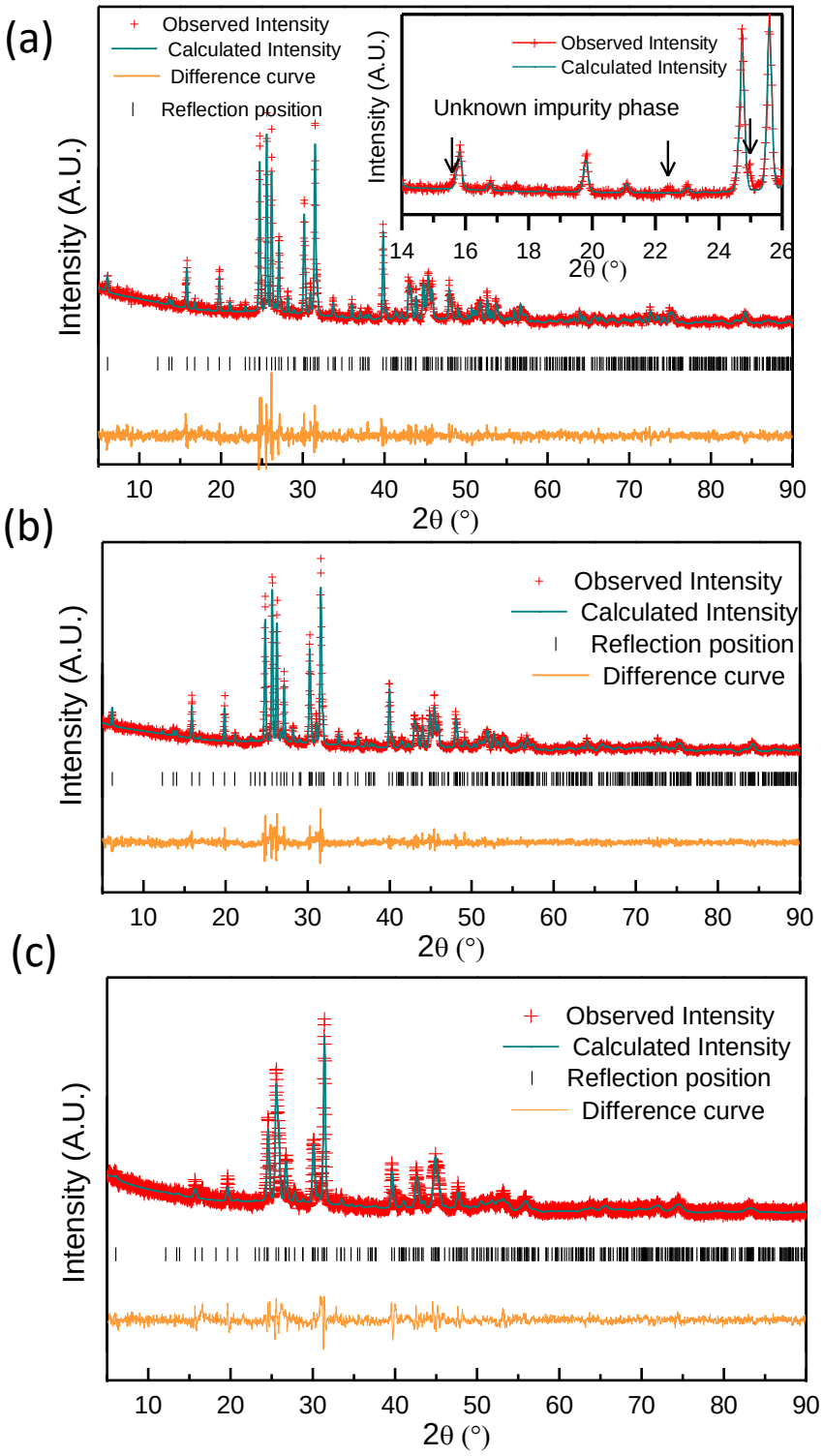

Figure S3. Rietveld refinement plots for (a) $Ag_{0.72}Bi_{5.48}Cu_{0.88}S_9$, **I** (b) $Ag_{0.70}Bi_{5.30}Cu_{1.3}S_9$, **II** (c) $Ag_{0.34}Bi_{4.54}Cu_{1.98}PbS_9$, **III**, showing the observed, calculated and difference curve. Inset in (a) shows an enlarged view of the segment for 2θ = 14 to 26°. The arrows indicate the presence of minute quantity of an unknown impurity phase.

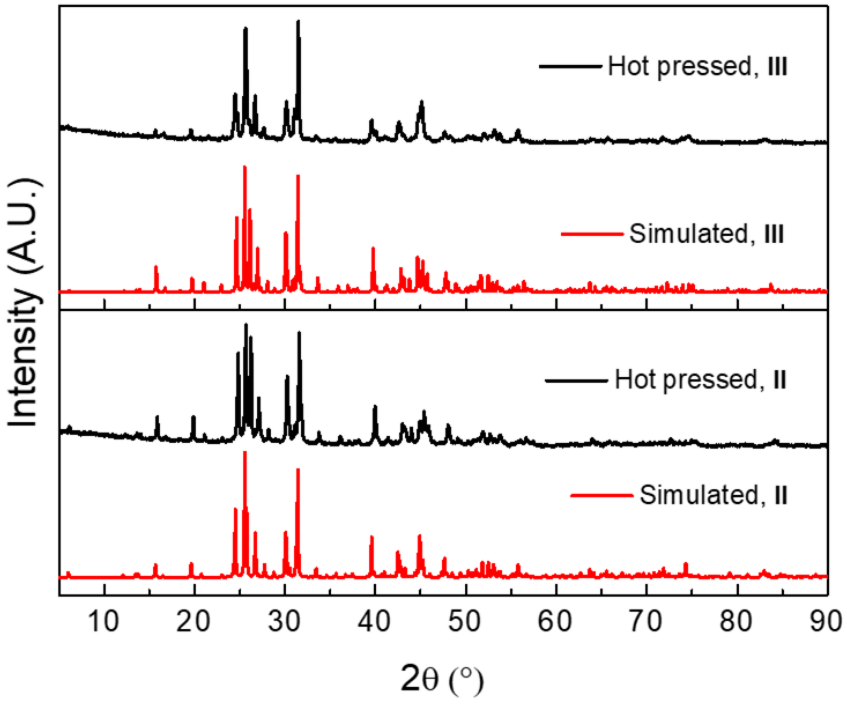

Figure S4. PXRD comparison with of hot-pressed samples with the simulated patterns for $Ag_{0.70}Bi_{5.30}Cu_{1.3}S_9$ (**II**), $Ag_{0.34}Bi_{4.54}Cu_{1.98}PbS_9$ (**III**).

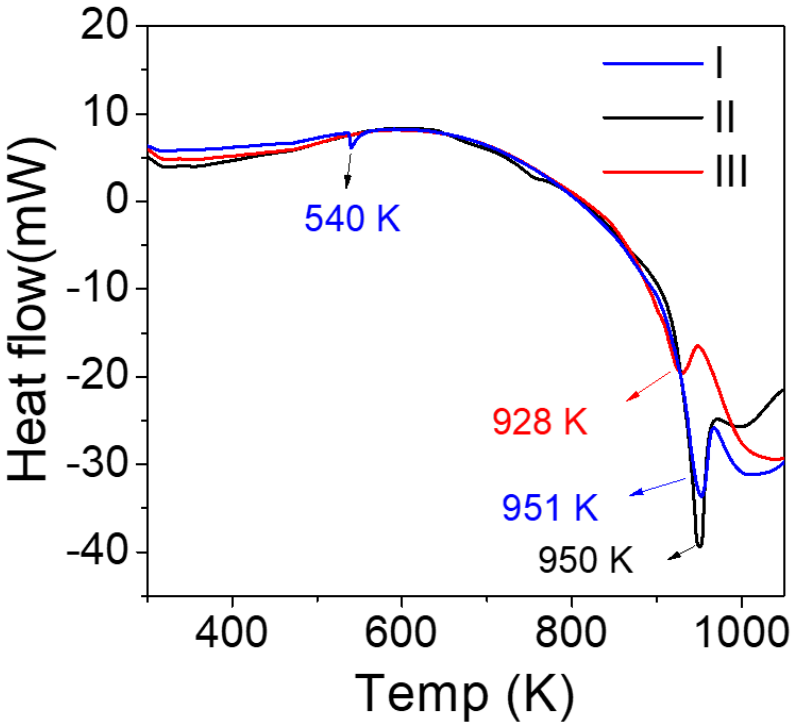

Figure S5. DSC curves for $Ag_{0.72}Bi_{5.48}Cu_{0.88}S_9$ (**I**), $Ag_{0.70}Bi_{5.30}Cu_{1.3}S_9$ (**II**), $Ag_{0.34}Bi_{4.54}Cu_{1.98}PbS_9$ (**III**).

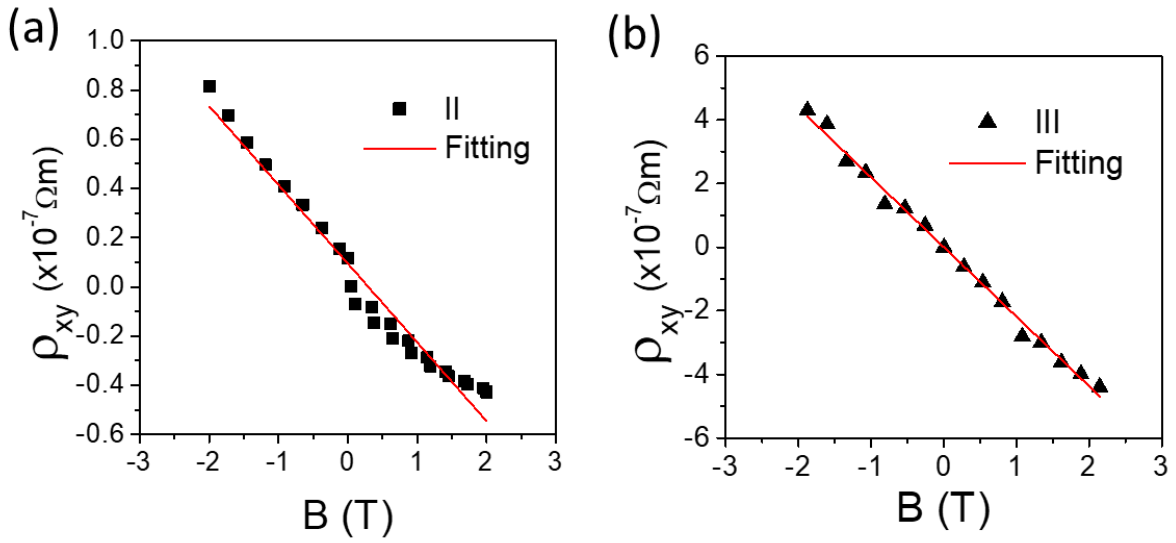

Figure S6. Magnetic field vs Hall resistivity (a) $Ag_{0.70}Bi_{5.30}Cu_{1.3}S_9$, **II** (b) $Ag_{0.34}Bi_{4.54}Cu_{1.98}PbS_9$, **III.**