RE$(SO_4)[B(OH)_4](H_2O)$, *RE*$(SO_4)[B(OH)_4](H_2O)_2$, and *RE*$(SO_4)[B(OH)_4](H_2O)\cdot H_2O$: Rare Earth Borate-Sulfates Featuring Three Types of Layered Structures

Wen-Wen Wang,[†,‡] Xiang Xu,*[,†] Jin-Tao Kong,[§] and Jiang-Gao Mao*[,†]

[†]*State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, People's Republic of China*

[‡]*College of Chemistry, Fuzhou University, Fuzhou 350108, People's Republic of China*

[§]*Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, People's Republic of China*

FAX: (+86)591-63173121; E-mail: mjg@fjirsm.ac.cn, xiangxu@fjirsm.ac.cn

Supporting Information

Excitation Spectra.

The excitation spectra have been recorded by monitoring the emission at 588 nm for compound **3**, 591 nm for compound **7**, and 602 nm for both compounds **2** and **6**. The excitation spectra of both Sm-containing compounds (**2** and **6**) show identical profile, as well as these of the two Eu-containing compounds (**3** and **7)** (Figure S4). A series of excitation peaks originating from 4f intra-configurational transitions of trivalent lanthanides (Sm^{3+} or Eu^{3+}) are identified at 305 ($^6H_{5/2}\rightarrow{}^4P_{5/2}$), 317 ($^6H_{5/2}\rightarrow{}^4P_{3/2}$), 332 ($^6H_{5/2}\rightarrow{}^4G_{9/2}$), 344 ($^6H_{5/2}\rightarrow{}^4D_{7/2}$), 354 ($^6H_{5/2}\rightarrow{}^4H_{7/2}$), 362 ($^6H_{5/2}\rightarrow{}^6P_{5/2}$), 375 ($^6H_{5/2}\rightarrow{}^6P_{7/2}$), 390 ($^6H_{5/2}\rightarrow{}^4L_{15/2}$), 402 ($^6H_{5/2}\rightarrow{}^4F_{7/2}$), 416 ($^6H_{5/2}\rightarrow{}^6P_{5/2}$), 438 ($^6H_{5/2}\rightarrow{}^4G_{9/2}$), 461 ($^6H_{5/2}\rightarrow{}^4I_{9/2}$), 477 ($^6H_{5/2}\rightarrow{}^4I_{13/2}$) and 500 nm ($^6H_{5/2}\rightarrow{}^4G_{7/2}$) for compounds **2** and **6**, and 317 ($^7F_0\rightarrow{}^5H_6$), 325 ($^7F_1\rightarrow{}^5H_7$), 362 ($^7F_0\rightarrow{}^5D_4$), 366 ($^7F_1\rightarrow{}^5D_4$), 376 ($^7F_0\rightarrow{}^5G_6$), 379 ($^7F_0\rightarrow{}^5G_2$), 385 ($^7F_1\rightarrow{}^5L_7$), 395 ($^7F_0\rightarrow{}^5L_6$), 415 ($^7F_1\rightarrow{}^5D_3$), 465 ($^7F_0\rightarrow{}^5D_2$) for compounds **3** and **7**. Among these excitation peaks, the ones centered at 402 and 395 nm for Sm- and Eu-containing compounds, respectively, exhibit relatively larger intensity than the others, which suggests that 402 nm and 395 nm should be a suitable excitation wavelength to extract efficient luminescence for compounds **2** and **6**, **3** and **7**, respectively.

Table S1. Compositions of the starting materials for the hydrothermal syntheses of compounds **1-16** [a]

Compound	Rare earth oxide (mmol)	H_3BO_3 (mmol)	H_2SO_4 (μL)	H_2O (mL)
1	0.25 (La_2O_3)	4.0	30	2
2	0.30 (Sm_2O_3)	3.0	30	3
3	0.25 (Eu_2O_3)	4.0	30	2
4	0.15 (Pr_6O_{11})	3.0	50	3
5	0.25 (Nd_2O_3)	2.0	30	3
6	0.25 (Sm_2O_3)	2.0	30	3
7	0.25 (Eu_2O_3)	2.0	30	3
8	0.50 (Gd_2O_3)	2.0	30	3
9	0.25 (Tb_4O_7)	2.0	30	4
10	0.25 (Dy_2O_3)	2.0	30	3
11	0.25 (Ho_2O_3)	2.0	30	3
12	0.50 (Er_2O_3)	2.0	30	3
13	0.25 (Tm_2O_3)	2.0	30	3
14	0.25 (Yb_2O_3)	2.0	30	3
15	0.25 (Lu_2O_3)	2.0	30	3
16	0.50 (Y_2O_3)	3.0	50	5

[a] RE_2O_3 (*RE* = La, Nd, Sm, Eu, Gd, Er, Dy, Ho, Tm, Yb, Lu, Y) (≥99.99%), Pr_6O_{11} (≥99.99%), and Tb_4O_7 (≥99.99%) were all purchased from Ruike National Engineering Research Centre of Rare Earth Metallurgy, and H_3BO_3 (≥99.8%) and H_2SO_4 (95.0-98.0%) were both from Sinopharm Chemical Reagent Co. Ltd. All reagents were used without further purification.

Table S2. Selected bond lengths (Å) and angles (°) of $RE(SO_4)[B(OH)_4](H_2O)$ (*RE* = La **1**, Sm **2**, Eu **3**) [a]

	La	Sm	Eu
RE(1)-O(3)#1	2.456(3)	2.387(4)	2.396(3)
RE(1)-O(5)	2.471(3)	2.386(4)	2.371(3)
RE(1)-O(7)#2	2.480(3)	2.409(5)	2.401(3)
RE(1)-O(4)#3	2.500(3)	2.424(4)	2.415(3)
RE(1)-O(6)	2.485(3)	2.428(4)	2.416(3)
RE(1)-O(8)#2	2.543(3)	2.470(4)	2.452(3)
RE(1)-O(1W)	2.553(3)	2.477(4)	2.454(4)
RE(1)-O(1)	2.630(3)	2.552(4)	2.541(3)
RE(1)-O(4)	2.678(3)	2.651(4)	2.645(4)
S(1)-O(2)	1.450(3)	1.459(4)	1.454(4)
S(1)-O(3)	1.457(3)	1.468(4)	1.453(3)
S(1)-O(1)	1.489(3)	1.489(4)	1.483(4)
S(1)-O(4)	1.499(3)	1.499(4)	1.492(3)
B(1)-O(5)	1.450(5)	1.463(8)	1.457(6)
B(1)-O(6)	1.462(6)	1.452(8)	1.460(6)
B(1)-O(7)	1.474(5)	1.495(8)	1.465(6)
B(1)-O(8)	1.489(5)	1.464(9)	1.468(6)
O(2)-S(1)-O(3)	112.0(2)	111.7(3)	111.9(2)
O(2)-S(1)-O(1)	111.0(2)	110.7(3)	110.7(2)
O(3)-S(1)-O(1)	108.9(2)	109.6(3)	109.1(2)
O(2)-S(1)-O(4)	110.4(2)	110.2(3)	110.4(2)
O(3)-S(1)-O(4)	110.1(2)	110.5(3)	110.3(2)
O(1)-S(1)-O(4)	104.1(2)	103.9(2)	104.0(2)
O(5)-B(1)-O(6)	101.9(3)	101.1(5)	100.6(4)
O(5)-B(1)-O(7)	114.5(4)	113.4(5)	114.8(4)
O(6)-B(1)-O(7)	113.5(3)	114.2(5)	114.5(4)
O(5)-B(1)-O(8)	113.7(3)	114.4(5)	113.7(4)
O(6)-B(1)-O(8)	113.3(4)	115.1(5)	114.4(4)
O(7)-B(1)-O(8)	100.5(3)	99.4(5)	99.6(4)

[a] Symmetry transformations used to generate equivalent atoms: #1 x, y+1, z; #2 x-1, y, z; #3 -x, -y, -z+2.

Table S3. Selected bond lengths (Å) and angles (°) of $RE(SO_4)[B(OH)_4](H_2O)_2$ (*RE* = Pr **4**, Nd **5**, Sm **6**, Eu **7**, Gd **8**) [a]

	Pr	Nd	Sm	Eu	Gd
RE(1)-O(6)#1	2.428(3)	2.416(5)	2.392(5)	2.381(3)	2.364(4)
RE(1)-O(6)#2	2.428(3)	2.416(5)	2.392(5)	2.381(3)	2.364(4)
RE(1)-O(4)	2.453(5)	2.436(7)	2.407(8)	2.396(5)	2.384(6)
RE(1)-O(1)#3	2.461(4)	2.445(7)	2.419(7)	2.412(5)	2.401(5)
RE(1)-O(5)	2.477(4)	2.475(7)	2.441(7)	2.427(4)	2.415(5)
RE(1)-O(1W)	2.511(4)	2.495(6)	2.457(5)	2.445(4)	2.425(4)
RE(1)-O(1W)#4	2.511(4)	2.495(6)	2.457(5)	2.445(4)	2.425(4)
RE(1)-O(3)#4	2.620(3)	2.607(5)	2.585(5)	2.586(4)	2.576(4)
RE(1)-O(3)	2.620(3)	2.607(5)	2.585(5)	2.586(4)	2.576(4)
S(1)-O(1)	1.457(4)	1.458(7)	1.459(7)	1.455(5)	1.453(6)
S(1)-O(2)	1.451(5)	1.459(7)	1.471(9)	1.456(5)	1.450(6)
S(1)-O(3)#4	1.485(3)	1.474(5)	1.478(6)	1.471(4)	1.478(4)
S(1)-O(3)	1.485(3)	1.474(5)	1.478(6)	1.471(4)	1.478(4)
B(1)-O(4)	1.457(8)	1.451(1)	1.456(1)	1.449(9)	1.447(9)
B(1)-O(5)	1.456(8)	1.451(1	1.437(2)	1.459(1)	1.453(9)
B(1)-O(6)	1.449(5)	1.449(8)	1.455(9)	1.445(6)	1.458(6)
B(1)-O(6)#4	1.449(5)	1.449(8)	1.455(9)	1.445(6)	1.458(6)
O(2)-S(1)-O(1)	112.2(3)	112.0(4)	111.6(5)	112.0(3)	112.7(3)
O(2)-S(1)- O(3)/O(3)#4	110.5(2)	110.5(3)	110.6(3)	110.5(2)	110.1(2)
O(1)-S(1)- O(3)/O(3)#4	109.5(2)	109.5(3)	109.9(3)	109.4(2)	109.6(2)
O(3)#4-S(1)-O(3)	104.3(3)	104.6(4)	104.0(5)	104.6(3)	104.3(3)
O(6) -B(1)-O(6)#4	99.7(5)	99.5(7)	98.4(8)	99.4(5)	98.7(5)
O(5)-B(1)-O(6)/O(6)#4	115.3(3)	114.9(5)	115.8(6)	115.0(4)	115.9(4)
O(4)-B(1)-O(6)/O(6)#4	114.0(4)	114.5(5)	114.0(6)	114.7(4)	114.3(4)
O(5)-B(1)-O(4)	99.3(5)	99.5(7)	99.8(9)	98.9(5)	98.6(5)

[a] Symmetry transformations used to generate equivalent atoms: #1 x-1, y, z; #2 x-1, -y+1/2, z; #3 x, y, z+1; #4 x, -y+1/2, z.

Table S4. Selected bond lengths (Å) and angles (°) of $RE(SO_4)[B(OH)_4](H_2O)\cdot H_2O$ (*RE* = Tb **9**, Dy **10**, Ho **11**, Er **12**, Tm **13**, Yb **14**, Lu **15**, Y **16**) [a]

	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
RE(1)-O(1)	2.279(5)	2.269(5)	2.264(5)	2.254(4)	2.239(6)	2.227(4)	2.219(4)	2.258(2)
RE(1)-O(2)#1	2.336(5)	2.321(4)	2.304(4)	2.302(4)	2.283(5)	2.282(3)	2.270(3)	2.301(2)
RE(1)-O(6)#2	2.350(4)	2.335(4)	2.331(4)	2.319(4)	2.311(5)	2.302(3)	2.290(3)	2.331(2)
RE(1)-O(4)#3	2.352(5)	2.353(4)	2.338(4)	2.335(4)	2.330(5)	2.315(3)	2.304(3)	2.338(2)
RE(1)-O(7)	2.364(4)	2.354(3)	2.351(3)	2.338(4)	2.331(5)	2.320(3)	2.310(3)	2.345(2)
RE(1)-O(5)	2.374(4)	2.372(3)	2.358(4)	2.347(4)	2.336(5)	2.331(3)	2.324(3)	2.357(2)
RE(1)-O(8)#2	2.398(4)	2.390(4)	2.382(4)	2.377(4)	2.357(5)	2.355(3)	2.345(3)	2.384(2)
RE(1)-O(1W)	2.475(4)	2.441(4)	2.444(4)	2.424(4)	2.412(5)	2.415(3)	2.382(4)	2.431(2)
S(1)-O(1)	1.460(5)	1.456(5)	1.452(5)	1.451(4)	1.455(6)	1.458(4)	1.453(4)	1.456(2)
S(1)-O(2)	1.462(5)	1.464(4)	1.468(5)	1.463(4)	1.469(5)	1.462(3)	1.467(3)	1.468(2)
S(1)-O(3)	1.466(4)	1.472(4)	1.470(4)	1.464(4)	1.470(5)	1.468(3)	1.469(3)	1.466(2)
S(1)-O(4)	1.479(5)	1.470(4)	1.477(4)	1.475(4)	1.461(5)	1.476(3)	1.475(3)	1.478(2)
B(1)-O(5)	1.464(8)	1.464(7)	1.457(7)	1.459(7)	1.468(9)	1.459(6)	1.453(5)	1.463(4)
B(1)-O(6)	1.449(8)	1.455(8)	1.460(7)	1.455(7)	1.459(9)	1.449(6)	1.456(6)	1.446(4)
B(1)-O(7)	1.461(8)	1.462(7)	1.467(7)	1.458(7)	1.453(9)	1.459(6)	1.460(5)	1.463(4)
B(1)-O(8)	1.502(8)	1.486(7)	1.489(7)	1.497(7)	1.491(9)	1.488(6)	1.490(6)	1.495(4)
O(1)-S(1)-O(2)	109.9(3)	109.8(3)	109.6(3)	110.3(3)	109.9(4)	110.4(2)	110.4(2)	109.8(1)
O(1)-S(1)-O(3)	110.1(3)	110.9(3)	110.5(3)	110.7(2)	110.2(3)	110.7(2)	110.2(2)	110.5(1)
O(2)-S(1)-O(3)	110.3(3)	110.3(2)	110.3(2)	110.0(2)	110.5(3)	109.8(2)	110.0(2)	110.2(1)
O(1)-S(1)-O(4)	109.1(3)	109.3(3)	109.3(3)	109.3(3)	109.2(3)	109.3(2)	109.5(2)	109.3(1)
O(2)-S(1)-O(4)	107.0(3)	106.9(2)	107.0(2)	106.4(2)	107.0(3)	106.7(2)	106.7(2)	107.0(1)
O(3)-S(1)-O(4)	110.4(3)	109.6(2)	110.1(2)	109.9(2)	110.0(3)	109.9 (2)	110.0(2)	110.1(1)
O(6)-B(1)-O(7)	115.6(6)	115.2(5)	114.7(5)	115.3(5)	115.5(6)	115.2(4)	115.0(4)	115.4(3)
O(6)-B(1)-O(5)	115.5(6)	114.8(5)	115.1(5)	114.7(5)	114.7(6)	115.4(4)	115.5(4)	115.0(2)
O(7)-B(1)-O(5)	100.8(4)	101.2(4)	101.3(4)	101.1(4)	101.1(5)	100.4(3)	100.5(3)	100.6(2)
O(6)-B(1)-O(8)	101.5(4)	101.6(4)	101.6(4)	101.4(4)	101.2(5)	101.7(3)	101.1(3)	102.1(2)
O(7)-B(1)-O(8)	112.7(5)	113.3(5)	112.4(5)	113.2(5)	113.4(6)	113.1(4)	113.3(4)	112.7(2)
O(5)-B(1)-O(8)	111.2(5)	111.3(5)	112.2(5)	111.7(5)	111.6(6)	111.6(4)	112.0(4)	111.5(2)

[a] Symmetry transformations used to generate equivalent atoms: #1 -x, -y, -z+1; #2 x-1, y, z; #3 -x, -y+1, -z+1.

Table S5. Hydrogen bonds in compounds **3**, **7** and **15**.

D-H···A	*d*(D-H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠(DHA) (°)
$Eu(SO_4)[B(OH)_4](H_2O)$ (**3**)				
O(5)-H(5)···O(2)#1	0.85	2.00	2.851(5)	175.6
O(8)-H(8)···O(2)#2	0.85	1.95	2.752(5)	156.2
O(1W)-H(1WB)···O(8)#3	0.85	2.07	2.905(5)	168.7
$Eu(SO_4)[B(OH)_4](H_2O)_2$ (**7**)				
O(4)-H(4)···O(2)#1	0.85	1.93	2.690(8)	148.5
O(5)-H(5)···O(2)#2	0.85	2.10	2.871(7)	151.4
O(6)-H(6)···O(3)#3	0.85	2.03	2.829(5)	155.6
O(1W)-H(1WB)···O(3)#3	0.85	2.02	2.856(5)	166.6
$Lu(SO_4)[B(OH)_4](H_2O)\cdot H_2O$ (**15**)				
O(6)-H(6)···O(3)	0.85	1.99	2.817(5)	162.3
O(8)-H(8)···O(2W)	0.85	1.87	2.688(5)	162.0
O(1W)-H(1WA)···O(2W)	0.85	2.08	2.906(5)	164.2
O(5)-H(5)···O(3)#1	0.85	2.03	2.830(4)	157.1
O(7)-H(7)···O(3)#2	0.85	1.95	2.767(4)	161.2
O(1W)-H(1WB)···O(8)#3	0.85	1.98	2.815(5)	167.6
O(2W)-H(2WA)···O(4)#4	0.85	2.01	2.811(5)	156.3

Symmetry transformations used to generate equivalent atoms:

For $Eu(SO_4)[B(OH)_4](H_2O)$: #1 -x+1, -y, -z+2; #2 x, y+1, z; #3 -x+1, -y+1, -z+1;

For $Eu(SO_4)[B(OH)_4](H_2O)_2$: #1 x+1, y, z+1; #2 x+1, y, z; #3 -x+1, y-1/2, -z+1;

For $Lu(SO_4)[B(OH)_4](H_2O)\cdot H_2O$: #1 -x+1, -y+1, -z+1; #2 -x+1, -y, -z+1; #3 -x+1, -y+1, -z; #4 x+1, y, z-1.

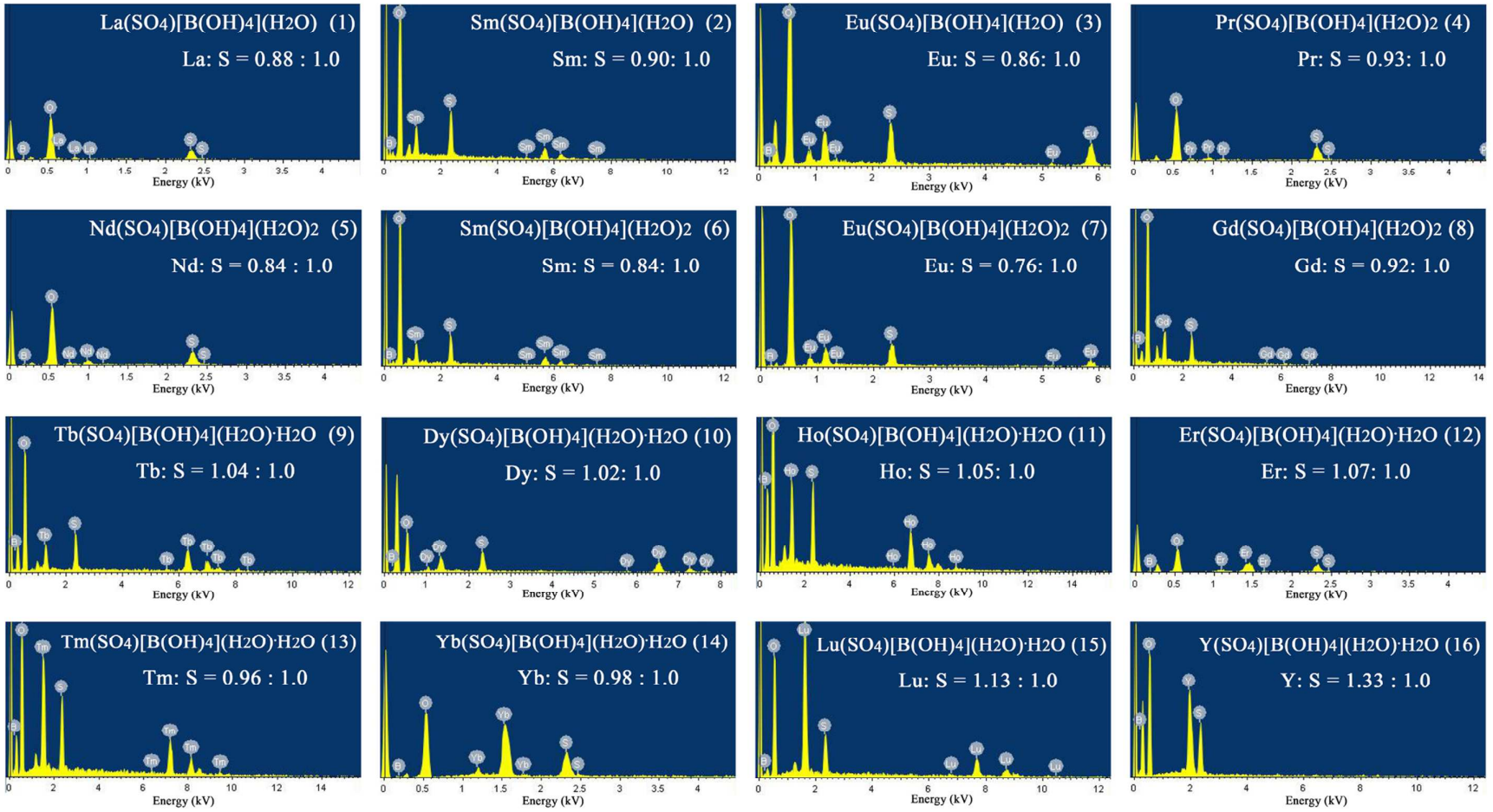


Figure S1. EDS results of compounds **1-16**.

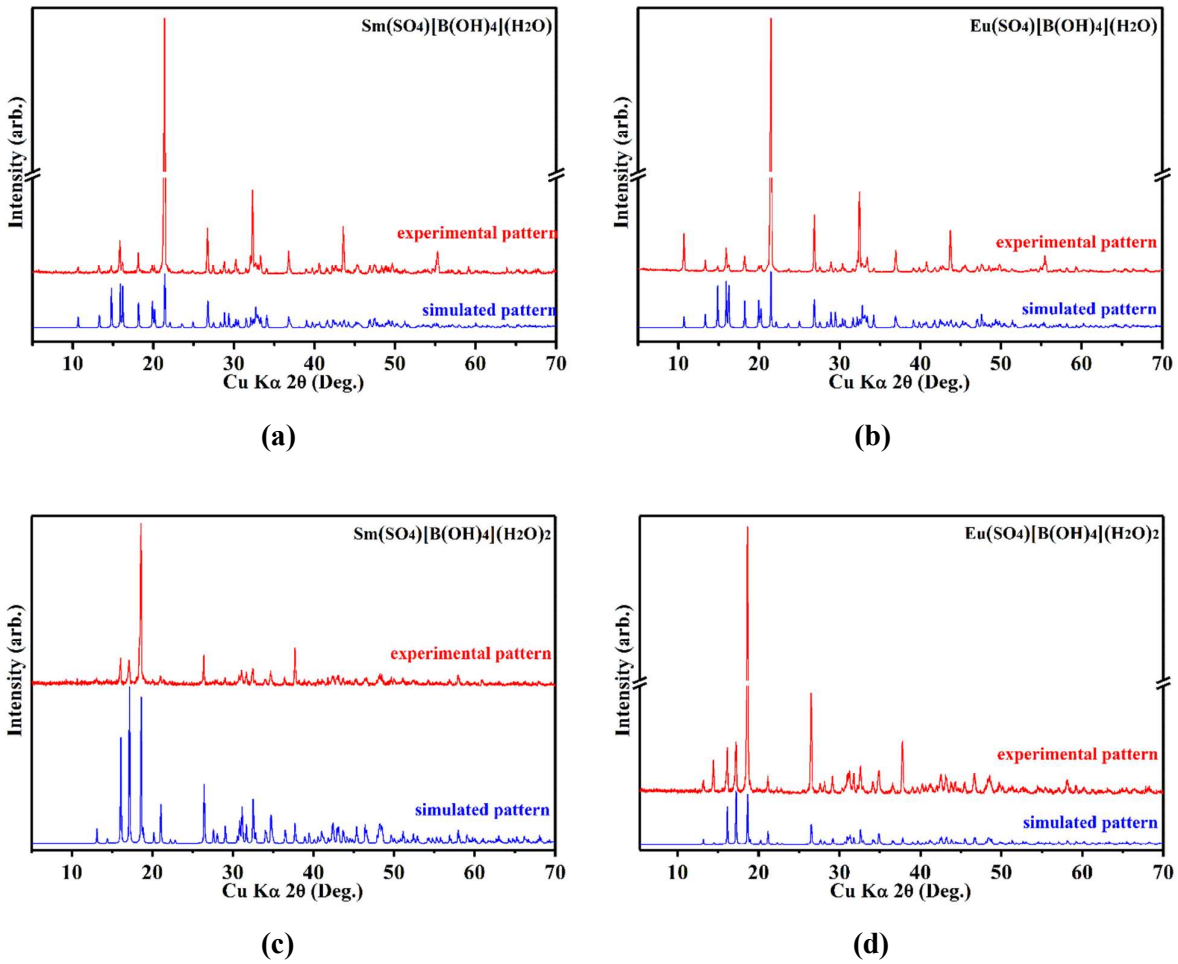


Figure S2. Experimental and simulated powder X-ray diffraction patterns of compounds **2** (a), **3** (b), **6** (c), and **7** (d).

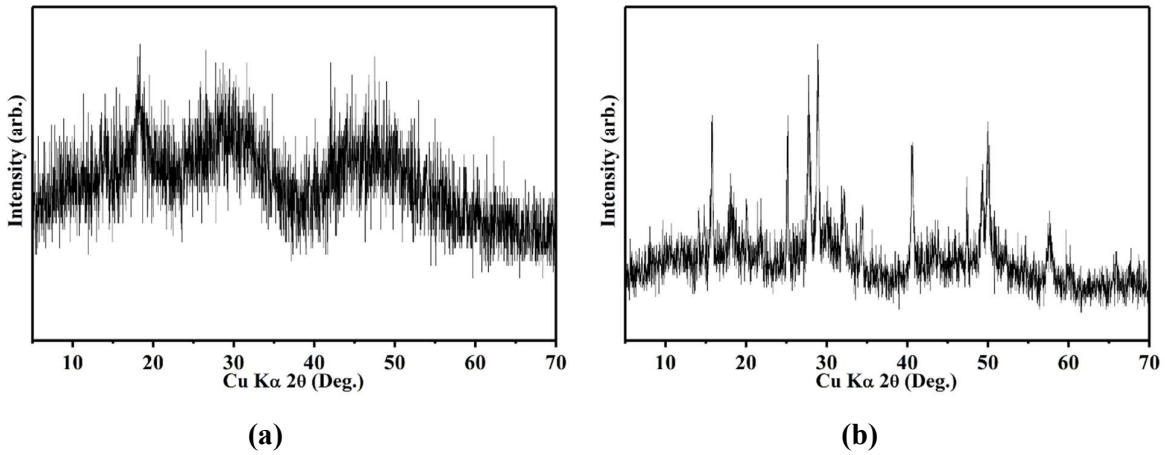
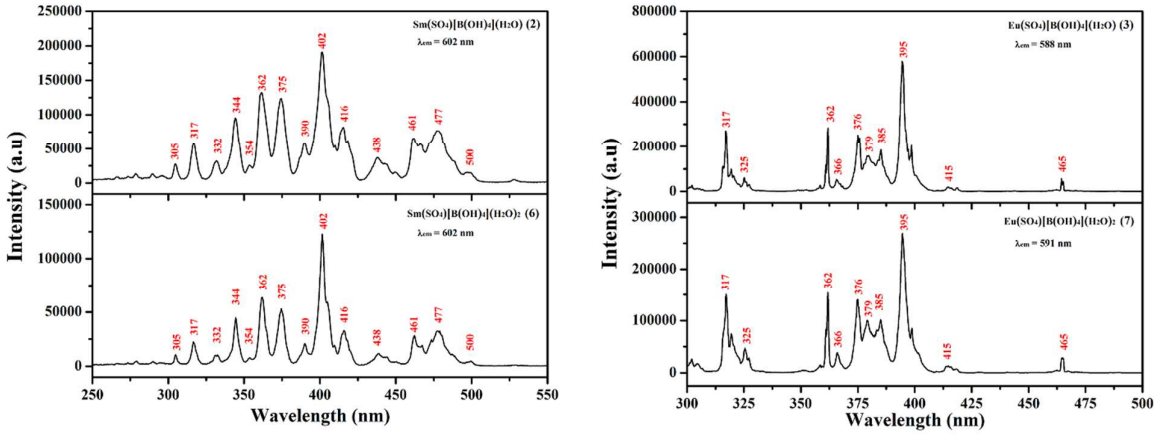
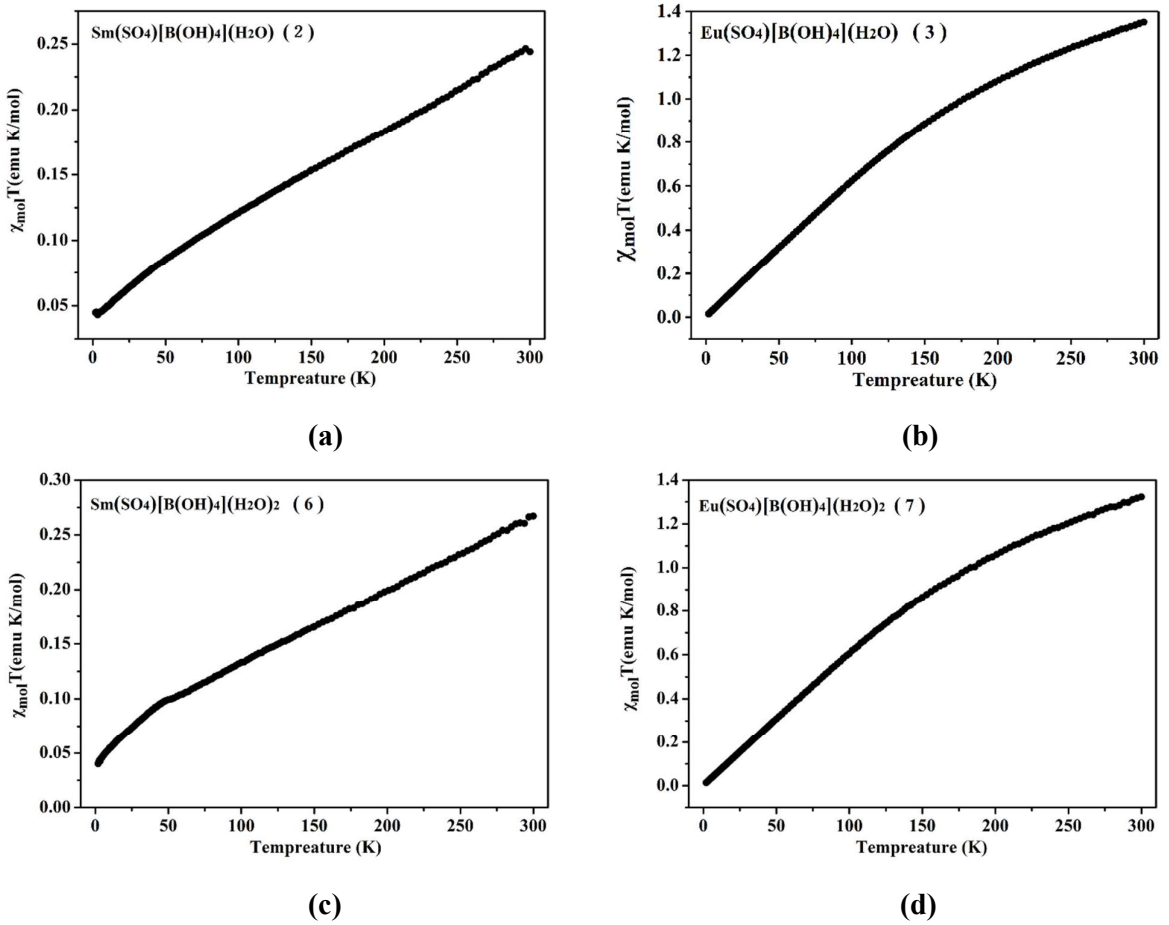


Figure S3. Powder X-ray diffraction patterns of the residuals of compounds **3** (a), and **6** (b) after heated at 300 °C.



(a) **(b)**

Figure S4. Solid state excitation spectra of compounds **2** and **6** (a), and compounds **3** and **7** (b).



(a) **(b)**

(c) **(d)**

Figure S5. Plots of $\chi_{mol}T$ vs. T for compounds **2** (a), **3** (b), **6** (c), and **7** (d).