Electronic Supplementary Information for

Approaching the structure of *RE*BaB_9O_{16} (*RE* = rare earth) by characterizations of its new analogue $Ba_6Bi_9B_{79}O_{138}$

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Table S1 Fractional atomic coordinates, occupancies and isotropic thermal displacement factors for **BBBO**.

Atom	site	*x*	*y*	*z*	Occupancy	U_{eq} /Å^2
Ba1	3*a*	0.0000	0.0000	0.06918(10)	1	0.0118(3)
Ba2	3*a*	0.0000	0.0000	0.92743(10)	1	0.0146(4)
Bi1	3*a*	0.0000	0.0000	0.1660	1	0.0070(2)
Bi2	3*a*	0.0000	0.0000	0.83060(2)	1	0.0070(2)
Bi3	3*a*	0.0000	0.0000	0.49833(4)	1	0.00539(14)
O1	3*a*	0.0000	0.0000	-0.0044(8)	1	0.042(5)
O2	9*b*	0.0003(15)	-0.3493(17)	0.0893(4)	1	0.007(3)
O3	9*b*	0.3446(17)	-0.0023(16)	0.9062(4)	1	0.008(3)
O4	9*b*	-0.3441(16)	0.0062(15)	0.9064(4)	1	0.008(3)
O5	9*b*	-0.3454(15)	-0.3531(16)	0.0893(3)	1	0.006(2)
O6	9*b*	-0.1329(19)	-0.266(2)	0.5308(3)	1	0.013(3)
O7	9*b*	-0.1333(17)	0.1303(17)	0.8662(2)	1	0.004(2)
O8	9*b*	-0.524(2)	-0.0473(17)	0.9983(3)	1	0.041(3)
O9	9*b*	-0.3882(15)	-0.1939(15)	0.8631(2)	1	0.005(2)
O10	9*b*	-0.031(2)	-0.519(2)	0.0468(4)	1	0.041(3)
O11	9*b*	-0.259(3)	-0.003(3)	0.9731(4)	1	0.065(4)
O12	9*b*	-0.490(2)	0.027(2)	0.9500(4)	1	0.041(3)
O13	9*b*	0.004(2)	-0.255(3)	0.0238(4)	1	0.056(4)
O14	9*b*	-0.5278(14)	-0.4726(14)	0.1351(2)	1	0.0011(18)
O15	9*b*	0.131(2)	-0.135(2)	0.1290(3)	1	0.012(3)
O16	9*b*	-0.2007(16)	-0.4031(17)	0.1309(2)	1	0.007(2)

B1	9*b*	-0.332(2)	0.008 (2)	0.8753 (4)	1	0.004(4)
B2	9*b*	0.340(2)	0.004 (2)	0.8756 (5)	1	0.002(4)
B3	9*b*	-0.003(3)	-0.336 (3)	0.1214(7)	1	0.010(5)
B4	9*b*	-0.333(2)	-0.343 (2)	0.1208(4)	1	0.005(4)
B5	9*b*	-0.497(3)	-0.001 (3)	0.9200(5)	1	0.014(4)
B6	9*b*	-0.005(3)	-0.500 (3)	0.0755(4)	1	0.011(4)
B7	9*b*	-0.418(4)	0.005 (4)	0.9722(6)	1	0.052(6)
B8	9*b*	0.014(4)	-0.407 (5)	0.0240(7)	1	0.058(6)
B9	9*b*	-0.166(8)	-0.006 (8)	-0.0019(12)	7/9	0.086(13)

Table S2 Selected bond distances for $Ba_6Bi_9B_{79}O_{138}$.

Bond	Distance (Å)	Bond	Distance (Å)
Bi1—O9 (×3)	2.36(1)	B4—O16	1.42(2)
Bi1—O15(×3)	2.49(1)	B4—O5	1.47(3)
		B4—O14	1.50(2)
Bi2—O7(×3)	2.44(1)	B4—O15	1.52(2)
Bi2—O16(×3)	2.36(1)		
		B5—O4	1.33(3)
Bi3—O6(×3)	2.36(1)	B5—O3	1.39(3)
Bi3—O14(×3)	2.35(1)	B5—O12	1.41(3)
Ba1—O2(×3)	2.90(1)		
Ba1—O5(×3)	2.90(1)	B6—O2	1.33(2)
Ba1—O13(×3)	2.92(2)	B6—O10	1.35(3)

		B6—O5	1.36(2)
Ba2—O3(×3)	2.89(1)		
Ba2—O4(×3)	2.89(1)	B7—O12	1.23(3)
Ba2—O11(×3)	2.93(2)	B7—O11	1.28(4)
		B7—O8	1.41(3)
B1—O7	1.42(2)		
B1—O6	1.44(2)	B8—O13	1.23(4)
B1—O4	1.45(3)	B8—O10	1.31(3)
B1—O9	1.53(2)	B8—O8	1.39(3)
B2—O3	1.43(3)	B9—O1	1.28(5)
B2—O6	1.44(2)	B9—O11	1.38(6)
B2—O7	1.48(2)	B9—O13	1.41(6)
B2—O9	1.51(2)		
B3—O16	1.43(2)		
B3—O15	1.44(2)		
B3—O2	1.50(4)		
B3—O14	1.50(2)		

Table S3 Unit Cell parameters of $Ba_6(Bi_{1-x}Eu_x)_9B_{79}O_{138}$.

x	a (Å)	c (Å)	V (Å^3)
0	7.850	46.577	2485.6
0.02	7.850	46.575	2485.4
0.04	7.848	46.565	2484.0
0.10	7.847	46.557	2482.8
0.20	7.844	46.540	2479.6
0.30	7.839	46.529	2476.0
0.40	7.838	46.512	2474.5
0.50	7.828	46.526	2468.9
0.70	7.821	46.507	2463.5
0.80	7.810	46.571	2459.8
0.90	7.808	46.536	2459.8
1	7.804	46.523	2453.9

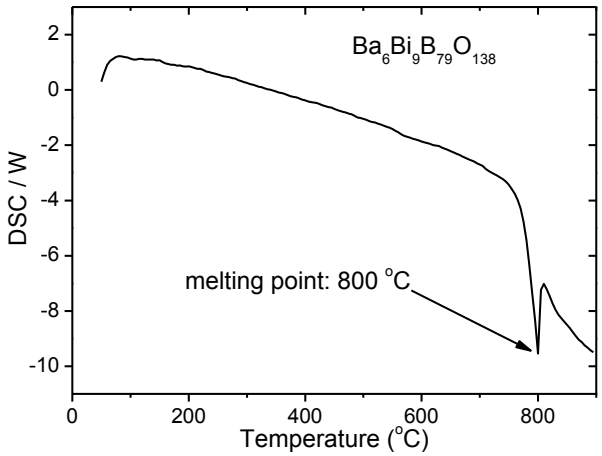

Fig. S1 DSC curve of the as-synthesized powder $Ba_6Bi_9B_{79}O_{138}$.

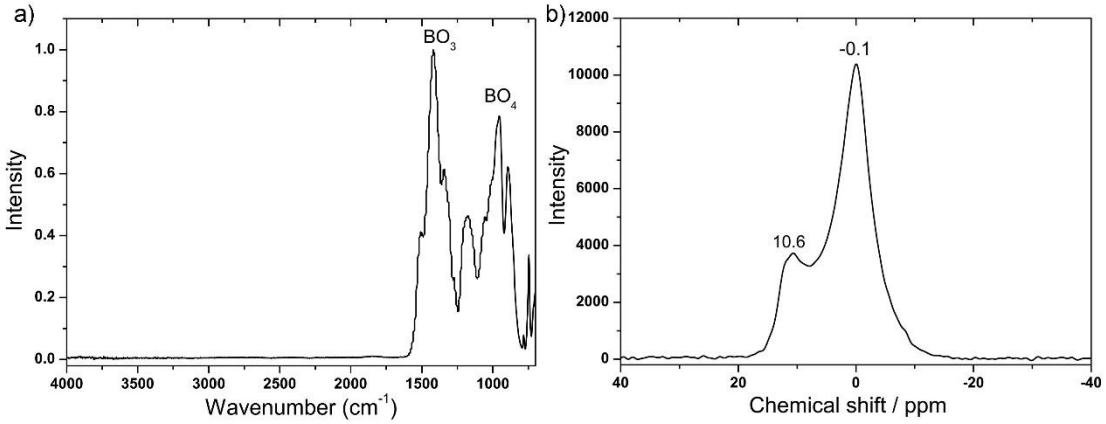

Fig. S2 The (a) IR and (b) ^{11}B MAS-NMR spectra indicate the co-presence of triangular and tetrahedral coordination of B atoms in the structure.

The absorption bands in the range of 1500-1100 cm^{-1} and 1100-800cm^{-1} in IR are generally assigned to the vibrations of the BO_3 and BO_4 groups, respectively. Generally, a single peak at around 0 ppm is related to the four-coordinated boron atoms, and the presence of three-coordinated boron atoms shows a broad bond with two peaks at around 10 and 1 ppm in the solid-state ^{11}B MAS-NMR spectrum. In detail, the strong peak at -0.1 ppm in Fig. S2b is typical for the four-coordinated boron atoms, and the peak at 10.6 ppm is related to the three-coordinated boron atoms, for which the other peak at around 1 ppm is overlapped with the signal of four-coordinated boron atoms.

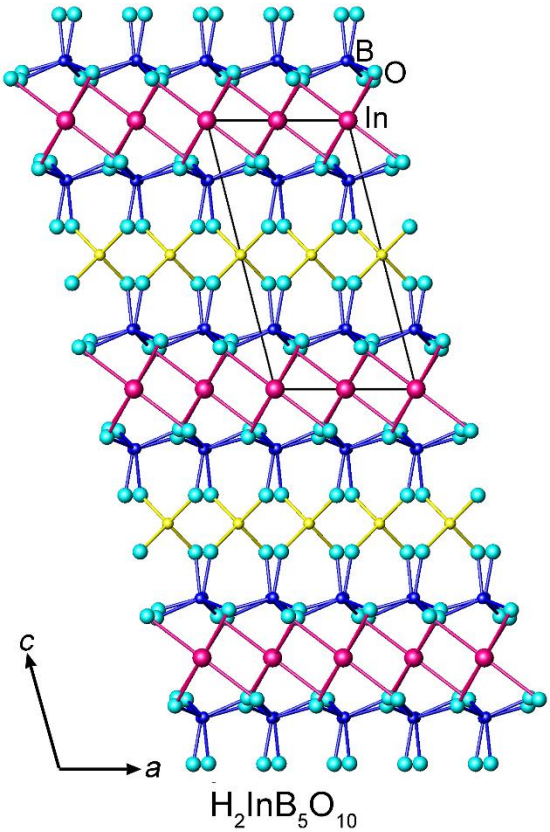

Fig. S3 Structure view of $H_2InB_5O_{10}$ showing a similar metal-centered sandwiched layer.