Supporting Information

Two new rare-earth borates $Sr_2Tb_3B_{27-\delta}O_{46}$ and $Ba_2Eu_3B_{27-\delta}O_{46}$ (δ = 2/3): Syntheses, crystal structures, and luminescent properties

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Content

Table S1 Atomic coordinates, site occupancies, and equivalent isotropic displacement parameters (Å^2) for $Sr_2Tb_3B_{27-\delta}O_{46}$ and $Ba_2Eu_3B_{27-\delta}O_{46}$ (δ = 2/3).

Atoms	Wyck sites	Site symmetry	X	Y	Z	Occupancies	U_{eq}
$Sr_2Tb_3B_{27-\delta}O_{46}$							
Sr1	3a	C_3	0.0000	0.0000	0.07410(9)	1	0.0253(3)
Sr2	3a	C_3	0.0000	0.0000	0.92588(9)	1	0.0257(3)
Tb1	3a	C_3	0.0000	0.0000	0.166330(16)	1	0.00938(11)
Tb2	3a	C_3	0.0000	0.0000	0.834530(11)	1	0.0095(2)
Tb3	3a	C_3	0.0000	0.0000	0.498865(14)	1	0.00849(17)
B1	9b	C_1	-0.3358(13)	0.0012(13)	0.8771(5)	1	0.0116(12)
B2	9b	C_1	0.3370(13)	-0.0013(13)	0.8771(5)	1	0.0112(13)
B3	9b	C_1	-0.0007(13)	-0.3369(14)	0.1228(6)	1	0.0134(13)
B4	9b	C_1	-0.3367(15)	-0.3385(13)	0.1228(6)	1	0.0141(13)
B5	9b	C_1	-0.4983(16)	0.0003(17)	0.9221(2)	1	0.0164(11)
B6	9b	C_1	-0.0041(18)	-0.5011(17)	0.0775(2)	1	0.0180(11)
B7	9b	C_1	-0.399(2)	0.009(2)	0.9737(3)	1	0.0339(16)
B8	9b	C_1	-0.012(2)	-0.412(2)	0.0258(3)	1	0.0332(15)
B9	9b	C_1	-0.148(2)	0.0000	0.0012(3)	7/9	0.0316(16)
O1	3a	C_3	0.0000	0.0000	-0.0067(3)	1	0.0296(12)
O2	9b	C_1	-0.0025(9)	-0.3475(10)	0.0913(3)	1	0.0145(11)
O3	9b	C_1	0.3444(9)	-0.0018(9)	0.9085(3)	1	0.0141(11)
O4	9b	C_1	-0.3480(10)	-0.0016(9)	0.9083(3)	1	0.0144(11)
O5	9b	C_1	-0.3452(10)	-0.3455(9)	0.0912(3)	1	0.0133(11)
O6	9b	C_1	-0.1327(8)	-0.2651(8)	0.53072(11)	1	0.0100(9)
O7	9b	C_1	-0.1299(9)	0.1276(9)	0.86793(11)	1	0.0137(9)
O8	9b	C_1	-0.5278(13)	-0.0514(12)	0.9999(2)	1	0.0421(15)
O9	9b	C_1	-0.3980(8)	-0.1991(8)	0.86490(11)	1	0.0122(8)
O10	9b	C_1	0.0274(13)	-0.4886(13)	0.04801(19)	1	0.0330(13)
O11	9b	C_1	-0.2424(15)	0.0016(14)	0.97387(19)	1	0.0461(15)
O12	9b	C_1	-0.5123(13)	-0.0262(13)	0.95170(18)	1	0.0350(14)
O13	9b	C_1	-0.0011(14)	-0.2455(14)	0.02663(19)	1	0.0432(14)
O14	9b	C_1	0.2017(9)	-0.1990(8)	0.13404(11)	1	0.0133(8)
O15	9b	C_1	-0.1279(9)	-0.2574(8)	0.13218(12)	1	0.0144(8)
O16	9b	C_1	-0.4669(8)	-0.5325(8)	0.13607(11)	1	0.0124(8)
$Ba_2Eu_3B_{27-\delta}O_{46}$							
Ba1	3a	C_3	1.0000	1.0000	0.92914(5)	1	0.01412(18)
Ba2	3a	C_3	1.0000	1.0000	0.07116(5)	1	0.01366(17)
Eu1	3a	C_3	1.0000	1.0000	0.833765(18)	1	0.00466(13)
Eu2	3a	C_3	1.0000	1.0000	0.165295(14)	1	0.00511(18)
Eu3	3a	C_3	1.0000	1.0000	0.50128(2)	1	0.00462(14)
B1	9b	C_1	1.3371(15)	0.9990(15)	0.1228(5)	1	0.0077(11)
B2	9b	C_1	0.6620(15)	0.9999(14)	0.1227(5)	1	0.0073(12)
B3	9b	C_1	1.0021(15)	1.3372(15)	0.8772(5)	1	0.0088(12)
B4	9b	C_1	1.3354(15)	1.3368(15)	0.8772(5)	1	0.0087(12)
B5	9b	C_1	1.5011(18)	1.0016(18)	0.0780(2)	1	0.0122(11)
B6	9b	C_1	1.0011(18)	1.5006(18)	0.9227(2)	1	0.0131(12)
B7	9b	C_1	1.4172(17)	0.9939(18)	0.0256(2)	1	0.0258(14)
B8	9b	C_1	1.0031(18)	1.4217(17)	0.9749(2)	1	0.0252(13)
B9	9b	C_1	1.1622(19)	1.0000	0.9999(3)	7/9	0.0240(15)
O1	3a	C_3	1.0000	1.0000	1.0056(2)	1	0.0155(6)
O2	9b	C_1	1.0020(11)	1.3486(12)	0.9084(3)	1	0.0113(6)
O3	9b	C_1	0.6526(11)	1.0009(11)	0.0916(3)	1	0.0114(6)
O4	9b	C_1	1.3503(11)	1.0023(11)	0.0918(3)	1	0.0110(6)
O5	9b	C_1	1.3468(12)	1.3471(12)	0.9086(3)	1	0.0116(6)
O6	9b	C_1	1.1346(8)	1.2686(8)	0.46920(12)	1	0.0102(6)
O7	9b	C_1	1.1315(9)	0.8693(9)	0.13203(12)	1	0.0123(6)
O8	9b	C_1	1.5246(10)	1.0463(9)	0.00000(15)	1	0.0207(7)
O9	9b	C_1	1.3960(8)	1.1982(8)	0.13527(12)	1	0.0113(6)
O10	9b	C_1	0.9612(11)	1.4821(10)	0.95172(15)	1	0.0192(7)
O11	9b	C_1	1.2515(11)	0.9963(10)	0.02567(15)	1	0.0225(7)
O12	9b	C_1	1.5150(10)	1.0325(11)	0.04831(15)	1	0.0203(7)
O13	9b	C_1	1.0022(10)	1.2536(10)	0.97431(14)	1	0.0213(7)
O14	9b	C_1	0.8018(8)	1.1985(8)	0.86586(12)	1	0.0113(6)
O15	9b	C_1	1.1301(8)	1.2614(9)	0.86770(12)	1	0.0118(6)
O16	9b	C_1	1.4687(9)	1.5308(9)	0.86387(12)	1	0.0117(6)

Note: U_{eq} is defined as one third of the trace of the orthogonalized **U** tensor.

Table S2 Selected bond lengths (Å) for $Sr_2Tb_3B_{27-\delta}O_{46}$ (δ = 2/3).

Sr1-O5 × 3	2.790(8)	B3-O16	1.475(15)
Sr1-O2 × 3	2.798(7)	B3-O14	1.481(14)
Sr1-O13 × 3	2.906(10)	Mean	1.471
Mean	2.831	B4-O16	1.463(15)
Sr2-O3 × 3	2.794(8)	B4-O5	1.464(29)
Sr2-O4 × 3	2.810(7)	B4-O14	1.473(14)
Sr2-O11 × 3	2.916(10)	B4-O15	1.478(13)
Mean	2.840	Mean	1.470
Tb1-O9 × 3	2.332(5)	B5-O4	1.334(13)
Tb1-O15 × 3	2.343(6)	B5-O3	1.366(14)
Mean	2.338	B5-O12	1.385(11)
Tb2-O7 × 3	2.320(5)	Mean	1.362
Tb2-O16 × 3	2.324(5)	B6-O2	1.345(14)
Mean	2.322	B6-O5	1.363(14)
Tb3-O14 × 3	2.305(5)	B6-O10	1.384(12)
Tb3-O6 × 3	2.312(5)	Mean	1.364
Mean	2.309	B7-O11	1.246(19)
B1-O4	1.451(28)	B7-O12	1.283(15)
B1-O7	1.457(12)	B7-O8	1.490(15)
B1-O6	1.475(13)	Mean	1.340
B1-O9	1.487(14)	B8-O13	1.248(18)
Mean	1.468	B8-O10	1.302(15)
B2-O3	1.454(29)	B8-O8	1.475(16)
B2-O6	1.471(14)	Mean	1.342
B2-O9	1.473(14)	B9-O1	1.204(17)
B2-O7	1.490(12)	B9-O13	1.399(18)
Mean	1.472	B9-O11	1.464(18)
B3-O2	1.464(31)	Mean	1.356
B3-O15	1.465(13)		

Table S3 Selected bond angles (°) for $Sr_2Tb_3B_{27-\delta}O_{46}$ (δ = 2/3).

O9-Tb1-O9 × 3	84.04(19)	O2-B3-O16	111.6(11)
O9-Tb1-O15 × 3	81.91(19)	O2-B3-O14	111.6(12)
O9-Tb1-O15 × 3	135.39(18)	O15-B3-O14	106.6(11)
O9-Tb1-O15 × 3	135.68(19)	O16-B3-O14	106.9(12)
O15-Tb1-O15 × 3	79.3(2)	O15-B3-O16	110.9(12)
		Mean	109.5
O7-Tb2-O7 × 3	80.3(2)	O5-B4-O15	109.3(12)
O7-Tb2-O16 × 3	81.26(19)	O5-B4-O14	110.9(11)
O7-Tb2-O16 × 3	135.1(2)	O16-B4-O14	106.4(12)
O7-Tb2-O16 × 3	135.6(2)	O16-B4-O15	111.0(12)
O16-Tb2-O16 × 3	84.0(2)	O16-B4-O5	112.8(11)
		O14-B4-O15	106.2(11)
O14-Tb3-O14 × 3	84.2(2)	Mean	109.4
O14-Tb3-O6 × 3	78.99(19)	O3-B5-O12	117.0(10)
O14-Tb3-O6 × 3	134.4(2)	O4-B5-O12	118.4(10)
O14-Tb3-O6 × 3	134.8(2)	O4-B5-O3	123.9(10)
O6-Tb3-O6 × 3	83.6(2)	Mean	119.8
		O2-B6-O10	119.0(11)
O4-B1-O7	110.0(11)	O2-B6-O5	123.8(11)
O4-B1-O6	111.4(10)	O5-B6-O10	116.2(10)
O4-B1-O9	112.3(10)	Mean	119.7
O6-B1-O9	106.8(11)	O11-B7-O8	119.6(11)
O7-B1-O6	110.8(11)	O11-B7-O12	124.8(12)
O7-B1-O9	105.4(10)	O12-B7-O8	107.7(11)
Mean	109.5	Mean	117.4
O3-B2-O7	108.5(11)	O10-B8-O8	107.1(11)
O3-B2-O6	112.2(10)	O13-B8-O8	121.0(11)
O3-B2-O9	113.0(10)	O13-B8-O10	122.4(11)
O6-B2-O9	107.6(12)	Mean	116.8
O6-B2-O7	109.8(11)	O1-B9-O11	102.6(12)
O9-B2-O7	105.5(10)	O1-B9-O13	140.0(15)
Mean	109.4	O13-B9-O11	117.3(13)
O2-B3-O15	109.2(12)	Mean	120.0

Table S4 Selected bond lengths (Å) for $Ba_2Eu_3B_{27-\delta}O_{46}$ (δ = 2/3).

Ba1-O5 × 3	2.868(9)	B3-O15	1.459(13)
Ba1-O2 × 3	2.877(9)	B3-O16	1.478(14)
Ba1-O13 × 3	2.879(7)	B3-O14	1.482(14)
Mean	2.875	Mean	1.469
Ba2-O3 × 3	2.874(8)	B4-O5	1.464(24)
Ba2-O4 × 3	2.887(8)	B4-O15	1.470(13)
Ba2-O11 × 3	2.894(7)	B4-O16	1.476(14)
Ba2-O1	3.051(10)	B4-O14	1.480(14)
Mean	2.902	Mean	1.473
Eu1-O9 × 3	2.352(6)	B5-O4	1.341(14)
Eu1-O15 × 3	2.368(6)	B5-O3	1.342(14)
Mean	2.360	B5-O12	1.398(11)
Eu2-O7 × 3	2.351(6)	Mean	1.360
Eu2-O16 × 3	2.357(6)	B6-O5	1.361(14)
Mean	2.354	B6-O2	1.362(14)
Eu3-O14 × 3	2.331(6)	B6-O10	1.376(11)
Eu3-O6 × 3	2.348(6)	Mean	1.366
Mean	2.340	B7-O12	1.250(13)
B1-O4	1.442(24)	B7-O11	1.301(15)
B1-O7	1.468(13)	B7-O8	1.392(13)
B1-O6	1.472(14)	Mean	1.314
B1-O9	1.500(14)	B8-O10	1.282(13)
Mean	1.471	B8-O13	1.307(15)
B2-O3	1.449(24)	B8-O8	1.371(13)
B2-O6	1.468(14)	Mean	1.320
B2-O7	1.481(13)	B9-O1	1.292(15)
B2-O9	1.492(14)	B9-O13	1.381(16)
Mean	1.473	B9-O11	1.395(16)
B3-O2	1.455(25)	Mean	1.356

Table S5 Selected bond angles (°) for $Ba_2Eu_3B_{27-\delta}O_{46}$ (δ = 2/3).

O9-Eu1-O9 × 3	84.6(2)	O2-B3-O16	111.4(10)
O9-Eu1-O15 × 3	80.8(2)	O2-B3-O14	111.5(11)
O9-Eu1-O15 × 3	135.0(2)	O15-B3-O14	106.4(10)
O9-Eu1-O15 × 3	135.3(2)	O15-B3-O16	110.9(11)
O15-Eu1-O15 × 3	80.4(2)	O16-B3-O14	106.0(11)
		Mean	109.4
O7-Eu2-O7 × 3	81.4(2)	O5-B4-O15	110.2(11)
O7-Eu2-O16 × 3	80.2(2)	O5-B4-O14	111.3(10)
O7-Eu2-O16 × 3	134.9(2)	O5-B4-O16	111.7(11)
O7-Eu2-O16 × 3	135.1(2)	O15-B4-O14	106.6(10)
O16-Eu2-O16 × 3	84.6(2)	O15-B4-O16	110.6(10)
		O16-B4-O14	106.3(11)
O14-Eu3-O14 × 3	85.2(2)	Mean	109.5
O14-Eu3-O6 × 3	78.0(2)	O4-B5-O12	117.7(10)
O14-Eu3-O6 × 3	134.2(2)	O4-B5-O3	123.4(10)
O14-Eu3-O6 × 3	134.3(2)	O3-B5-O12	118.3(10)
O6-Eu3-O6× 3	84.0(2)	Mean	119.8
		O5-B6-O10	117.7(10)
O4-B1-O7	110.4(11)	O5-B6-O2	122.0(10)
O4-B1-O6	111.3(10)	O2-B6-O10	119.1(10)
O4-B1-O9	112.8(10)	Mean	119.6
O7-B1-O9	105.3(10)	O12-B7-O8	116.5(10)
O7-B1-O6	110.3(11)	O12-B7-O11	118.9(10)
O6-B1-O9	106.5(11)	O11-B7-O8	117.1(10)
Mean	109.4	Mean	117.5
O3-B2-O7	109.5(10)	O10-B8-O8	115.7(11)
O3-B2-O6	111.8(10)	O10-B8-O13	118.5(9)
O3-B2-O9	113.5(10)	O13-B8-O8	118.6(10)
O6-B2-O9	106.7(11)	Mean	117.6
O6-B2-O7	109.8(10)	O1-B9-O11	108.8(11)
O7-B2-O9	105.2(10)	O1-B9-O13	132.5(13)
Mean	109.4	O13-B9-O11	118.7(12)
O2-B3-O15	110.4(11)	Mean	120

Table S6 SHG intensities of the $Sr_2Tb_3B_{27-\delta}O_{46}$ and $Ba_2Eu_3B_{27-\delta}O_{46}$ ($\delta = 2/3$) samples compared with the KDP reference.

Sample name		KDP		$Sr_2Tb_3B_{27-\delta}O_{46}$		$Ba_2Eu_3B_{27-\delta}O_{46}$	
		$I_{observed}$	$I_{corrected}$	$I_{observed}$	$I_{corrected}$	$I_{observed}$	$I_{corrected}$
Measurement number	1	388	408	371	391	203	223
	2	418	438	333	353	193	213
	3	413	433	324	344	215	235
	4	367	387	395	415	210	230
	5	473	493	383	403	220	240
	6	454	474	373	393	200	220
	7	392	412	376	396	176	196
	8	386	406			189	209
	9					243	263
	10					171	191
Average SHG intensity			431.375		385		222

Note: Background counts is -20, $I_{observed}$ is the observed SHG intensity in counts, $I_{corrected} = I_{observed}$ – Background, and it is the SHG intensity after correction. The KDP, $Sr_2Tb_3B_{27-\delta}O_{46}$ and $Ba_2Eu_3B_{27-\delta}O_{46}$ samples were each repeatedly measured 8, 7 and 10 times, respectively, and the average SHG intensity was used for comparison.

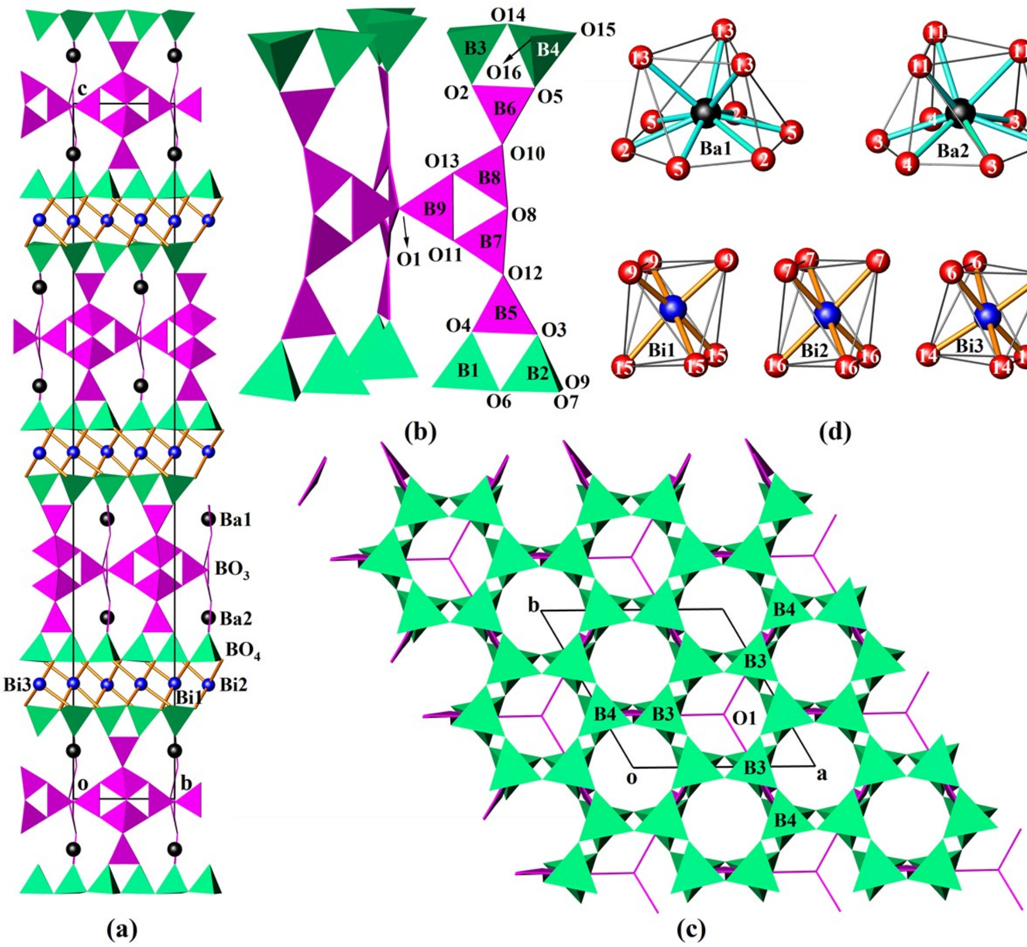

Fig. S1 Crystal structure of $Ba_6Bi_9B_{79}O_{138}$ projected along the [100] direction (a), the $[B_{27}O_{58}]^{35-}$ polyborate anionic group (b), a single layer $[B_{27}O_{46}]_n^{11n-}$ viewed along the [001] direction (c), and the local environment of each Ba^{2+} and Bi^{3+} site (the numbers correspond to the oxygen atom designations) (d). Ba: black balls; Bi: blue balls; BO_3: magenta triangles; BO_4: green tetrahedra. Note: the structural data of $Ba_6Bi_9B_{79}O_{138}$ are taken from ref.28; the crystal structure of $Ba_6Bi_9B_{79}O_{138}$ is plotted in the same way as that of $Sr_2Tb_3B_{27-\delta}O_{46}$, and the atom designations and the plot orientation of these two structures remain the same for the convenience of the structural comparison.

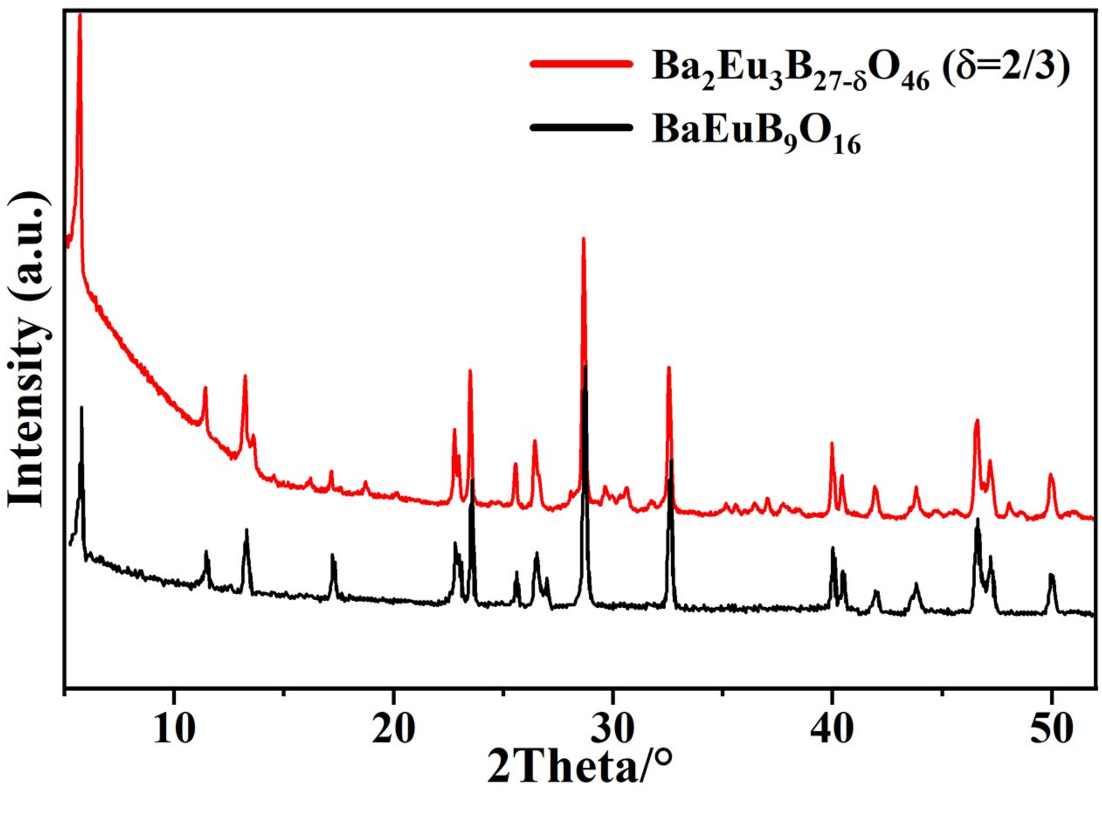

Fig. S2 Comparison of the observed XRD pattern of $Ba_2Eu_3B_{27-\delta}O_{46}$ (δ = 2/3) (presented in this work) with that of "$BaEuB_9O_{16}$" (cited from ref. 21).

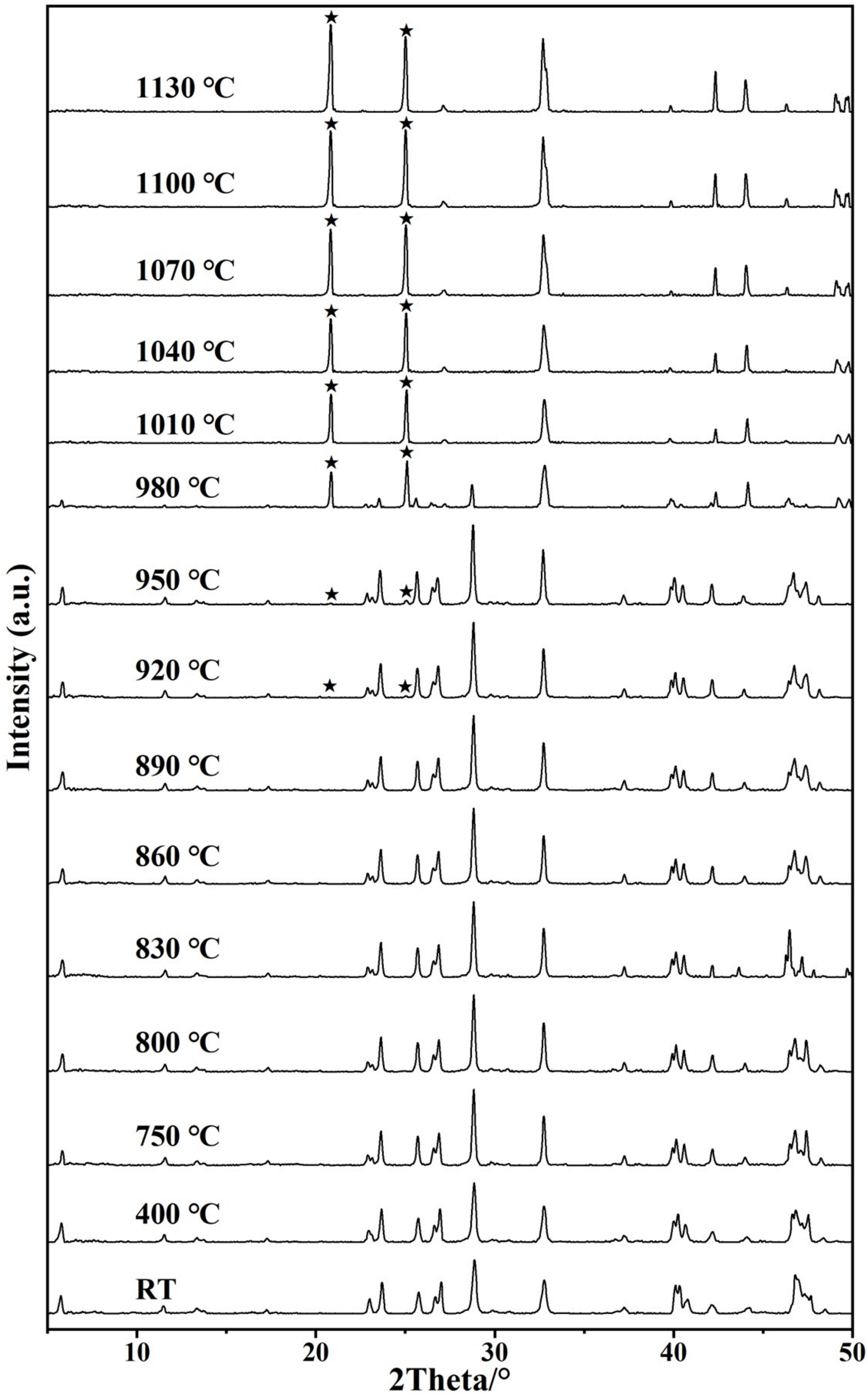

Fig. S3 XRD patterns of $Sr_2Tb_3B_{27-\delta}O_{46}$ ($\delta = 2/3$) under different temperatures. ★: an unknown phase.

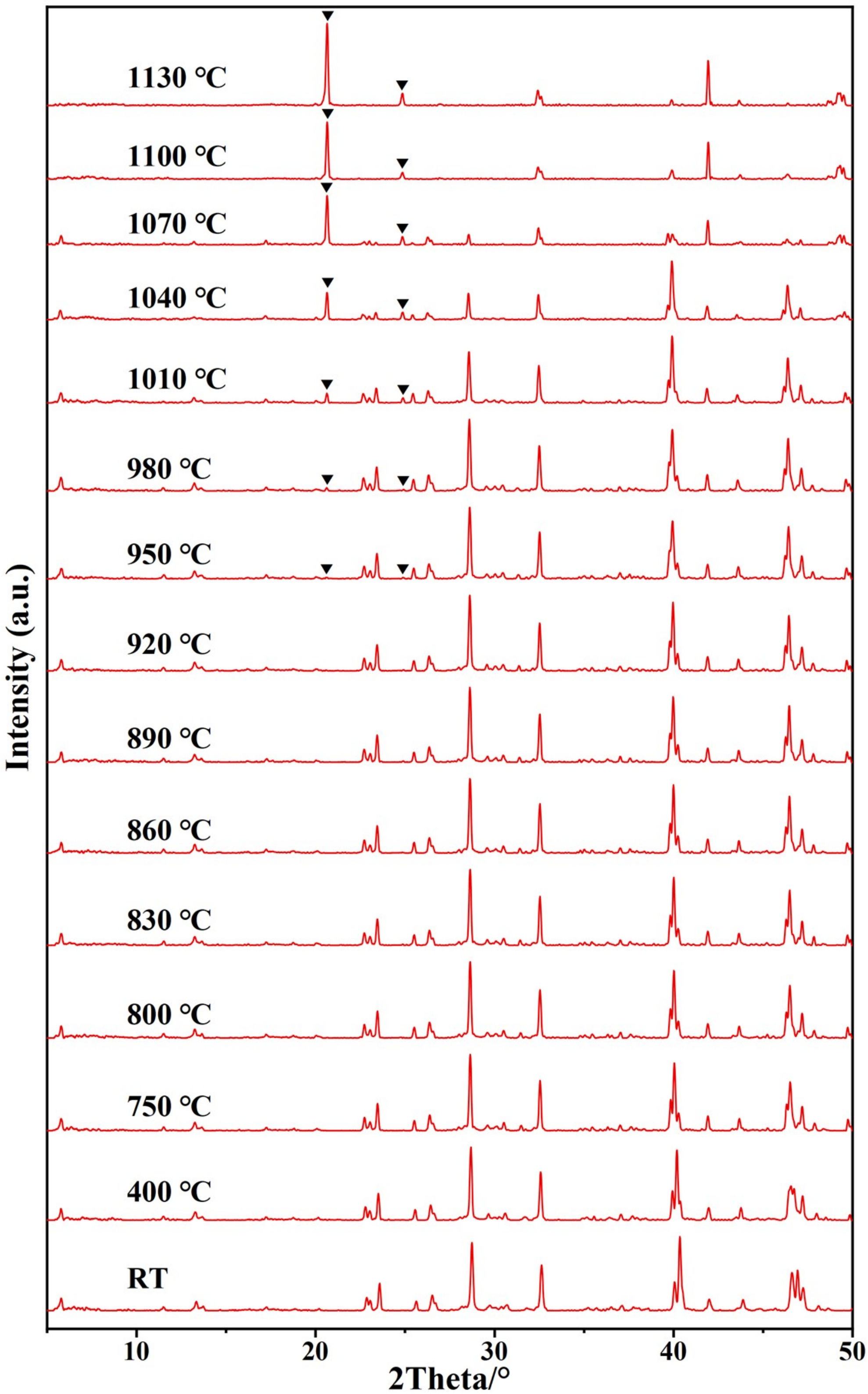

Fig. S4 XRD patterns of $Ba_2Eu_3B_{27-\delta}O_{46}$ (δ = 2/3) under different temperatures. ▼: $EuBO_3$ (PDF 89-7888).

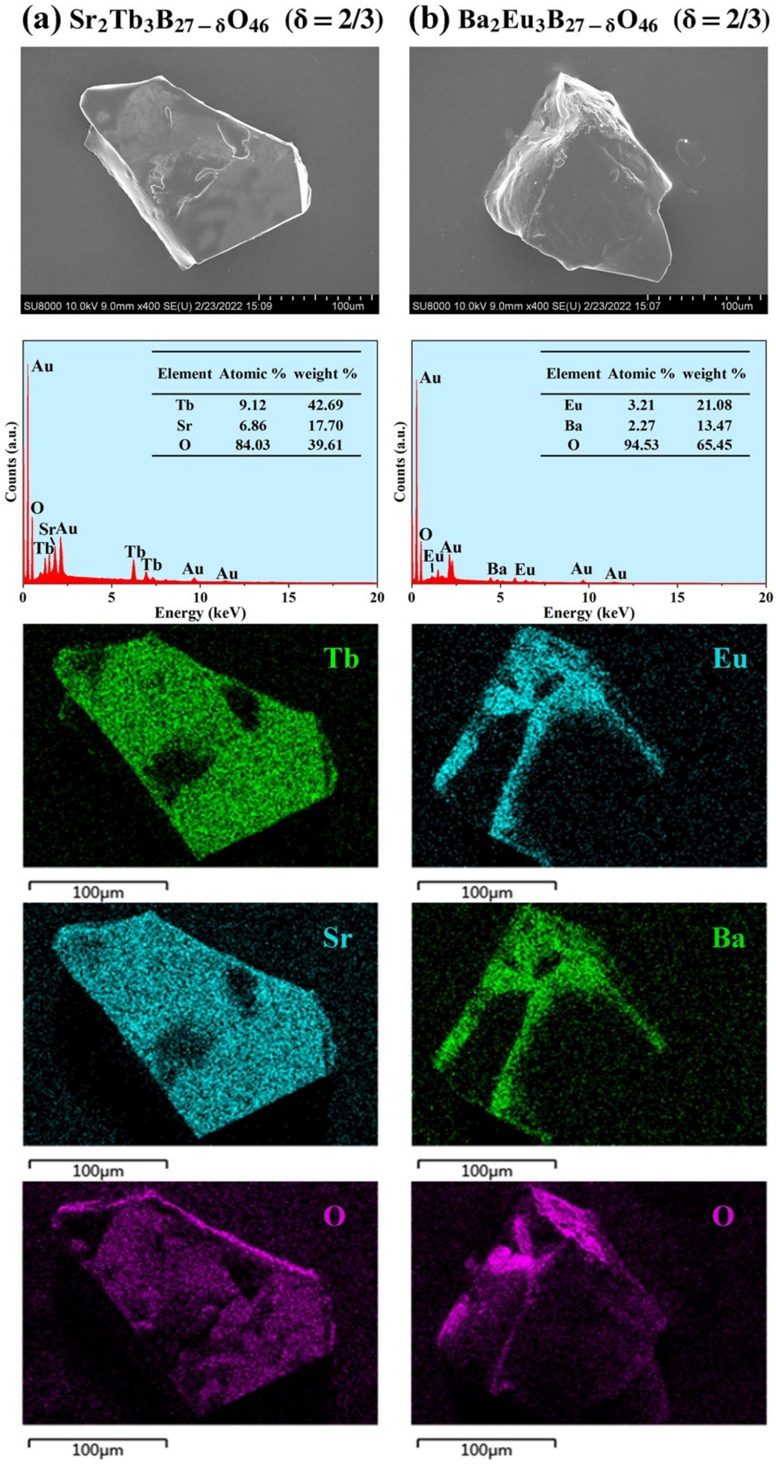

Fig. S5 FE-SEM images, typical EDX spectra, and elemental mapping of the $Sr_2Tb_3B_{27-\delta}O_{46}$ (a) and $Ba_2Eu_3B_{27-\delta}O_{46}$ (b) crystals. Au element comes from the pretreatment process. Note: The single crystal displayed in (b) has a size suitable for the crystal structure determination, which was cut from a big and thick $Ba_2Eu_3B_{27-\delta}O_{46}$ ($\delta = 2/3$) plate.

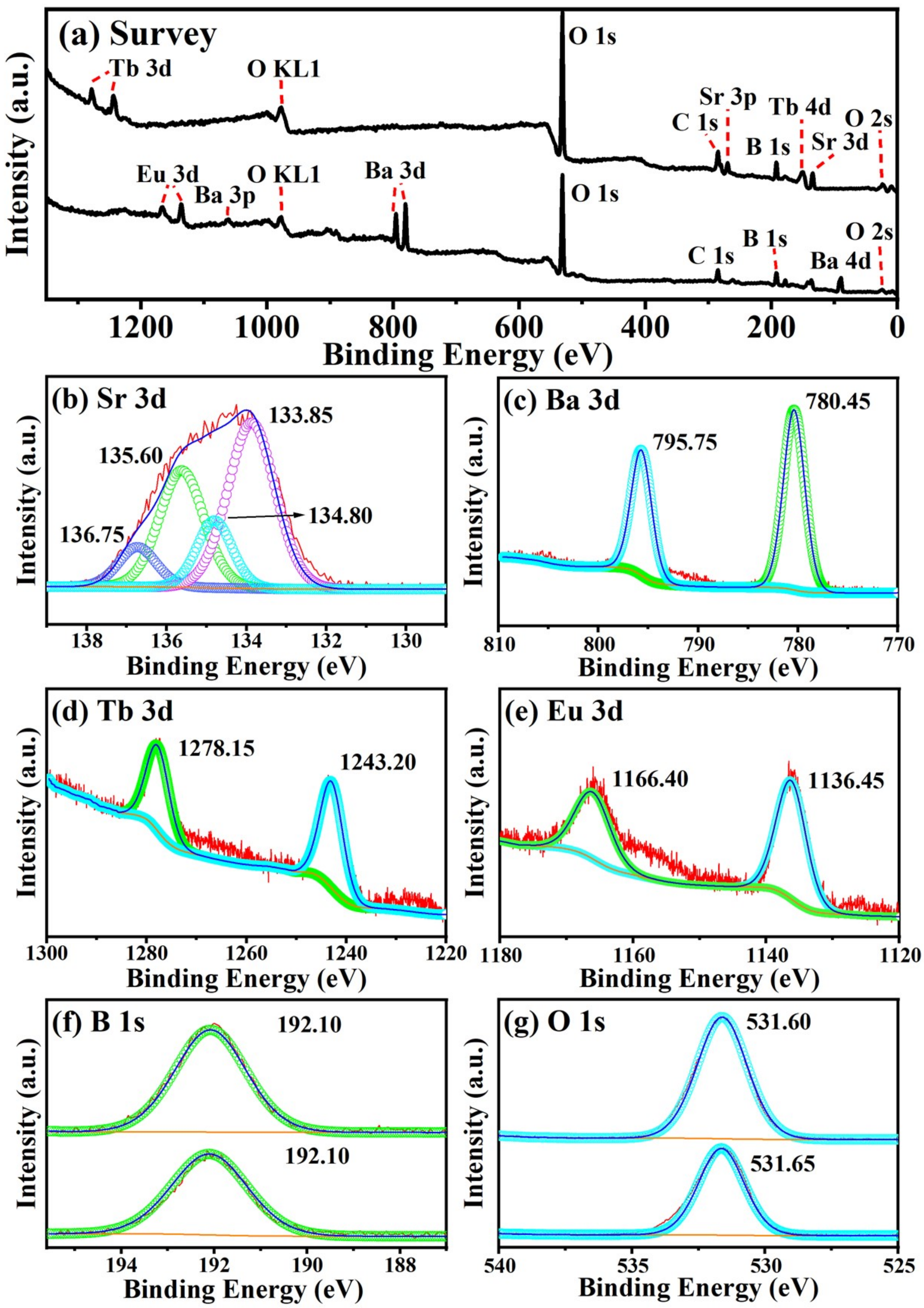

Fig. S6 Survey (a) and core-level spectra of Sr 3d (b), Ba 3d (c), Tb 3d (d), Eu 3d (e) B 1s (f), and O 1s (g) for $Sr_2Tb_3B_{27-\delta}O_{46}$ (top) and $Ba_2Eu_3B_{27-\delta}O_{46}$ (bottom).