Dalton Transactions

SUPPORTING INFORMATION

Supporting Information

for

Structure and thermoelectric properties of the silver lead bismuth selenides $Ag_5Pb_9Bi_{19}Se_{40}$ and $AgPb_3Bi_7Se_{14}$

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Table S1: Synthesis parameters of ternary silver lead bismuth selenides: nominal compositions, local sample identifiers, melting and annealing conditions (including remarks on quenching to room temperature) and information on the utilization of the respective samples.

nominal composition **sample name**	**used for ...**	**pre-reaction**	**melting**	**annealing at ... –** **then quenched in ...**
$Ag_2Pb_6Bi_{10}Se_{22}$ (FRHS49)	a) SCXRD b) PXRD c) thermoelectric characterization	650 °C for 72 h (subsequently quenched at air)	950 °C for 24 h (subsequently water-quenched)	650 °C for 480 h and again 408 h after pellet-pressing (water-quenched after each step)
$AgPb_8Bi_9Se_{22}$ (FRHS04)	a) SCXRD	---	---	660 °C for 186 h (water-quenched)

Table S2: Atom positions, site occupancies and equivalent isotropic displacement parameters (in Å^2) of $Ag_5Pb_9Bi_{19}Se_{40}$ at RT, $U_{eq} = 1/3 \cdot [U_{11} + U_{22} + U_{33}]$.

stom	site	x	y	z	U_{eq}	s.o.f.	overall occupancy
Ag1 Pb1 Bi1	2*d*	0	0.40746(4)	0.42170(2)	0.02776(16)	0.14825(9) 0.39827(6) 0.23896(3)	0.78548(18)
Ag2 Pb2 Bi2	2*d*	0.5	0.63720(3)	0.47371(2)	0.02962(15)	0.11960(9) 0.24725(3) 0.57692(6)	0.94377(18)
Ag3 Bi3	2*d*	0.5	0.18115(3)	0.36701(2)	0.02779(15)	0.06408(8) 0.93592(8)	1*
Ag4 Pb4	2*d*	0	0.23079(6)	0.25	0.0584(3)	0.03810(14) 0.96190(14)	1*
Ag5 Bi5	4*d*	0.5	0.46011(4)	0.31735(2)	0.03427(17)	0.27403(9) 0.62173(9)	0.89576(18)
Se6	4*d*	0	0.5	0.5	0.0265(3)	1	1
Se7	2*d*	0.5	0.27355(6)	0.44995(3)	0.0243(2)	1	1
Se8	2*d*	0.5	0.54754(7)	0.39743(3)	0.0256(2)	1	1
Se9	2*d*	0	0.31052(7)	0.34117(3)	0.0301(2)	1	1
Se10	2*d*	0.5	0.09027(7)	0.29798(3)	0.0245(2)	1	1
Se11	4*d*	0.5	0.37209(12)	0.25	0.0390(4)	1	1

* Overall site occupancy was restricted to 1 to prevent slight (numerically insignificant) overpopulation.

Table S3: Anisotropic displacement parameters (in Å^2) of $Ag_5Pb_9Bi_{19}Se_{40}$ at RT, defined as exp $[-2\pi^2 (U_{11}h^2 a^{*2} + U_{22}k^2 b^{*2} + U_{33}l^2 c^{*2} + U_{12}hka^* b^* + U_{13}hla^* c^* + U_{23}klb^* c^*)]$.

Atom	U_{11}	U_{22}	U_{33}	$U_{12} = U_{13}$	U_{23}
Ag1 Pb1 Bi1	0.0231(3)	0.0254(3)	0.0347(3)	0	0.0016(2)
Ag2 Pb2 Bi2	0.0264(2)	0.0328(3)	0.0296(2)	0	-0.00251(18)
Ag3 Bi3	0.0247(2)	0.0303(3)	0.0284(2)	0	-0.00481(14)
Ag4 Pb4	0.0310(3)	0.0504(5)	0.0936(7)	0	0
Ag5 Bi5	0.0265(3)	0.0340(3)	0.0423(3)	0	-0.0002(2)
Se6	0.0212(6)	0.0249(7)	0.0335(7)	0	0.0036(5)
Se7	0.0225(5)	0.0237(5)	0.0267(5)	0	0.0003(4)
Se8	0.0210(4)	0.0257(5)	0.0302(5)	0	0.0045(4)
Se9	0.0203(4)	0.0255(5)	0.0446(6)	0	0.0103(4)
Se10	0.0246(4)	0.0272(5)	0.0217(4)	0	-0.0008(3)
Se11	0.0249(7)	0.0320(8)	0.0600(10)	0	0

Table S4: Atom positions, site occupancies and equivalent isotropic displacement parameters (in Å^2) of $Ag_5Pb_9Bi_{19}Se_{40}$ at 100 °C, $U_{eq} = 1/3 \cdot [U_{11} + U_{22} + U_{33}]$.

Atom	Site	x	y	z	U_{eq}	s.o.f.	overall occupancy
Ag1 Pb1 Bi1	2*d*	0	0.40697(4)	0.42202(2)	0.03244(19)	0.15548(8) 0.39843(5) 0.22412(3)	0.77803(16)
Ag2 Pb2 Bi2	2*d*	0.5	0.63720(3)	0.47385(2)	0.03345(18)	0.13979(8) 0.24300(2) 0.56702(6)	0.94981(16)
Ag3 Bi3	2*d*	0.5	0.18025(3)	0.36740(2)	0.03124(17)	0.06033(7) 0.93967(7)	1*
Ag4 Pb4	2*d*	0	0.22887(7)	0.25	0.0671(3)	0.03188(12) 0.96812(12)	1*
Ag5 Bi5	4*d*	0.5	0.45871(5)	0.31780(2)	0.03704(19)	0.25346(8) 0.64370(8)	0.89716(16)
Se6	4*d*	0	0.50	0.5	0.0311(4)	1	1
Se7	2*d*	0.5	0.27343(7)	0.44993(3)	0.0282(3)	1	1
Se8	2*d*	0.5	0.54706(8)	0.39778(3)	0.0289(3)	1	1
Se9	2*d*	0	0.31013(9)	0.34165(4)	0.0349(3)	1	1
Se10	2*d*	0.5	0.08976(8)	0.29822(3)	0.0280(2)	1	1
Se11	4*d*	0.5	0.37016(14)	0.25	0.0402(4)	1	1

* Overall site occupancy was restricted to 1 to prevent slight (numerically insignificant) overpopulations.

Table S5: Anisotropic displacement parameters (in Å^2) of $Ag_5Pb_9Bi_{19}Se_{40}$ at 100 °C, defined as $\exp[-2\pi^2 (U_{11}h^2 a^{*2} + U_{22}k^2 b^{*2} + U_{33}l^2 c^{*2} + U_{12}hka^* b^* + U_{13}hla^* c^* + U_{23}klb^* c^*)]$.

Atom	U_{11}	U_{22}	U_{33}	$U_{12} = U_{13}$	U_{23}
Ag1 Pb1 Bi1	0.0285(3)	0.0293(4)	0.0396(4)	0	0.0021(3)
Ag2 Pb2 Bi2	0.0313(3)	0.0360(4)	0.0331(3)	0	-0.0026(2)
Ag3 Bi3	0.0292(2)	0.0330(3)	0.0315(2)	0	-0.00419(16)
Ag4 Pb4	0.0377(4)	0.0562(6)	0.1073(9)	0	0
Ag5 Bi5	0.0305(3)	0.0365(4)	0.0441(3)	0	-0.0002(2)
Se6	0.0260(7)	0.0290(8)	0.0382(8)	0	0.0031(6)
Se7	0.0273(5)	0.0277(6)	0.0298(5)	0	-0.0006(4)
Se8	0.0256(5)	0.0279(6)	0.0331(5)	0	0.0043(4)
Se9	0.0244(5)	0.0291(6)	0.0513(7)	0	0.0123(5)
Se10	0.0290(5)	0.0308(6)	0.0242(5)	0	0.0001(4)
Se11	0.0307(8)	0.0364(9)	0.0536(11)	0	0

Table S6: Atom positions, site occupancies and equivalent isotropic displacement parameters (in Å^2) of $Ag_5Pb_9Bi_{19}Se_{40}$ at 200 °C, $U_{eq} = 1/3 \cdot [U_{11} + U_{22} + U_{33}]$.

Atom	Site	x	y	z	U_{eq}	s.o.f.	overall occupancy
Ag1 Pb1 Bi1	2*d*	0	0.40644(4)	0.42259(2)	0.03926(19)	0.15345(11) 0.38953(7) 0.20975(4)	0.7527(2)
Ag2 Pb2 Bi2	2*d*	0.5	0.63722(3)	0.47410(2)	0.04004(18)	0.09705(11) 0.24634(3) 0.57479(8)	0.9182(2)
Ag3 Bi3	2*d*	0.5	0.17919(3)	0.36815(2)	0.03716(17)	0.06872(9) 0.93128(9)	1*
Ag4 Pb4	2*d*	0	0.22580(7)	0.25	0.0821(4)	0.01727(17) 0.98273(17)	1*
Ag5 Bi5	4*d*	0.5	0.45698(4)	0.31854(2)	0.04200(18)	0.29714(11) 0.65694(11)	0.9541(2)
Se6	4*d*	0	0.5	0.5	0.0383(3)	1	1
Se7	2*d*	0.5	0.27340(7)	0.44991(3)	0.0346(3)	1	1
Se8	2*d*	0.5	0.54641(7)	0.39831(3)	0.0343(3)	1	1
Se9	2*d*	0	0.30997(8)	0.34243(4)	0.0428(3)	1	1
Se10	2*d*	0.5	0.08932(8)	0.29867(3)	0.0342(2)	1	1
Se11	4*d*	0.5	0.36733(13)	0.25	0.0438(4)	1	1

* Overall site occupancy was restricted to 1 to prevent slight (numerically insignificant) overpopulations.

Table S7: Anisotropic displacement parameters (in Å^2) of $Ag_5Pb_9Bi_{19}Se_{40}$ at 200 °C, defined as $\exp[-2\pi^2 (U_{11}h^2 a^{*2} + U_{22}k^2 b^{*2} + U_{33}l^2 c^{*2} + U_{12}hka^* b^* + U_{13}hla^* c^* + U_{23}klb^* c^*)]$.

Atom	U_{11}	U_{22}	U_{33}	$U_{12} = U_{13}$	U_{23}
Ag1 Pb1 Bi1	0.0334(3)	0.0364(4)	0.0480(4)	0	0.0036(3)
Ag2 Pb2 Bi2	0.0366(3)	0.0423(3)	0.0412(3)	0	-0.0018(2)
Ag3 Bi3	0.0335(2)	0.0389(3)	0.0391(2)	0	-0.00350(16)
Ag4 Pb4	0.0459(4)	0.0680(6)	0.1323(10)	0	0
Ag5 Bi5	0.0348(3)	0.0422(3)	0.0490(3)	0	0.0006(2)
Se6	0.0303(7)	0.0349(8)	0.0498(9)	0	0.0059(6)
Se7	0.0326(5)	0.0342(6)	0.0370(5)	0	-0.0003(4)
Se8	0.0301(5)	0.0348(6)	0.0379(5)	0	0.0036(4)
Se9	0.0277(5)	0.0364(6)	0.0642(7)	0	0.0168(5)
Se10	0.0332(5)	0.0382(6)	0.0313(4)	0	0.0011(4)
Se11	0.0365(7)	0.0437(9)	0.0511(9)	0	0

Table S8: Atom positions, site occupancies and equivalent isotropic displacement parameters (in Å^2) of $Ag_5Pb_9Bi_{19}Se_{40}$ at 300 °C, $U_{eq} = 1/3 \cdot [U_{11} + U_{22} + U_{33}]$.

Atom	Site	x	y	z	U_{eq}	s.o.f.	overall occupancy
Ag1 Pb1 Bi1	2*d*	0	0.40634(5)	0.42287(2)	0.0476(2)	0.14494(9) 0.39711(6) 0.21383(3)	0.75588(18)
Ag2 Pb2 Bi2	2*d*	0.5	0.63716(4)	0.47427(2)	0.04787(19)	0.11439(9) 0.23942(3) 0.55865(6)	0.91246(18)
Ag3 Bi3	2*d*	0.5	0.17897(3)	0.36859(2)	0.04435(18)	0.09448(8) 0.90551(8)	1*
Ag4 Pb4	2*d*	0	0.22414(9)	0.25	0.1003(5)	0.01761(14) 0.98239(14)	1*
Ag5 Bi5	4*d*	0.5	0.45651(4)	0.31882(2)	0.0493(2)	0.26238(9) 0.69428(9)	0.95666(18)
Se6	4*d*	0	0.5	0.5	0.0453(4)	1	1
Se7	2*d*	0.5	0.27345(8)	0.44990(3)	0.0421(3)	1	1
Se8	2*d*	0.5	0.54610(8)	0.39855(3)	0.0411(3)	1	1
Se9	2*d*	0	0.31059(9)	0.34304(4)	0.0514(3)	1	1
Se10	2*d*	0.5	0.08966(9)	0.29890(3)	0.0422(3)	1	1
Se11	4*d*	0.5	0.36564(14)	0.25	0.0503(4)	1	1

* Overall site occupancy was restricted to 1 to prevent slight (numerically insignificant) overpopulations.

Table S9: Anisotropic displacement parameters (in Å^2) of $Ag_5Pb_9Bi_{19}Se_{40}$ at 300 °C, defined as $\exp[-2\pi^2 (U_{11}h^2 a^{*2} + U_{22}k^2 b^{*2} + U_{33}l^2 c^{*2} + U_{12}hka^* b^* + U_{13}hla^* c^* + U_{23}klb^* c^*)]$.

Atom	U_{11}	U_{22}	U_{33}	$U_{12} = U_{13}$	U_{23}
Ag1 Pb1 Bi1	0.0429(4)	0.0435(4)	0.0564(4)	0	0.0044(3)
Ag2 Pb2 Bi2	0.0455(3)	0.0490(4)	0.0490(3)	0	-0.0012(2)
Ag3 Bi3	0.0408(3)	0.0450(3)	0.0472(3)	0	-0.00251(19)
Ag4 Pb4	0.0587(5)	0.0809(7)	0.1613(14)	0	0
Ag5 Bi5	0.0431(3)	0.0485(4)	0.0563(3)	0	0.0013(2)
Se6	0.0381(8)	0.0402(9)	0.0577(10)	0	0.0066(7)
Se7	0.0408(6)	0.0410(7)	0.0447(6)	0	-0.0006(5)
Se8	0.0387(6)	0.0408(7)	0.0437(6)	0	0.0042(5)
Se9	0.0346(5)	0.0433(7)	0.0763(9)	0	0.0190(6)
Se10	0.0422(5)	0.0448(6)	0.0397(5)	0	0.0018(4)
Se11	0.0475(8)	0.0495(10)	0.0539(10)	0	0

Table S10: Atom positions, site occupancies and equivalent isotropic displacement parameters (in Å^2) of $Ag_5Pb_9Bi_{19}Se_{40}$ at 350 °C, $U_{eq} = 1/3 \cdot [U_{11} + U_{22} + U_{33}]$.

Atom	Site	x	y	z	U_{eq}	s.o.f.	overall occupancy
Ag1 Pb1 Bi1	2*d*	0	0.40624(6)	0.42282(3)	0.0534(3)	0.14066(11) 0.40492(7) 0.24295(4)	0.7585(2)
Ag2 Pb2 Bi2	2*d*	0.5	0.63695(5)	0.47444(2)	0.0527(3)	0.09411(11) 0.23674(3) 0.55240(8)	0.8833(2)
Ag3 Bi3	2*d*	0.5	0.17936(5)	0.36887(2)	0.0491(2)	0.13368(9) 0.86632(9)	1*
Ag4 Pb4	2*d*	0	0.22283(13)	0.25	0.1103(7)	0.03234(17) 0.96766(17)	1*
Ag5 Bi5	4*d*	0.5	0.45685(6)	0.31891(2)	0.0547(3)	0.24039(11) 0.71283(11)	0.9532(2)
Se6	4*d*	0	0.5	0.5	0.0511(6)	1	1
Se7	2*d*	0.5	0.27373(11)	0.44995(5)	0.0490(4)	1	1
Se8	2*d*	0.5	0.54572(11)	0.39872(5)	0.0472(4)	1	1
Se9	2*d*	0	0.31136(12)	0.34368(6)	0.0572(5)	1	1
Se10	2*d*	0.5	0.09019(12)	0.29903(5)	0.0485(4)	1	1
Se11	4*d*	0.5	0.36484(19)	0.25	0.0557(6)	1	1

* Overall site occupancy was restricted to 1 to prevent slight (numerically insignificant) overpopulations.

Table S11: Anisotropic displacement parameters (in Å^2) of $Ag_5Pb_9Bi_{19}Se_{40}$ at 350 °C, defined as exp $[-2\pi^2 (U_{11}h^2 a^{*2} + U_{22}k^2 b^{*2} + U_{33}l^2 c^{*2} + U_{12}hka^* b^* + U_{13}hla^* c^* + U_{23}klb^* c^*)]$.

Atom	U_{11}	U_{22}	U_{33}	$U_{12} = U_{13}$	U_{23}
Ag1 Pb1 Bi1	0.0473(5)	0.0482(5)	0.0646(6)	0	0.0047(4)
Ag2 Pb2 Bi2	0.0495(5)	0.0522(5)	0.0566(5)	0	-0.0007(3)
Ag3 Bi3	0.0435(4)	0.0479(4)	0.0558(4)	0	-0.0017(3)
Ag4 Pb4	0.0670(8)	0.0872(10)	0.177(2)	0	0
Ag5 Bi5	0.0477(4)	0.0525(5)	0.0640(5)	0	0.0015(4)
Se6	0.0426(12)	0.0449(11)	0.0657(15)	0	0.0057(11)
Se7	0.0456(9)	0.0473(9)	0.0542(9)	0	-0.0011(7)
Se8	0.0432(9)	0.0469(9)	0.0517(9)	0	0.0051(7)
Se9	0.0383(8)	0.0475(9)	0.0858(13)	0	0.0188(9)
Se10	0.0470(8)	0.0500(9)	0.0486(8)	0	0.0022(7)
Se11	0.0544(13)	0.0522(13)	0.0604(14)	0	0

Table S12: Atom positions, site occupancies and equivalent isotropic displacement parameters (in Å^2) of $Ag_5Pb_9Bi_{19}Se_{40}$ at 400 °C, $U_{eq} = 1/3 \cdot [U_{11} + U_{22} + U_{33}]$.

Atom	Site	x	y	z	U_{eq}	s.o.f.	overall occupancy
Ag1 Pb1 Bi1	2*d*	0	0.40634(8)	0.42271(4)	0.0633(4)	0.11545(11) 0.40557(7) 0.27038(4)	0.7914(2)
Ag2 Pb2 Bi2	2*d*	0.5	0.63689(7)	0.47455(3)	0.0626(3)	0.05083(11) 0.23987(3) 0.55971(8)	0.8504(2)
Ag3 Bi3	2*d*	0.5	0.17984(6)	0.36898(3)	0.0588(3)	0.15506(9) 0.84494(9)	1*
Ag4 Pb4	2*d*	0	0.22195(17)	0.25	0.1246(9)	0.04234(17) 0.95766(17)	1*
Ag5 Bi5	4*d*	0.5	0.45709(8)	0.31888(3)	0.0651(4)	0.28249(11) 0.70070(11)	0.9832(2)
Se6	4*d*	0	0.5	0.5	0.0625(8)	1	1
Se7	2*d*	0.5	0.27364(16)	0.44994(6)	0.0597(6)	1	1
Se8	2*d*	0.5	0.54553(15)	0.39881(6)	0.0577(5)	1	1
Se9	2*d*	0	0.31220(16)	0.34416(8)	0.0676(6)	1	1
Se10	2*d*	0.5	0.09111(16)	0.29919(6)	0.0592(5)	1	1
Se11	4*d*	0.5	0.3645(2)	0.25	0.0661(8)	1	1

* Overall site occupancy was restricted to 1 to prevent slight (numerically insignificant) overpopulations.

Table S13: Anisotropic displacement parameters (in Å^2) of $Ag_5Pb_9Bi_{19}Se_{40}$ at 400 °C, defined as exp $[-2\pi^2 (U_{11}h^2 a^{*2} + U_{22}k^2 b^{*2} + U_{33}l^2 c^{*2} + U_{12}hka^* b^* + U_{13}hla^* c^* + U_{23}klb^* c^*)]$.

Atom	U_{11}	U_{22}	U_{33}	$U_{12} = U_{13}$	U_{23}
Ag1 Pb1 Bi1	0.0560(7)	0.0590(7)	0.0749(8)	0	0.0048(6)
Ag2 Pb2 Bi2	0.0586(6)	0.0630(6)	0.0662(7)	0	-0.0006(5)
Ag3 Bi3	0.0525(5)	0.0587(6)	0.0651(6)	0	-0.0019(4)
Ag4 Pb4	0.0798(12)	0.1012(14)	0.193(3)	0	0
Ag5 Bi5	0.0575(6)	0.0640(6)	0.0737(7)	0	0.0007(5)
Se6	0.0533(16)	0.0556(16)	0.079(2)	0	0.0063(15)
Se7	0.0552(13)	0.0586(13)	0.0654(13)	0	-0.0010(10)
Se8	0.0532(12)	0.0585(12)	0.0613(12)	0	0.0048(10)
Se9	0.0481(12)	0.0581(12)	0.0967(18)	0	0.0207(12)
Se10	0.0571(12)	0.0600(12)	0.0603(12)	0	0.0025(9)
Se11	0.0644(19)	0.0637(18)	0.070(2)	0	0

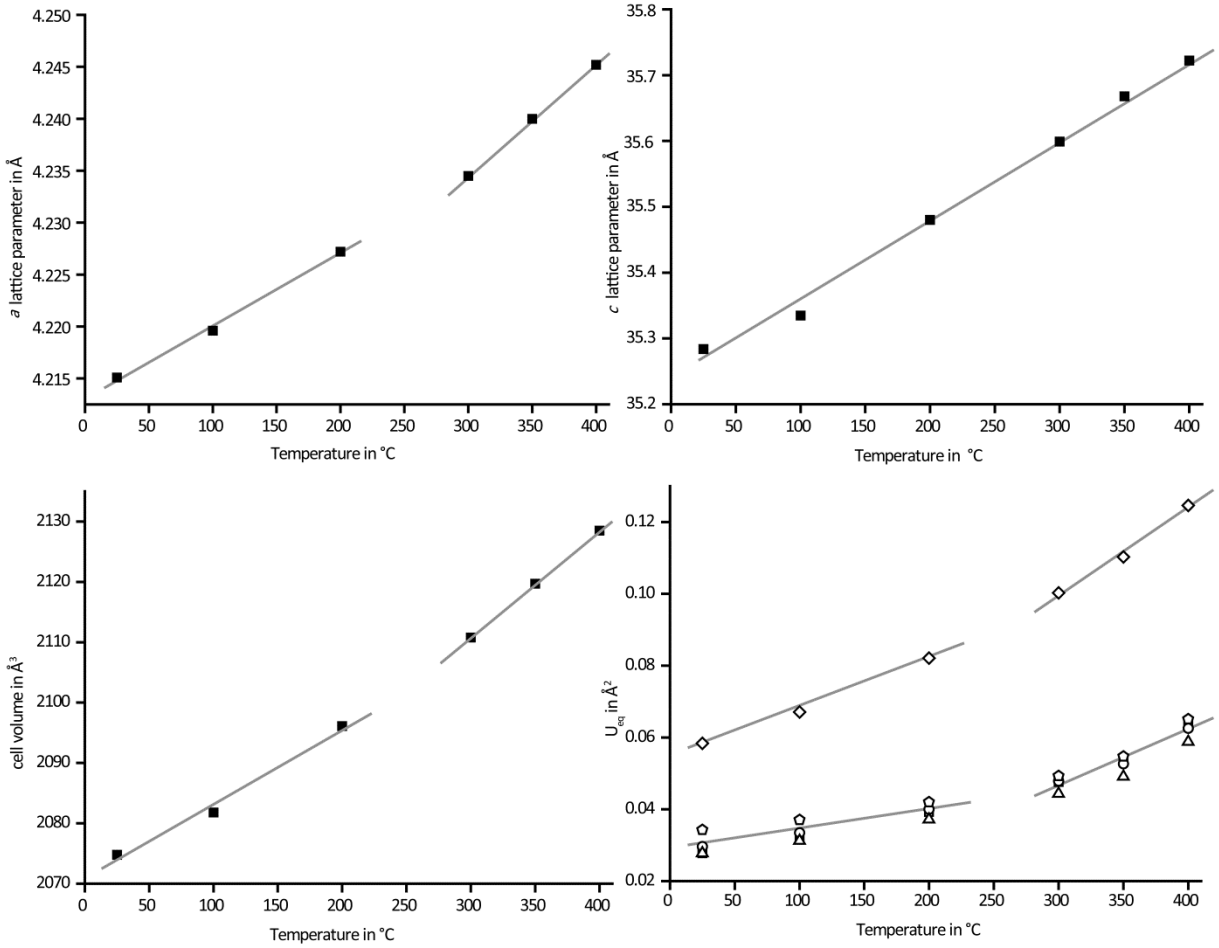

Figure S1: Temperature-dependent evolution of the *a* and *c* lattice parameters (top left and right, respectively) and the cell volume (bottom left) of $Ag_5Pb_9Bi_{19}Se_{40}$ as well as of the isotropic displacement parameters for all cation sites (bottom right; squares for Ag1/Pb1/Bi1, circles for Ag2/Pb2/Bi2, triangles for Ag3/Bi3, rhombi for site Ag4/Pb4 and pentagons for site Ag5/Bi5); the corresponding graph for *b* is shown in Fig. 3 in the manuscript; standard deviations are smaller than the symbols.

Table S14: Atom positions, site occupancies and equivalent isotropic displacement parameters (in Å^2) of $AgPb_3Bi_7Se_{14}$ at RT, $U_{eq} = 1/3 \cdot [U_{11} + U_{22} + U_{33}]$.

Atom	Site	x	y	z	U_{eq}	s.o.f.	overall occupancy
Ag1 Pb1 Bi1	2*d*	0	0.26691(8)	0.57775(4)	0.0286(3)	0.08087(9) 0.62042(6) 0.29871(3)	1*
Ag2 Bi2	2*d*	0	0.45629(9)	0.35111(4)	0.0295(3)	0.12804(10) 0.82577(10)	0.9538(2)
Ag3 Bi3	4*d*	0.5	0.68916(16)	0.25	0.0646(7)	0.00392(16) 0.99608(16)	1*
Ag4 Pb4 Bi4	4*d*	0.5	0.5	0.5	0.0239(5)	0.0783(2) 0.25695(10) 0.25695(10)	0.5922(4)
Se4	2*d*	0	0.36430(19)	0.46263(10)	0.0254(5)	1	1
Se5	4*d*	0	0.5457(3)	0.25	0.0283(7)	1	1
Se6	2*d*	0.5	0.3997(2)	0.61639(14)	0.0389(7)	1	1
Se7	2*d*	0	0.17722(19)	0.67926(9)	0.0249(5)	1	1

* Overall site occupancy was restricted to 1 to prevent slight (numerically insignificant) overpopulations.

Table S15: Anisotropic displacement parameters (in Å^2) of $AgPb_3Bi_7Se_{14}$ at RT, defined as exp $[-2\pi^2 (U_{11}h^2 a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)]$.

Atom	U_{11}	U_{22}	U_{33}	$U_{12} = U_{13}$	U_{23}
Ag1 Pb1 Bi1	0.0263(5)	0.0315(5)	0.0279(5)	0	0.0061(4)
Ag2 Bi2	0.0245(5)	0.0325(6)	0.0314(5)	0	0.0023(4)
Ag3 Bi3	0.0317(10)	0.0461(11)	0.1160(19)	0	0
Ag4 Pb4 Bi4	0.0217(11)	0.0213(11)	0.0288(11)	0	-0.0027(8)
Se4	0.0244(13)	0.0288(12)	0.0230(10)	0	-0.0007(9)
Se5	0.0288(18)	0.0268(17)	0.0292(16)	0	0
Se6	0.0210(13)	0.0298(13)	0.0658(19)	0	-0.0213(13)
Se7	0.0254(13)	0.0278(13)	0.0214(10)	0	0.0018(9)

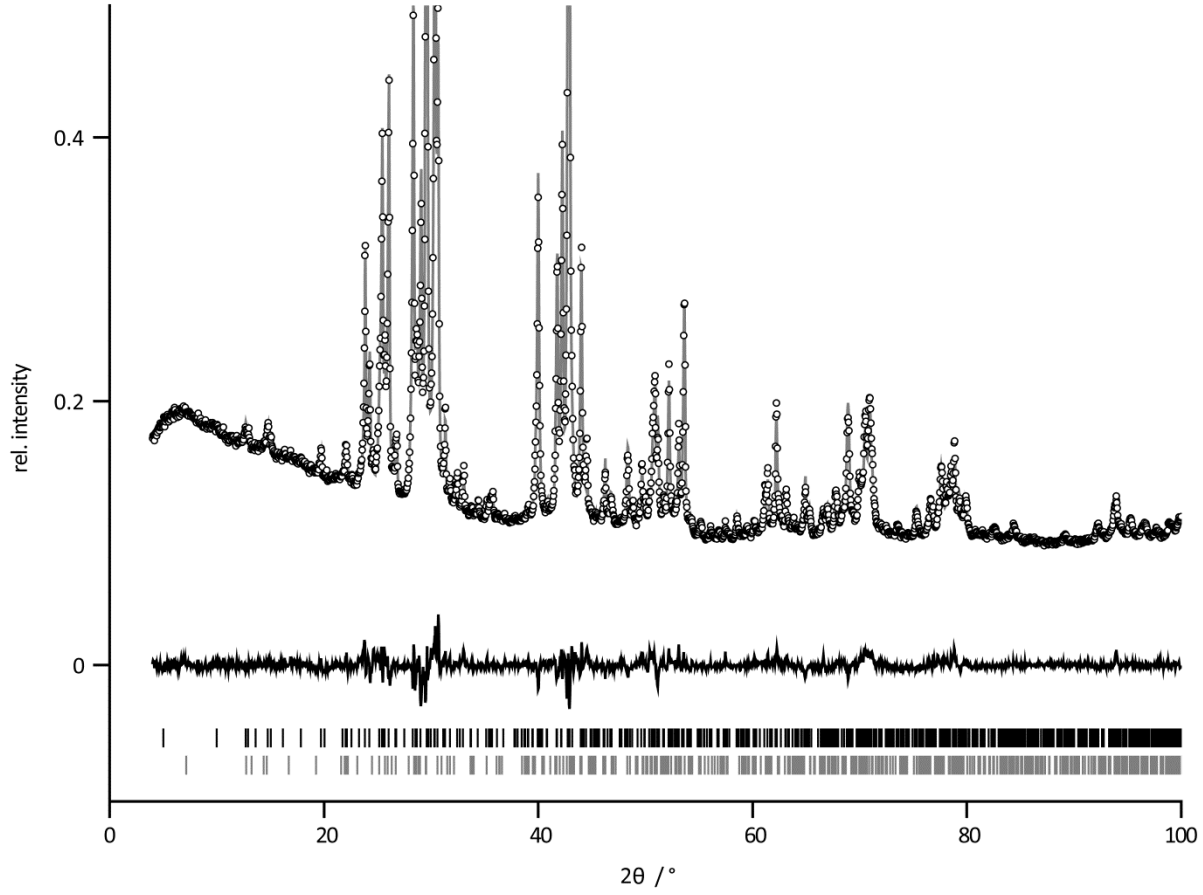

Figure S2: Rietveld refinement for powder diffraction data (truncated at 50% of the maximum intensity) of a sample (sintered pellet) with the nominal composition $Ag_2Pb_6Bi_{10}Se_{22}$; measurement (black dots), calculated profile (gray line), difference plot (black line below), black reflection markers for ^{8,8}L-$Ag_5Pb_9Bi_{19}Se_{40}$ and gray reflection markers for ^{5,5}L-$AgPb_3Bi_7Se_{14}$.

Table S16: Crystallographic data from the Rietveld refinement (Fig. S2) for powder diffraction data of a sintered pellet with the nominal composition $Ag_2Pb_6Bi_{10}Se_{22}$.

Nominal composition	$Ag_2Pb_6Bi_{10}Se_{22}$	
Wavelength / Å	1.540596	
Temperature / K	295	
2θ range / °	4 – 100	
Profile function	fundamental parameters	
R_P / R_{wp}	0.0175 / 0.0224	
GooF	1.076	
Parameters / thereof background	33 / 18	
Phase	$Ag_5Pb_9Bi_{19}Se_{40}$ (^{8,8}L-type) *	$AgPb_3Bi_7Se_{14}$ (^{5,5}L-type) *
Phase fraction	90.8 wt.-%	9.2 wt.-%
Molar mass /g·mol^{-1}	9533.08	3297.74
F(000)	3910	2700
Z	1	2
Crystal system	orthorhombic	
Space group	*Cmcm*	
lattice parameters		
a / Å	4.21693(9)	4.2337 **
b / Å	13.9447(3)	13.864 **
c / Å	35.3489(7)	24.653 **
Volume / Å^3	2078.65	1447.03 **
Density / g·cm^{-3}	7.6156(3)	7.5685*
R_{Bragg}	0.0187	0.0137

* Atom coordinates, occupancy parameters and isotropic displacement parameters were taken from the corresponding single crystal data and remained unrefined. Effects of crystallite-size broadening were taken into account by a Lorentzian function for both phases. In addition, for $Ag_5Pb_9Bi_{19}Se_{40}$ microstrain peak broadening was considered by a Lorentzian function and preferred orientation was refined by spherical harmonics of the fourth order.

** The lattice parameters of the phase $AgPb_3Bi_7Se_{14}$ remained unrefined. The small fraction of the phase ($AgPb_3Bi_7Se_{14}$) combined with the strong overlap of reflections prevented a reliable refinement of the lattice parameters. A test run with unrestricted cell parameters for the ^{5,5}L-type yielded no improvement of the fit.

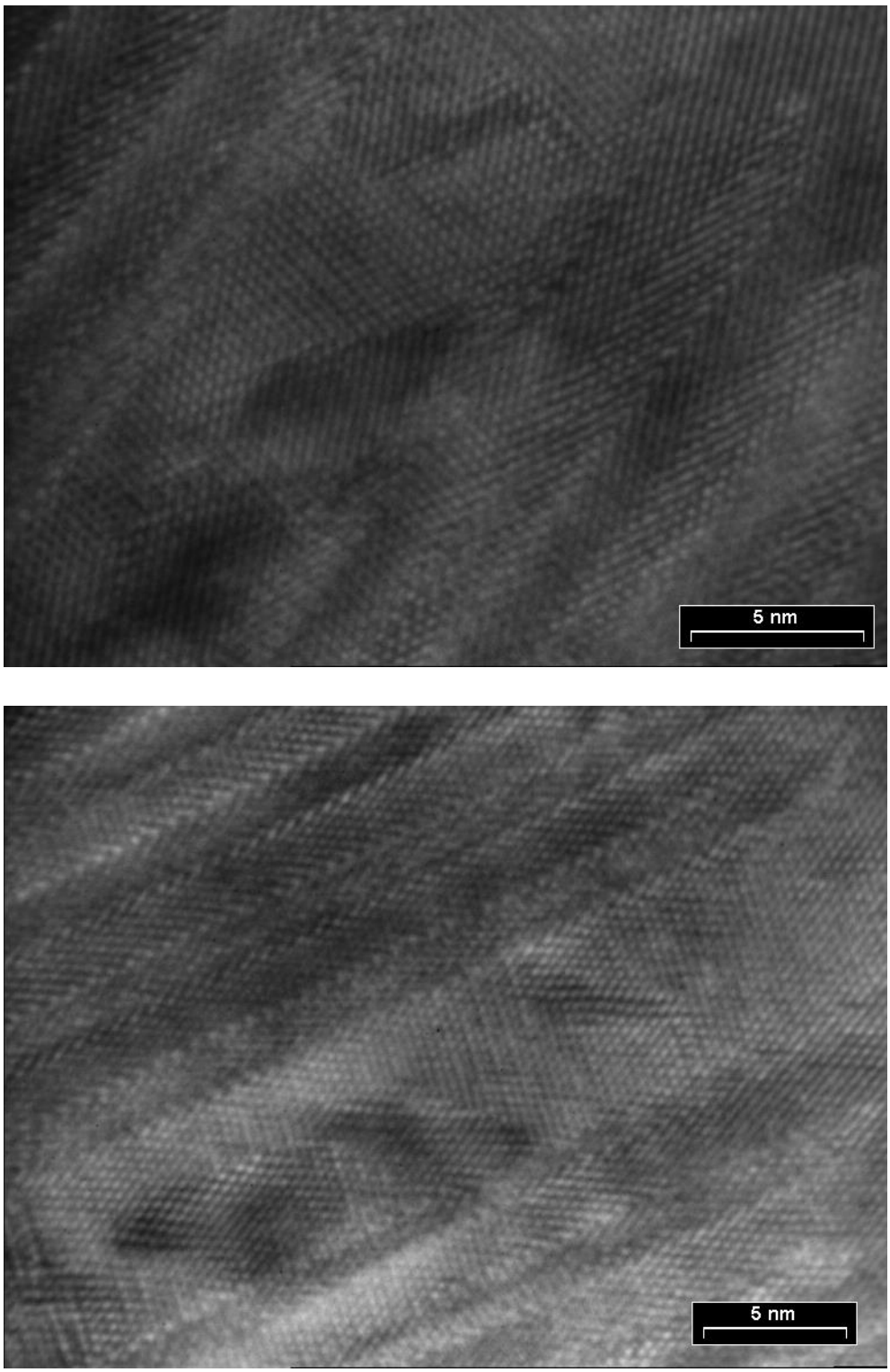

Figure S3: HRTEM images of a sample with the nominal composition $Ag_2Pb_6Bi_{10}Se_{22}$ ($\Delta f \approx$ -78 nm) displaying a highly disordered area of separating well-ordered slabs of ^{8,8}L-$Ag_5Pb_9Bi_{19}Se_{40}$.