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Supporting information for article:

The first silver bismuth borate, AgBi2B5O11

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S1. Rietveld refinement.

Pseudo-Voigt functions were used for fitting the reflection profiles. The background was described by a Chebyshev polynomial function (30th order); the preferred orientation (direction [010]) was modelled by the March-Dollase approach. Only atomic coordinates for the bismuth and silver atoms were refined and isotropic temperature factor was constrained to be the same for all atoms. Final Rietveld refinement plot is given in Fig. S3. The final refinement resulted in values of 3.17 % for R_{exp} and 6.13 % for R_{wp}.

S1. High-temperature X-ray powder diffraction.

Temperature dependences of unit-cell parameters and volume in the 303–823 K temperature range (Fig. S7) can be described by the following linear equations:

$a = 13.1602(8) + 0.000271(3)t$

$b = 7.7633(4) + 0.000061(1)t$

$c = 18.1565(8) + 0.000057(2)t$

$V = 1854.8(1) + 0.0592(4)t$

Table S1 Atomic coordinates, displacement parameters (Å^2) and site-occupancy factors (SOFs) in the structure of $AgBi_2B_5O_{11}$.

Atom	Wyckoff site	SOF	*x*	*y*	*z*	*U* eq
Bi1	4*a*	1	0.60824(3)	0.71542(5)	0.40703(2)	0.01617(9)
Bi2	4*a*	1	0.38139(3)	0.51716(4)	0.320446(18)	0.01557(8)
Bi3	4*a*	1	0.13714(3)	0.54085(5)	0.61769(2)	0.01636(9)
Bi4	4*a*	1	0.36116(3)	0.72982(5)	0.52786(2)	0.01623(10)
Ag1	4*a*	1	0.38274(7)	0.97671(11)	0.32360(6)	0.0264(2)
Ag2	4*a*	1	0.36692(7)	0.50199(11)	0.11168(5)	0.0258(2)
O1	4*a*	1	0.1902(7)	0.2640(10)	0.3025(6)	0.025(3)
O2	4*a*	1	0.4426(7)	0.2546(9)	0.6343(6)	0.024(3)
O3	4*a*	1	0.3838(5)	0.3134(10)	0.7556(4)	0.0185(19)
O4	4*a*	1	0.1321(6)	0.1824(11)	0.1844(4)	0.022(2)
O5	4*a*	1	0.2143(7)	0.7422(9)	0.5690(5)	0.022(2)
O6	4*a*	1	0.0787(6)	0.4414(10)	0.3750(4)	0.021(2)
O7	4*a*	1	0.4583(6)	0.7158(10)	0.3738(5)	0.021(2)
O8	4*a*	1	0.2681(5)	0.2040(11)	0.6671(4)	0.021(2)
O9	4*a*	1	0.0139(6)	0.3006(11)	0.2697(4)	0.021(2)
O10	4*a*	1	0.2699(6)	0.7070(10)	0.2972(5)	0.024(2)
O11	4*a*	1	0.5660(6)	0.5184(9)	0.4883(4)	0.022(2)
O12	4*a*	1	0.0598(6)	0.1323(9)	0.3754(4)	0.0185(19)
O13	4*a*	1	0.5684(7)	0.2133(10)	0.4887(5)	0.023(2)
O14	4*a*	1	0.4535(6)	0.5941(10)	0.2182(4)	0.025(2)
O15	4*a*	1	0.3124(8)	0.2270(9)	0.4481(5)	0.027(3)
O16	4*a*	1	0.3048(6)	0.5286(9)	0.4514(4)	0.020(2)
O17	4*a*	1	0.5595(5)	0.9130(9)	0.4870(4)	0.0181(19)
O18	4*a*	1	0.2032(5)	0.6027(10)	0.7247(4)	0.021(2)
O19	4*a*	1	0.3371(6)	0.0741(9)	0.5605(4)	0.021(2)

O20	4*a*	1	0.3123(6)	0.9246(9)	0.4501(5)	0.022(2)
O21	4*a*	1	0.3106(6)	0.3810(10)	0.5628(4)	0.022(2)
O22	4*a*	1	0.9768(6)	0.2771(10)	0.1402(5)	0.022(2)
B1	4*a*	1	0.0370(9)	0.2533(11)	0.1980(8)	0.012(3)
B2	4*a*	1	0.2064(8)	0.1809(16)	0.2375(6)	0.019(3)
B3	4*a*	1	0.2909(10)	0.2357(15)	0.7372(9)	0.021(3)
B4	4*a*	1	0.4590(8)	0.3242(14)	0.7022(6)	0.016(3)
B5	4*a*	1	0.5649(8)	0.3667(14)	0.4515(6)	0.017(3)
B6	4*a*	1	0.0895(9)	0.2850(14)	0.3294(7)	0.018(3)
B7	4*a*	1	0.3193(9)	0.0755(15)	0.4848(7)	0.020(3)
B8	4*a*	1	0.3417(10)	0.2231(15)	0.6063(6)	0.018(3)
B9	4*a*	1	0.5700(8)	0.0599(15)	0.4487(6)	0.015(3)
B10	4*a*	1	0.3091(9)	0.3804(16)	0.4870(7)	0.021(3)

Table S2 Anisotropic parameters of atomic displacements the structure of $AgBi_2B_5O_{11}$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi1	0.01471(17)	0.01751(15)	0.01628(17)	0.00043(12)	0.00033(14)	0.00014(16)
Bi2	0.01569(14)	0.01625(15)	0.01478(14)	0.00040(11)	–0.00070(14)	–0.00080(14)
Bi3	0.01577(15)	0.01705(16)	0.01628(15)	0.00032(11)	0.00077(14)	0.00037(14)
Bi4	0.01499(18)	0.01682(16)	0.01688(18)	–0.00046(11)	–0.00096(14)	–0.00029(16)
Ag1	0.0301(4)	0.0271(4)	0.0219(4)	–0.0034(3)	–0.0052(4)	0.0058(4)
Ag2	0.0279(4)	0.0281(4)	0.0214(4)	0.0026(3)	–0.0042(3)	–0.0058(4)
O1	0.017(4)	0.037(5)	0.020(5)	–0.002(3)	–0.001(3)	–0.008(3)
O2	0.019(4)	0.033(4)	0.021(5)	–0.001(3)	0.001(3)	–0.006(3)
O3	0.013(3)	0.024(4)	0.019(3)	–0.006(2)	0.000(2)	0.004(3)
O4	0.021(4)	0.033(4)	0.011(3)	0.009(3)	0.000(2)	–0.006(3)
O5	0.015(4)	0.028(4)	0.023(4)	–0.001(2)	0.011(3)	0.002(3)
O6	0.026(4)	0.027(4)	0.010(3)	0.002(3)	0.001(2)	–0.001(3)
O7	0.018(4)	0.019(3)	0.027(4)	0.001(3)	0.001(3)	–0.006(3)
O8	0.011(3)	0.035(4)	0.017(3)	–0.009(3)	–0.001(2)	0.004(3)
O9	0.014(3)	0.038(4)	0.013(3)	0.004(3)	0.000(2)	–0.005(3)
O10	0.024(4)	0.029(4)	0.019(4)	0.008(3)	–0.005(3)	–0.001(3)
O11	0.028(4)	0.020(4)	0.018(3)	–0.003(3)	–0.005(3)	–0.001(3)
O12	0.027(4)	0.016(3)	0.013(3)	–0.002(3)	–0.002(3)	0.001(3)
O13	0.031(4)	0.020(3)	0.017(4)	–0.005(3)	–0.004(3)	–0.001(3)
O14	0.020(4)	0.039(4)	0.016(3)	–0.008(3)	–0.001(3)	0.003(3)
O15	0.046(6)	0.016(3)	0.018(4)	0.000(3)	–0.003(4)	–0.002(3)
O16	0.020(3)	0.019(3)	0.021(3)	–0.003(2)	0.000(3)	–0.003(3)
O17	0.022(3)	0.016(3)	0.016(3)	0.005(2)	–0.001(3)	0.006(3)
O18	0.018(3)	0.031(4)	0.014(3)	–0.006(3)	–0.001(2)	0.000(3)
O19	0.034(4)	0.016(3)	0.013(3)	0.002(3)	0.006(3)	–0.005(3)
O20	0.027(4)	0.012(3)	0.026(4)	–0.001(2)	0.002(3)	0.002(3)
O21	0.026(4)	0.019(4)	0.022(4)	0.001(3)	0.001(3)	–0.001(3)
O22	0.013(3)	0.037(4)	0.016(3)	0.006(3)	–0.002(3)	0.003(3)
B1	0.013(5)	0.009(5)	0.014(5)	0.003(3)	–0.001(4)	0.003(3)
B2	0.011(5)	0.032(6)	0.014(4)	–0.002(4)	–0.003(3)	–0.001(4)
B3	0.018(6)	0.023(6)	0.020(6)	–0.005(4)	–0.006(5)	–0.007(4)
B4	0.016(5)	0.016(5)	0.015(4)	–0.001(3)	–0.001(3)	0.000(4)
B5	0.017(5)	0.017(5)	0.016(5)	0.005(3)	0.004(4)	–0.003(4)
B6	0.021(5)	0.016(5)	0.017(5)	0.005(3)	0.001(4)	0.002(5)
B7	0.025(6)	0.018(5)	0.017(5)	–0.003(4)	0.004(4)	0.006(4)
B8	0.026(6)	0.023(5)	0.007(4)	–0.003(4)	0.005(4)	0.002(4)
B9	0.019(5)	0.020(5)	0.007(4)	–0.002(4)	–0.004(3)	0.002(4)
B10	0.015(5)	0.025(6)	0.022(6)	–0.003(4)	0.011(4)	–0.011(5)

Table S3 Selected bond length and bond valences (BV, v.u.) in the $AgBi_2B_5O_{11}$ structure.

Bond	Distance (Å)	BV	Bond	Distance (Å)	BV	Bond	Distance (Å)	BV	Bond	Distance (Å)	BV

Bi1–O7	2.073(8)	1.06Bi4–O5	2.083(9)	1.03B1–O4	1.394(14)	0.94B6–O1	1.428(16)	0.86
Bi1–O11	2.199(8)	0.75Bi4–O20	2.169(8)	0.82B1–O9	1.387(16)	0.96B6–O6	1.478(14)	0.75
Bi1–O17	2.210(7)	0.73Bi4–O16	2.220(7)	0.71B1–O22^{xii}	1.330(16)	1.12B6–O9	1.479(15)	0.75
Bi1–O3^{i}	2.760(7)	0.17Bi4–O19^{viii}	2.762(7)	0.16<B(1)–O>$_{III}$	1.370	3.01B6–O12	1.504(14)	0.70
Bi1–O6^{ii}	2.760(8)	0.17Bi4–O21	2.865(8)	0.12		<B(6)–O>$_{IV}$	1.472	3.05
Bi1–O12^{iii}	2.838(7)	0.13Bi4–O4^{vii}	2.866(7)	0.12B2–O1	1.362(15)	1.02		
<Bi(1)–O>$_{III}$	2.161	2.54<Bi(4)–O>$_{III}$	2.157	2.56B2–O4	1.377(13)	0.98B7–O15	1.358(14)	1.04
<Bi(1)–O>$_{VI}$	2.473	3.01<Bi(4)–O>$_{VI}$	2.494	2.97B2–O18^{xi}	1.361(13)	1.03B7–O19	1.394(14)	0.94
				<B(2)–O>$_{III}$	1.367	3.04B7–O20^{xiv}	1.336(14)	1.10
		Ag1–O18^{x}	2.341(7)	0.26		<B(7)–O>$_{III}$	1.363	3.07
Bi2–O7	2.088(8)	1.02Ag1–O7	2.438(8)	0.20B3–O3	1.409(15)	0.90		
Bi2–O10	2.129(8)	0.91Ag1–O20	2.510(8)	0.16B3–O8	1.331(18)	1.11B8–O2	1.449(16)	0.81
Bi2–O14	2.171(7)	0.81Ag1–O10	2.618(8)	0.12B3–O10^{xiii}	1.372(18)	1.00B8–O8	1.479(14)	0.75
Bi2–O16	2.586(8)	0.26Ag1–O9^{ii}	2.639(8)	0.12<B(3)–O>$_{III}$	1.371	3.01B8–O19	1.427(14)	0.86
Bi2–O12^{iii}	2.813(7)	0.14Ag1–O6^{ii}	2.826(8)	0.07		B8–O21	1.517(14)	0.67
<Bi(2)–O>$_{III}$	2.129	2.74<Ag(1)–O>$_{V}$	2.509	0.86B4–O2	1.363(15)	1.02<B(8)–O>$_{IV}$	1.468	3.09
<Bi(2)–O>$_{VI}$	2.492	3.20<Ag(1)–O>$_{VI}$	2.562	0.93B4–O3	1.391(13)	0.95		
				B4–O14^{vi}	1.352(13)	1.05B9–O6^{iii}	1.343(12)	1.08
		Ag2–O14	2.358(7)	0.25<B(4)–O>$_{III}$	1.369	3.02B9–O13	1.397(14)	0.93
Bi3–O5	2.067(8)	1.08Ag2–O11^{i}	2.414(8)	0.21		B9–O17^{xiv}	1.344(13)	1.08
Bi3–O22^{vi}	2.107(8)	0.97Ag2–O5^{xi}	2.415(8)	0.21B5–O11	1.355(13)	1.04<B(9)–O>$_{III}$	1.361	3.09
Bi3–O18	2.183(7)	0.79Ag2–O8^{x}	2.582(8)	0.14B5–O12^{iii}	1.383(13)	0.97		
Bi3–O17^{v}	2.610(7)	0.25Ag2–O22^{iv}	2.664(8)	0.11B5–O13	1.372(14)	1.00B10–O15	1.387(15)	0.96
Bi3–O21	2.792(8)	0.15Ag2–O19^{x}	2.907(8)	0.06<B(5)–O>$_{III}$	1.370	3.01B10–O16	1.322(14)	1.14
<Bi(3)–O>$_{III}$	2.119	2.83<Ag(2)–O>$_{V}$	2.487	0.92		B10–O21	1.376(15)	0.99
<Bi(3)–O>$_{V}$	2.352	3.23<Ag(2)–O>$_{VI}$	2.557	0.97		<B(10)–O>$_{III}$	1.362	3.09

Symmetry codes: (i) –*x*+1,–*y*+1,*z*–½; (ii) *x*+½,–*y*+3/2,*z*; (iii) *x*+½,–*y*+½,*z*; (iv) *x*–½,–*y*+½,*z*; (v) *x*–½,–*y*+3/2,*z*; (vi) – *x*+1,–*y*+1,*z*+½; (vii) – *x*+½,*y*+½,*z*+½; (viii) *x*,*y*+1,*z*; (ix) – *x*+3/2,*y*+½,*z*+½; (x) – *x*+½,*y*+½,*z*–½; (xi) – *x*+½,*y*–½,*z*–½; (xii) *x*–1,*y*,*z*; (xiii) – x+½,*y*–½,*z*+½; (xiv) *x*,*y*–1,*z*.

Table S4 O–Bi–O, O–Ag–O and O–B–O angles (°) in the $AgBi_2B_5O_{11}$ structure.

O3^{i}–Bi1–O6^{ii}	82.8(2)	O4^{vii}–Bi4–O5	71.3(3)	O4–B1–O9	118.0(10)
O3^{i}–Bi1–O7	75.3(3)	O4^{vii}–Bi4–O16	122.6(3)	O4–B1–O22^{xii}	117.0(11)
O3^{i}–Bi1–O11	128.4(3)	O4^{vii}–Bi4–O19^{viii}	85.2(2)	O9–B1–O22^{xii}	124.9(10)
O3^{i}–Bi1–O12^{iii}	74.3(2)	O4^{vii}–Bi4–O20	138.1(3)		
O3^{i}–Bi1–O17	136.2(2)	O4^{vii}–Bi4–O21	70.5(2)	O1–B2–O4	119.4(9)
O6^{ii}–Bi1–O7	78.6(3)	O5–Bi4–O16	86.8(3)	O1–B2–O18^{xi}	119.9(9)
O6^{ii}–Bi1–O11	141.2(2)	O5–Bi4–O19^{viii}	76.7(3)	O4–B2–O18^{xi}	120.6(9)
O6^{ii}–Bi1–O12^{iii}	147.9(2)	O5–Bi4–O20	85.6(3)		
O6^{ii}–Bi1–O17	54.9(2)	O5–Bi4–O21	75.3(3)	O3–B3–O8	120.2(12)
O7–Bi1–O11	87.3(3)	O7–Bi4–O22^{ix}	109.0(2)	O3–B3–O10^{xiii}	113.1(12)
O7–Bi1–O12^{iii}	74.1(3)	O16–Bi4–O19^{viii}	141.2(2)	O8–B3–O10^{xiii}	126.7(11)
O7–Bi1–O17	84.9(3)	O16–Bi4–O20	89.2(3)		
O11–Bi1–O12^{iii}	54.1(2)	O16–Bi4–O21	52.6(2)	O2–B4–O3	119.5(9)
O11–Bi1–O17	88.3(3)	O19^{viii}–Bi4–O20	55.1(2)	O2–B4–O14^{vi}	121.1(9)
O12^{iii}–Bi1–O17	136.9(2)	O19^{viii}–Bi4–O21	147.6(2)	O3–B4–O14^{vi}	119.4(9)
		O20–Bi4–O21	137.4(3)		
				O11–B5–O12^{iii}	119.1(9)
				O11–B5–O13	121.0(10)
		O6^{ii}–Ag1–O7	71.9(2)	O12^{iii}–B5–O13	119.9(9)
		O6^{ii}–Ag1–O9^{ii}	51.1(2)		
O7–Bi2–O10	85.1(3)	O6^{ii}–Ag1–O10	139.8(2)	O1–B6–O6	112.1(9)
O7–Bi2–O12^{iii}	74.5(3)	O6^{ii}–Ag1–O18^{x}	127.1(2)	O1–B6–O9	112.9(10)
O7–Bi2–O14	88.8(3)	O6^{ii}–Ag1–O20	94.3(2)	O1–B6–O12	110.0(8)
O7–Bi2–O16	74.9(3)	O7–Ag1–O9^{ii}	114.6(3)	O6–B6–O9	106.1(8)
O10–Bi2–O12^{iii}	159.7(3)	O7–Ag1–O10	68.6(3)	O6–B6–O12	108.3(9)
O10–Bi2–O14	86.8(3)	O7–Ag1–O18^{x}	146.5(3)	O9–B6–O12	107.2(8)
O10–Bi2–O16	83.5(3)	O7–Ag1–O20	71.1(3)		
O12^{iii}–Bi2–O14	92.8(2)	O9^{ii}–Ag1–O10	146.4(3)	O15–B7–O19	120.1(10)
O12^{iii}–Bi2–O16	90.9(2)	O9^{ii}–Ag1–O18^{x}	76.1(2)	O15–B7–O20^{xiv}	121.8(11)
O14–Bi2–O16	161.6(3)	O9^{ii}–Ag1–O20	133.5(2)	O19–B7–O20^{xiv}	118.1(10)
		O10–Ag1–O18^{x}	85.3(3)		
		O10–Ag1–O20	80.0(2)	O2–B8–O8	111.1(9)
				O2–B8–O19	112.4(10)
				O2–B8–O21	107.2(9)
		O18^{x}–Ag1–O20	126.1(2)	O8–B8–O19	108.9(9)

O5–Bi3–O17^{v}	72.6(3)	O5^{xi}–Ag2–O8^{x}	109.1(3)	O8–B8–O21	107.0(9)
O5–Bi3–O18	90.9(3)	O5^{xi}–Ag2–O11^{i}	79.1(3)	O19–B8–O21	110.1(9)
5–Bi3–O21	77.3(3)	O5^{xi}–Ag2–O14	137.1(3)		
O5–Bi3–O22^{vi}	85.8(3)	O5^{xi}–Ag2–O22^{iv}	67.8(3)	O6^{iii}–B9–O13	121.7(9)
O17^{v}–Bi3–O18	159.3(2)	O8^{x}–Ag2–O11^{i}	130.9(3)	O6^{iii}–B9–O17^{xiv}	121.2(9)
O17^{v}–Bi3–O21	93.4(2)	O8^{x}–Ag2–O14	80.3(3)	O13–B9–O17^{xiv}	117.1(9)
O17^{v}–Bi3–O22^{vi}	78.6(3)	O8^{x}–Ag2–O22^{iv}	142.9(3)		
O18–Bi3–O21	95.0(2)	O11^{i}–Ag2–O14	127.0(3)	O15–B10–O16	120.2(11)
O18–Bi3–O22^{vi}	88.0(3)	O11^{i}–Ag2–O22^{iv}	85.8(3)	O15–B10–O21	120.8(10)
O21–Bi3–O22^{vi}	162.8(3)	O14–Ag2–O22^{iv}	79.8(3)	O16–B10–O21	119.0(10)

Symmetry codes: (i) –*x*+1,–*y*+1,*z*–½; (ii) *x*+½,–*y*+3/2,*z*; (iii) *x*+½,–*y*+½,*z*; (iv) *x*–½,–*y*+½,*z*; (v) *x*–½,–*y*+3/2,*z*; (vi) – *x*+1,–*y*+1,*z*+½; (vii) – *x*+½,*y*+½,*z*+½; (viii) *x*,*y*+1,*z*; (ix) – *x*+3/2,*y*+½,*z*+½; (*x*) – *x*+½,*y*+½,*z*–½; (*x*i) – *x*+½,*y*–½,*z*–½; (*x*ii) *x*–1,*y*,*z*; (*x*iii) – *x*+½,*y*–½,*z*+½; (*x*iv) *x*,*y*–1,*z*

Table S5 Assignment of the vibrational bands observed in the infrared and Raman spectra for $AgBi_2B_5O_{11}$.

Raman	IR	Modes
95		Translational modes of heavy Bi^{3+} ions
125		
137		Translational and librational modes of BO_4 groups
171		
197		
215		
261		
271		
302		Bending vibrations of BO_4 groups
346		
419	420	
444	439	
459	460	
	472	
	480	
512	513	
551	551	Symmetric stretching vibration modes of BO_4 groups
	589	In-plane O–B–O bending vibration
613	613	Out-of plane bending vibrations of BO_3 groups
627		
636	637	
649		
680		
	685	
748	748	
762	762	Symmetric stretching vibration modes of BO_4 groups
	790	
	798	
	886	
	907	
930	932	Symmetric stretching vibration modes of BO_3 groups
	950	
	1006	Asymmetric stretching vibration modes of BO_4 groups
	1043	

Figure S1 (*a*) Photograph and (*b*) schematic diagram of experimental setup for the synthesis of $AgBi_2B_5O_{11}$.

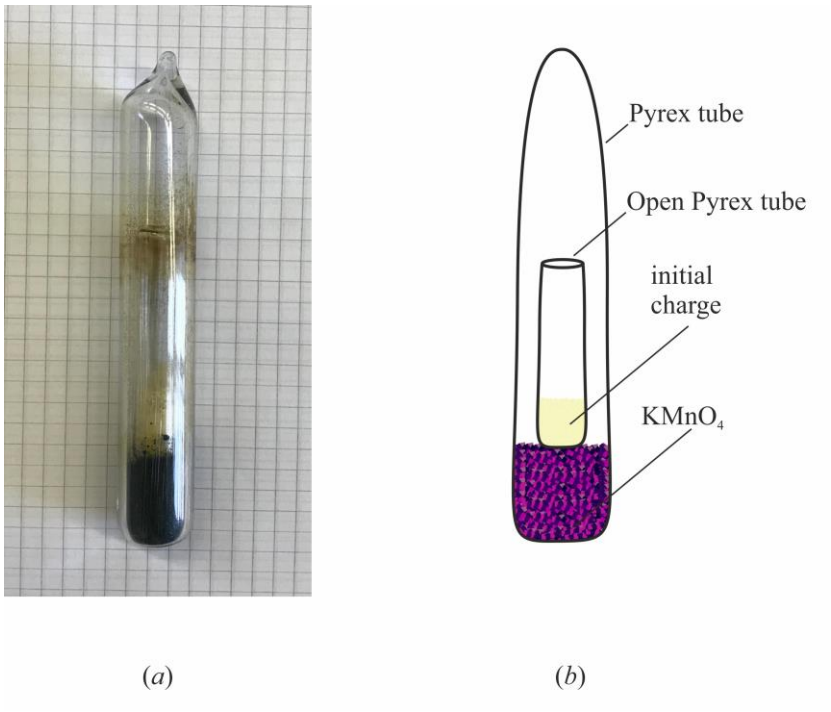


Figure S2 X-ray diffraction pattern for $AgBi_2B_5O_{11}$ obtained by solid-phase synthesis.

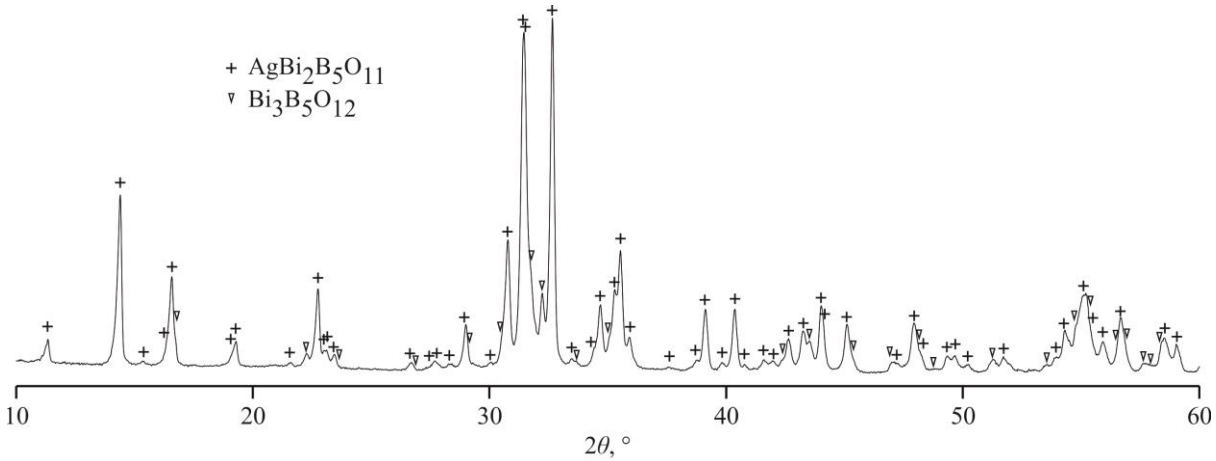


Figure S3 Experimental and calculated X-ray diffraction patterns for $AgBi_2B_5O_{11}$.

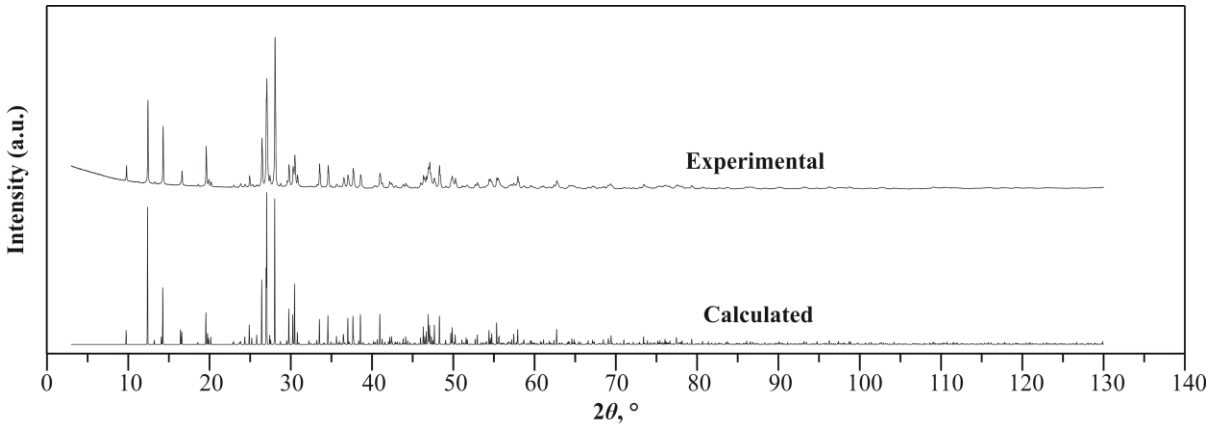


Figure S4 Single crystal of $AgBi_2B_5O_{11}$.

Figure S5 Intensity profiles for the powder X-ray Rietveld refinement of $AgBi_2B_5O_{11}$. The observed and calculated profiles are represented in blue and red lines, respectively. The difference profile is plotted at the bottom. Vertical bars indicate the positions of the Bragg reflections.

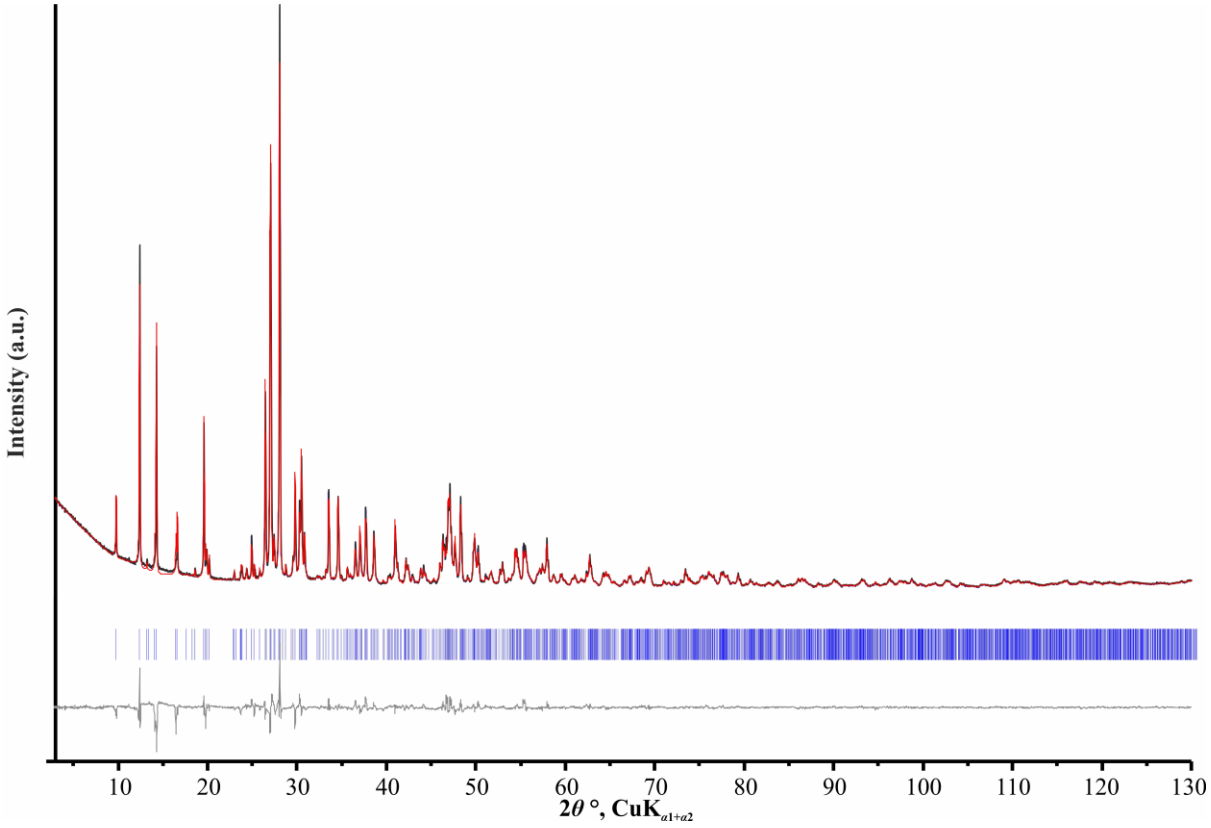


Figure S6 High-temperature X-ray powder diffraction measurements of $AgBi_2B_5O_{11}$. $Bi_3B_5O_{12}$ and Ag peaks are marked by arrows. The dashed lines indicates the onset of observation of metallic silver.

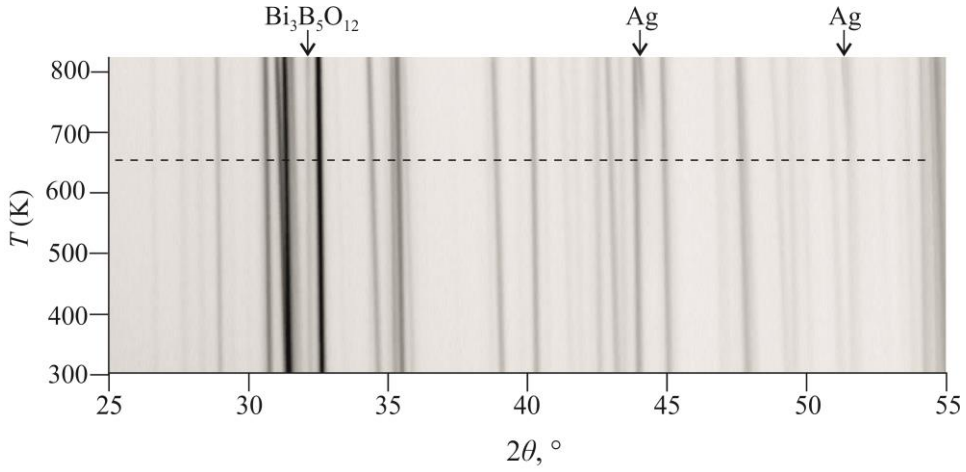


Figure S7 Temperature dependences of the unit-cell parameters and volume for $AgBi_2B_5O_{11}$. Uncertainties are smaller than used symbols.

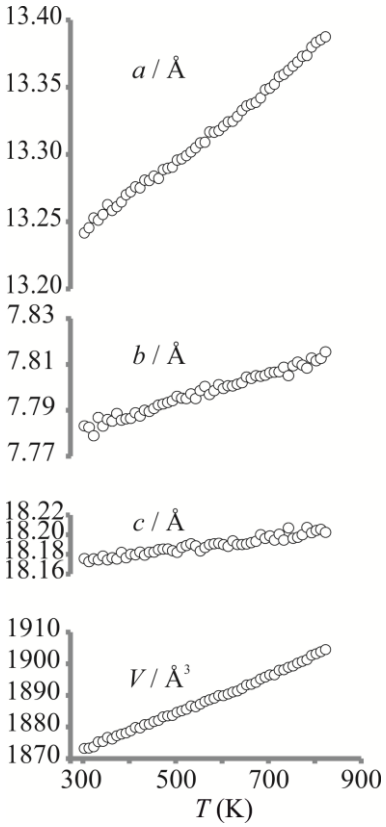


Figure S8 IR spectrum of $AgBi_2B_5O_{11}$.

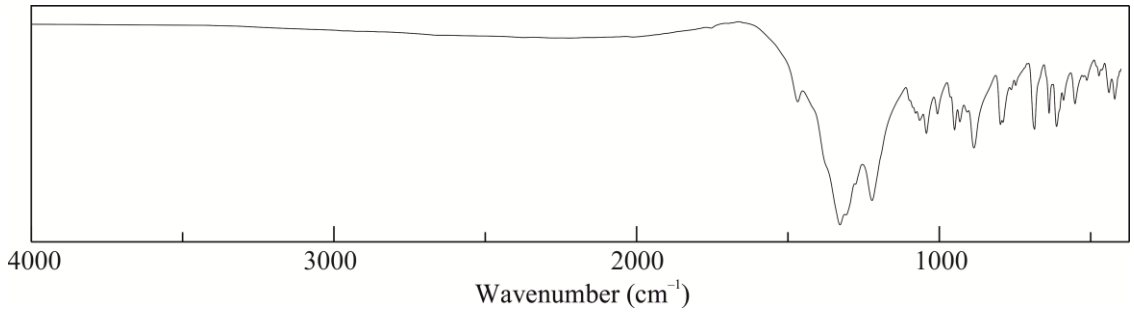
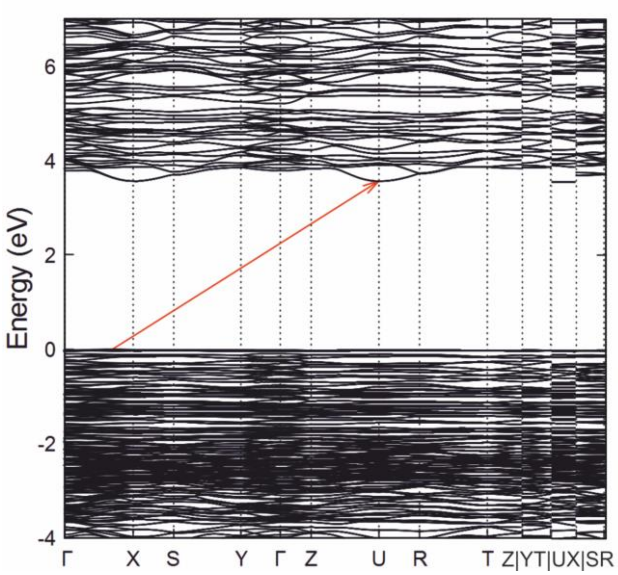


Figure S9 The band structure of $AgBi_2B_5O_{11}$. The arrow indicates the indirect bandgap.



References

Filatov, S., Shepelev, Yu., Bubnova, R., Sennova, N., Egorysheva, A. V. & Kargin, Yu. F. (2004) *J. Sol. St. Chem.* **177**, 515–522.