Supplementary materials

Layered Gadolinium-Europium-Terbium Hydroxides Sensitised with 4-Sulfobenzoate as All Solid-State Luminescent Thermometers

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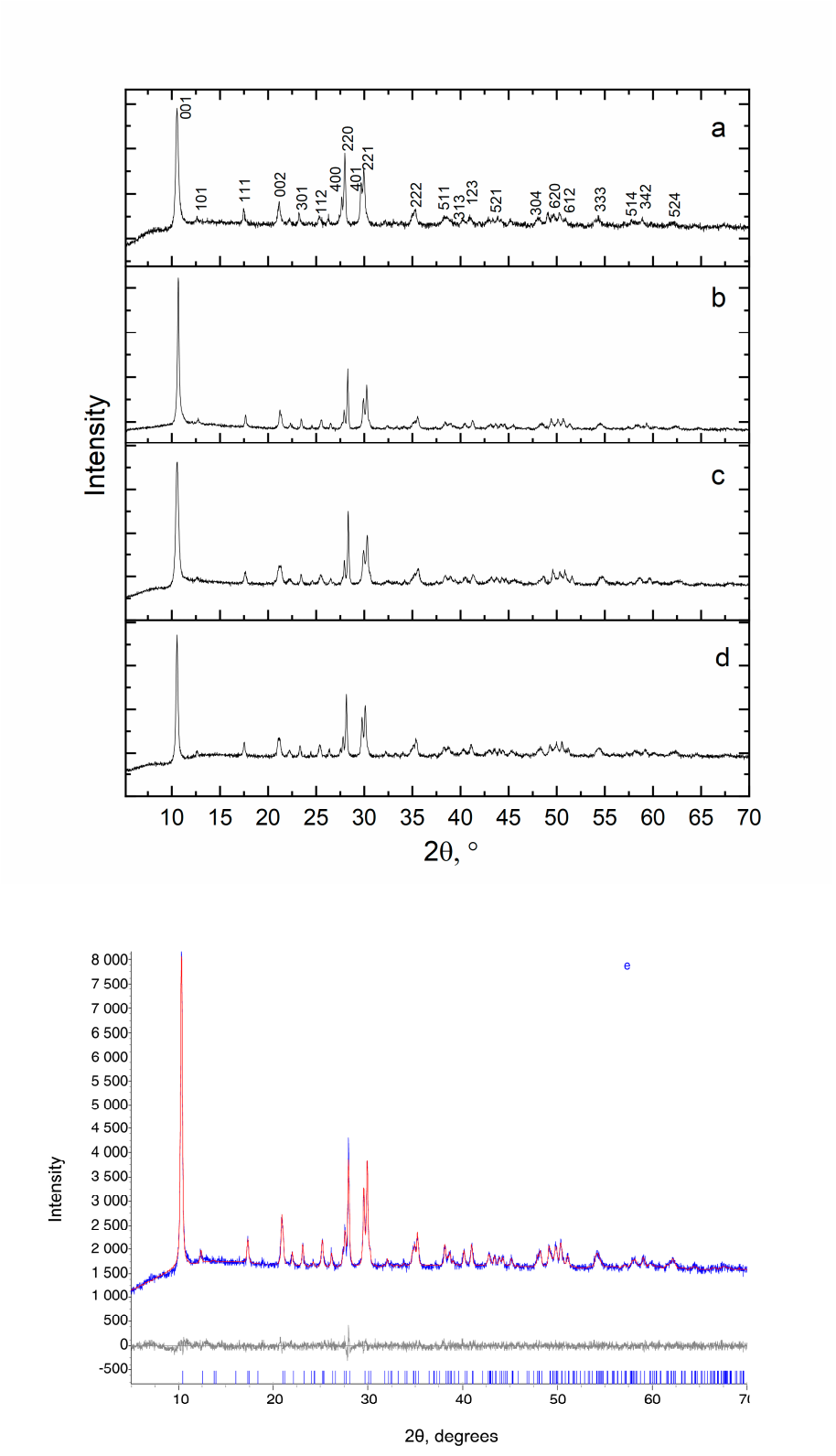


Figure S1. X-ray powder diffraction patterns of the hydrothermal-microwave treatment products of a solutions mixture containing HMT, potassium chloride and (a) europium chloride, (b) gadolinium chloride, (c) terbium chloride and (d) mixtures of solutions of europium, gadolinium and terbium chlorides in a ratio of 1:1:1, respectively. (e) Difference curve, experimental and refined X-ray profiles of the layered basic chloride with the composition $Gd_{0.76}Eu_{0.6}Tb_{0.64}(OH)_5Cl\cdot nH_2O$.

Table S1. Composition of LRHs and refined *a*, *b*, *c* parameters of their crystal lattice.

$Gd_{2-x-y}Eu_xTb_y$	Ln/Cl molar ratio	*a*, Å	*b*, Å	*c*, Å	*V*, Å^3	<*R*>, pm	R_p
Gd_2	2	12.85(2)	7.292(9)	8.43(2)	790(3)	105	2.05
Eu_2	2.298	12,94(2)	7,357(8)	8,44(2)	803(2)	107	2,16
Tb_2	1.818	12.80(1)	7.256(6)	8.42(1)	782(2)	104	2.47
$Gd_{0.12}Eu_{1.52}Tb_{0.36}$	1.851	12.91(1)	7.335(6)	8.44(1)	799(2)	106.32	2.12
$Gd_{0.36}Eu_{1.3}Tb_{0.34}$	2.127	12.899(9)	7.329(5)	8.46(1)	799(1)	106.10	2.14
$Gd_{0.12}Eu_{0.98}Tb_{0.9}$	2.127	12.88(1)	7.321(6)	8.44(2)	796(2)	105.44	2.12
$Gd_{0.34}Eu_{0.9}Tb_{0.76}$	2.173	12.87(1)	7.313(5)	8.45(1)	796(1)	105.52	2.15
$Gd_{0.78}Eu_{0.9}Tb_{0.32}$	2.040	12.89(1)	7.319(5)	8.45(1)	797(2)	105.73	2.08
$Gd_{1.08}Eu_{0.6}Tb_{0.32}$	2.083	12.88(1)	7.319(6)	8.45(1)	797(2)	105.45	2.19
$Gd_{1.46}Eu_{0.25}Tb_{0.29}$	2	12.88(1)	7.314(6)	8.45(2)	796(2)	105.11	2.15
$Gd_{0.75}Eu_{0.31}Tb_{0.94}$	1.923	12.85(1)	7.291(6)	8.44(1)	791(2)	104.86	2.26
$Gd_{1.18}Eu_{0.82}$	1.960	12.886(9)	7.319(5)	8.45(1)	797(1)	105.82	1.97
$Eu_{0.88}Tb_{1.12}$	1.923	12.83(1)	7.300(6)	8.49(1)	796(1)	105.33	2.17
$Gd_{0.1}Eu_{0.28}Tb_{1.62}$	2	12.81(1)	7.270(6)	8.42(1)	785(1)	104.46	2.32
$Gd_{0.32}Eu_{0.04}Tb_{1.64}$	1.886	12.827(9)	7.275(5)	8.42(1)	786(1)	104.22	2.29
$Gd_{0.32}Eu_{0.27}Tb_{1.41}$	2.173	12.83(2)	7.282(7)	8.42(2)	787(2)	104.56	2.31
$Gd_{0.99}Tb_{1.01}$	2	12.84(1)	7.283(6)	8.44(1)	789(2)	104.49	2.32
$GdEu_{0.3}Tb_{0.97}$	2.040	12.843(9)	7.285(5)	8.43(1)	789(1)	104.55	2.04
$Gd_{1.01}Eu_{0.89}Tb_{0.1}$	2.083	12.885(9)	7.318(5)	8.45(1)	797(1)	105.82	2.01
$Gd_{1.14}Eu_{0.4}Tb_{0.46}$	1.851	12.88(1)	7.311(6)	8.44(1)	795(2)	105.17	2.03
$Gd_{1.1}Eu_{0.24}Tb_{0.66}$	2	12.86(1)	7.299(6)	8.44(2)	792(2)	104.92	2.12
$Gd_{0.36}Eu_{1.5}Tb_{0.14}$	1.960	12.93(1)	7.339(6)	8.45(1)	801(2)	106.42	2.17
$Gd_{0.7}Eu_{1.3}$	2	12.91(1)	7.330(5)	8.44(1)	799(1)	106.40	2.04
$Gd_{1.5}Eu_{0.51}$	2.040	12.89(1)	7.318(5)	8.44(1)	796(2)	105.60	2.01
$Gd_{0.76}Eu_{0.6}Tb_{0.64}$	2	12.865(8)	7.299(4)	8.44(1)	792(1)	105.33	2.12
$Tb_{1.2}Eu_{0.8}$	2	12.85(1)	7.297(7)	8.42(2)	790(2)	105.2	2.11
$Tb_{0.1}Eu_{1.9}$	2	12.93(1)	7.341(6)	8.44(1)	801(2)	106.85	2.35
$Tb_{1.9}Eu_{0.1}$	2	12.81(1)	7.265(6)	8.44(1)	785(2)	104.15	2.02
$Tb_{0.3}Eu_{1.7}$	2	12.913(8)	7.333(4)	8.443(9)	800(1)	106.55	1.89
$Tb_{1.7}Eu_{0.3}$	2	12.822(9)	7.272(4)	8.42(1)	785(1)	104.45	2.08

Table S2. Composition of LRHs before and after anion exchange

$Gd_{2-x-y}Eu_xTb_y$	Cl/Ln molar ratio	$Gd_{2-x-y}Eu_xTb_y$ before anion exchange	S/Ln molar ratio	Cl/Ln molar ratio after anion exchange
Eu_2	0.44	Eu_2	0.18	0
$Gd_{0.12}Eu_{1.52}Tb_{0.36}$	0.54	$Gd_{0.13}Eu_{1.5}Tb_{0.37}$	0.21	0
$Gd_{0.36}Eu_{1.3}Tb_{0.34}$	0.47	$Gd_{0.38}Eu_{1.25}Tb_{0.27}$	0.28	0.0042
$Gd_{0.36}Eu_{1.5}Tb_{0.14}$	0.51	$Gd_{0.4}Eu_{1.5}Tb_{0.1}$	0.22	0.0027
$Gd_{0.7}Eu_{1.3}$	0.5	$Gd_{0.72}Eu_{1.28}(OH)_5$	0.23	0.0042
$Gd_{0.76}Eu_{0.6}Tb_{0.64}$	0.5	$Gd_{0.76}Eu_{0.61}Tb_{0.63}$	0.19	0.0049
$Gd_{0.75}Eu_{0.31}Tb_{0.94}$	0.52	$Gd_{0.75}Eu_{0.32}Tb_{0.93}$	0.21	0
$Gd_{0.78}Eu_{0.9}Tb_{0.32}$	0.49	$Gd_{0.8}Eu_{0.87}Tb_{0.33}$	0.21	0
$GdEu_{0.3}Tb_{0.97}$	0.49	$Gd_{0.99}Eu_{0.04}Tb_{0.97}$	0.23	0
$Gd_{1.01}Eu_{0.89}Tb_{0.1}$	0.48	$Gd_{1.01}Eu_{0.87}Tb_{0.12}$	0.24	0.0147
$Gd_{1.1}Eu_{0.24}Tb_{0.66}$	0.5	$Gd_{1.1}Eu_{0.24}Tb_{0.66}$	0.21	0
$Gd_{1.08}Eu_{0.6}Tb_{0.32}$	0.48	$Gd_{1.08}Eu_{0.6}Tb_{0.32}$	0.22	0.0009
$Gd_{1.13}Eu_{0.66}Tb_{0.21}$	0.48	$Gd_{1.13}Eu_{0.66}Tb_{0.21}$	0.23	0
$Gd_{1.18}Eu_{0.82}$	0.51	$Gd_{1.19}Eu_{0.81}$	0.31	0.0024
Gd_2	0.5	Gd_2	0.25	0.0108
Tb_2	0.47	Tb_2	0.26	0.0089

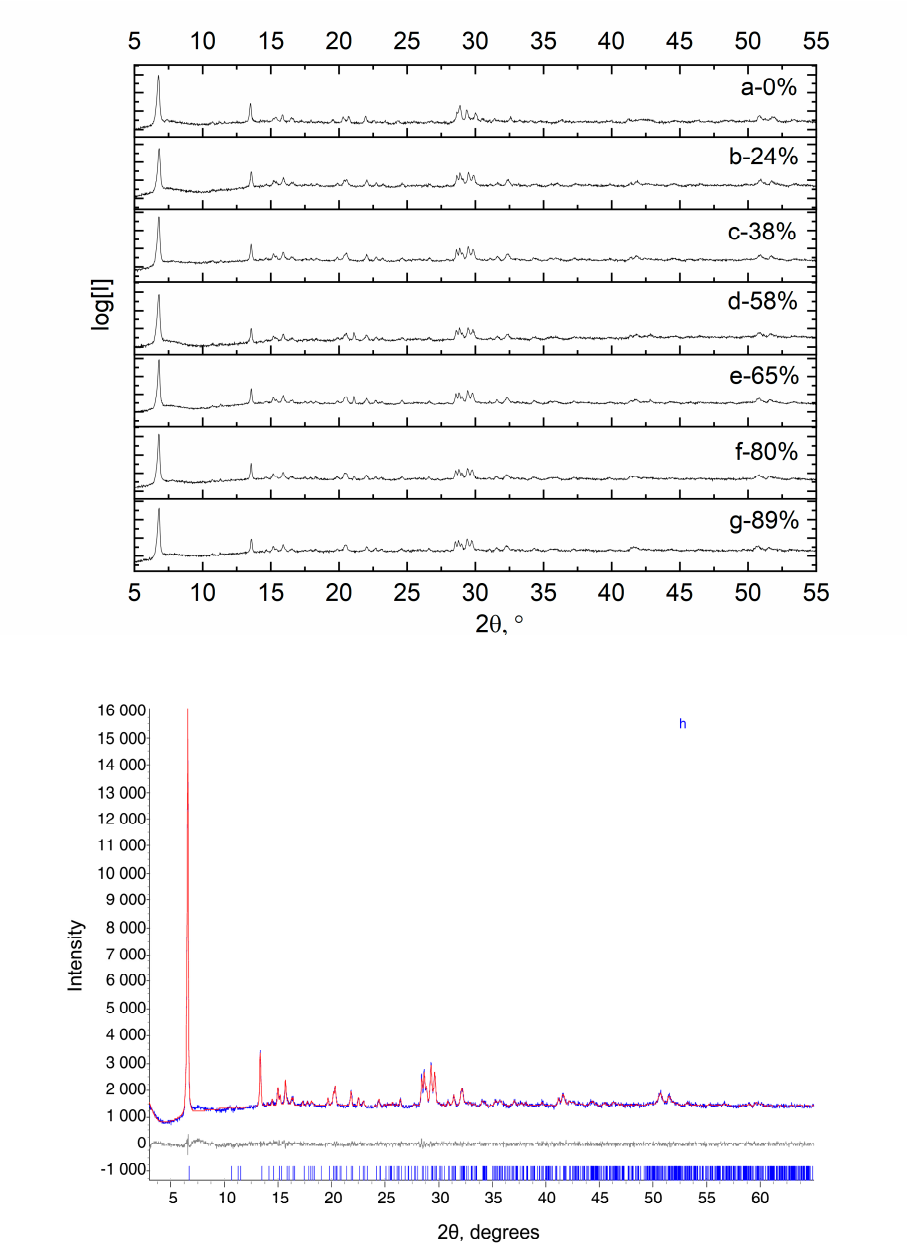


Figure S2. X-ray powder diffraction patterns of $(Gd_{1-x}Tb_{0.9x}Eu_{0.1x})_3(OH)_7(C_7H_4O_5S)\cdot nH_2O$ (a) x = 1, (b) x = 0.76, (c) x = 0.62, (d) x = 0.42, (e) x = 0.35, (f) x = 0.2, (g) x = 0.11 obtained by homogeneous precipitation in the presence of 4-sulfobenzoate anion and a mixture of gadolinium, europium and terbium chlorides in 0.0:0.1:0.9, 0.150:0.765:0.085, 0.50:0.45:0.05, 0.560:0.396:0.044, 0.630:0.333:0.037, 0.770:0.207:0.023 and 0.90:0.09:0.01 ratios. (h) The difference curve, experimental and refined X-ray diffraction profiles of layered Gd-Eu-Tb basic sulfobenzoates with the composition $(Gd_{1-x}Tb_{0.9x}Eu_{0.1x})_3(OH)_7(C_7H_4O_5S)\cdot nH_2O$, x = 0.76.

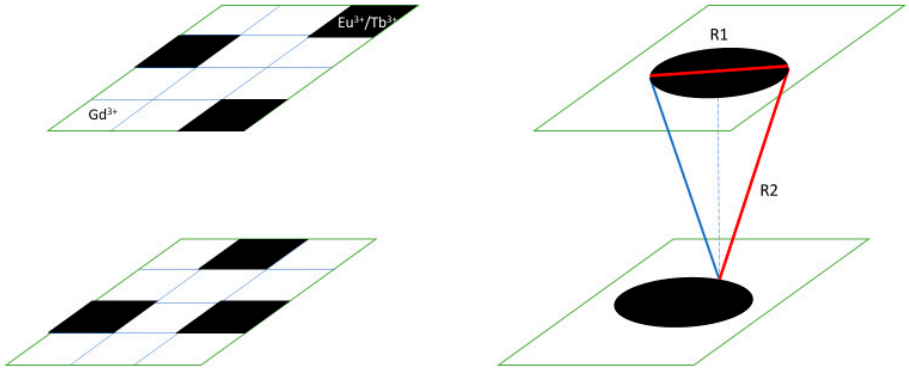
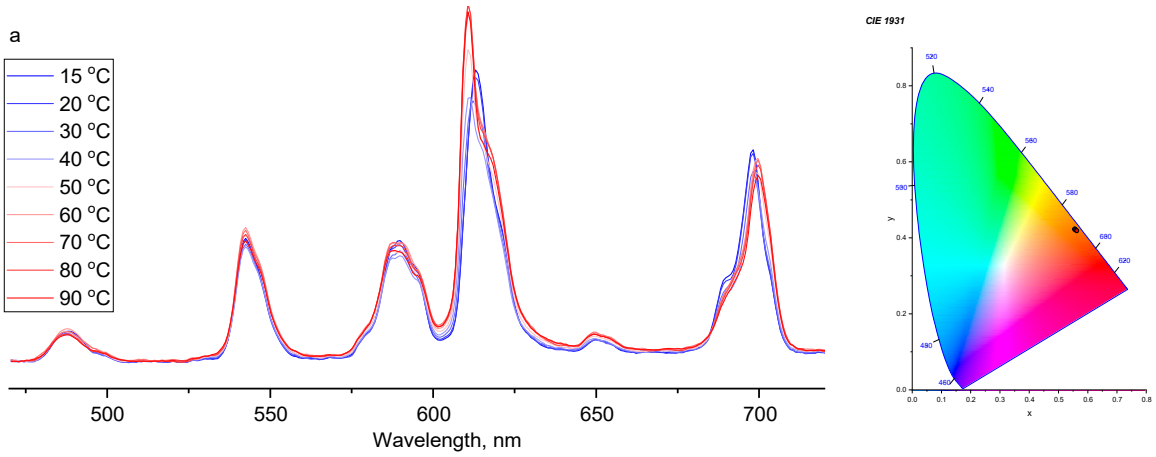


Figure S3. The geometric scheme used to calculate the average distances between the Eu^{3+} and Tb^{3+} cations in the $(Gd_{1-x}Tb_{0.9x}Eu_{0.1x})_3(OH)_7(C_7H_4O_5S)\cdot nH_2O$. Black sectors indicate the area in the layer plane corresponding to Eu^{3+} and Tb^{3+} cations, and white areas correspond to Gd^{3+} cations.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30 °C
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80 °C
90 °C
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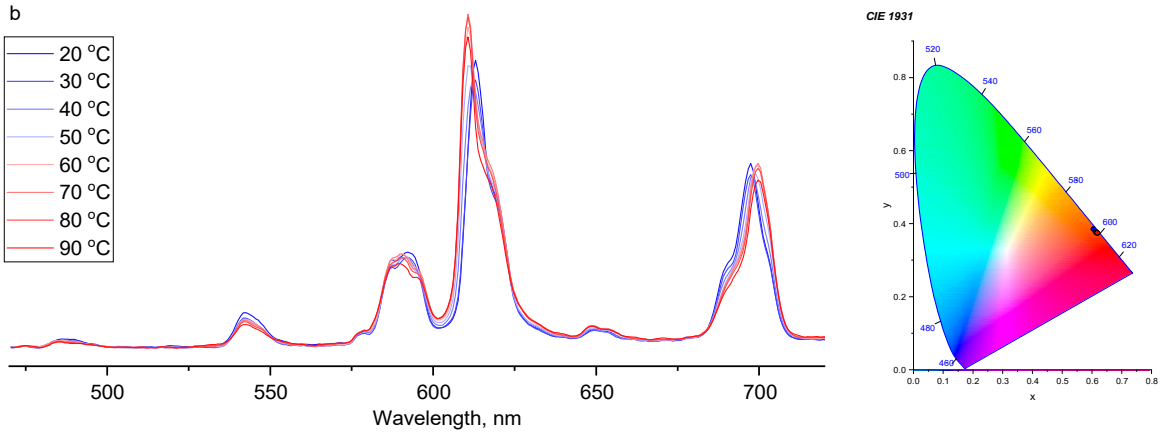
Wavelength, nm
CIE 1931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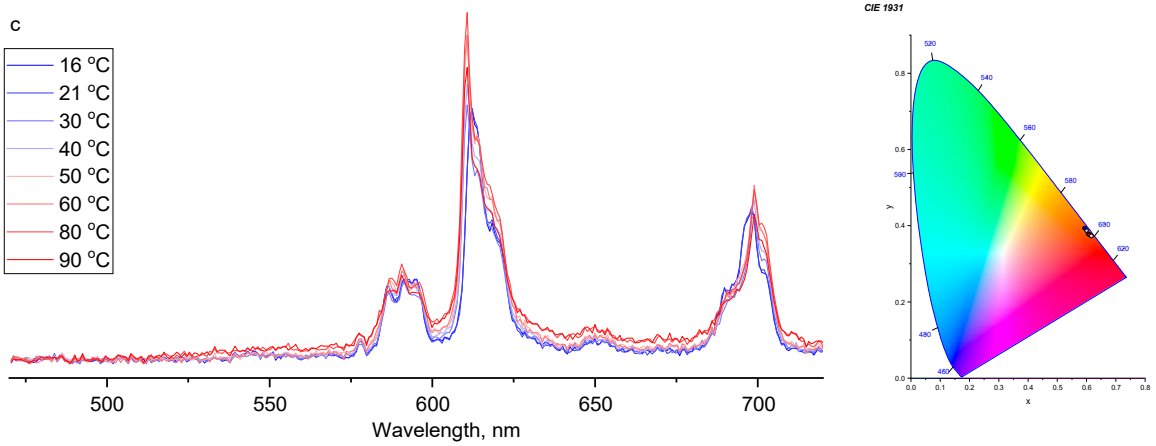
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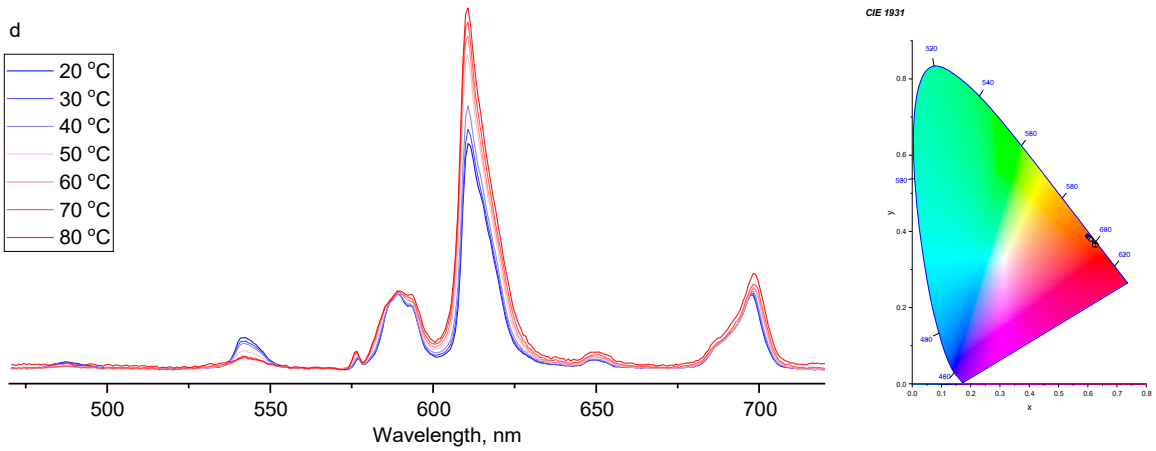
CIE 1931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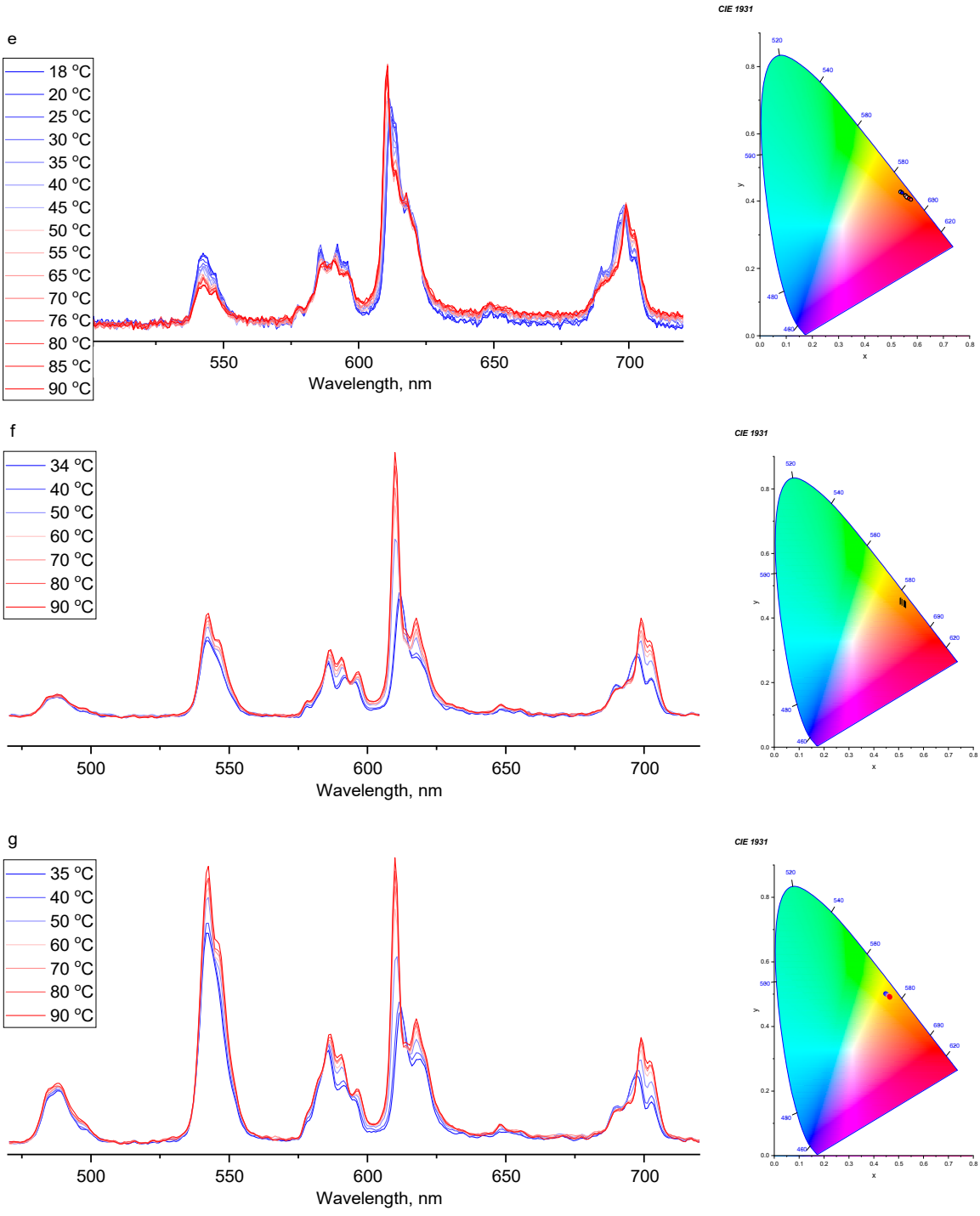
Wavelength, nm
CIE 1931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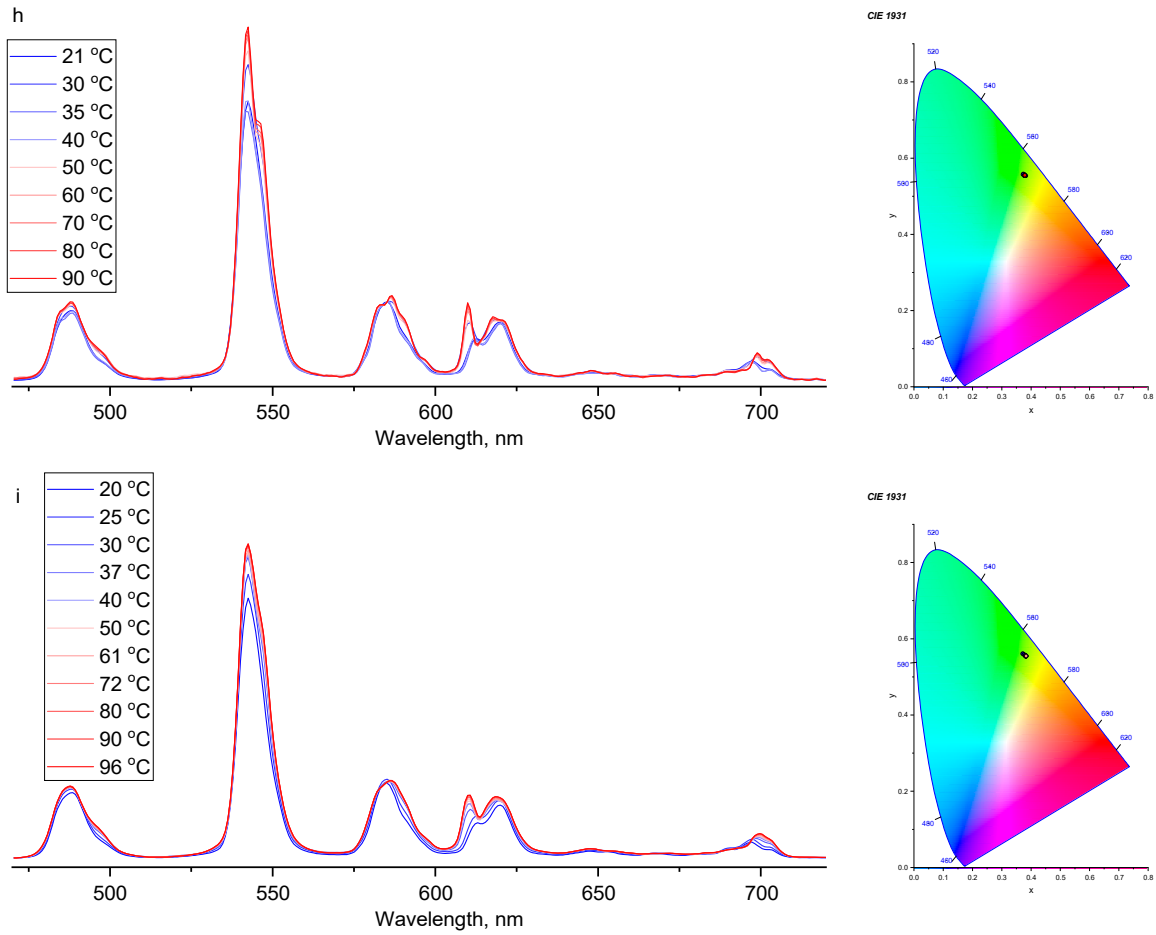

Figure S4. Luminescence spectra at 15–96°C (left) and corresponding luminescence colour coordinates (right) for the samples:
(a) $(Gd_{0.5}Tb_{0.48}Eu_{0.02})_3(OH)_7(C_7H_4O_5S)\cdot nH_2O$,
(b) $(Gd_{0.55}Tb_{0.33}Eu_{0.12})_3(OH)_7(C_7H_4O_5S)\cdot nH_2O$,
(c) $(Gd_{0.54}Tb_{0.16}Eu_{0.30})_3(OH)_7(C_7H_4O_5S)\cdot nH_2O$,
(d) $(Gd_{0.73}Tb_{0.14}Eu_{0.13})_3(OH)_7(C_7H_4O_5S)\cdot nH_2O$,
(e) $(Gd_{0.80}Tb_{0.05}Eu_{0.15})_3(OH)_7(C_7H_4O_5S)\cdot nH_2O$,
(f) $(Gd_{0.58}Tb_{0.39}Eu_{0.03})_3(OH)_7(C_7H_4O_5S)\cdot nH_2O$,
(g) $(Gd_{0.65}Tb_{0.33}Eu_{0.02})_3(OH)_7(C_7H_4O_5S)\cdot nH_2O$,
(h) $(Gd_{0.80}Tb_{0.20}Eu_{0.01})_3(OH)_7(C_7H_4O_5S)\cdot nH_2O$,
(i) $(Gd_{0.89}Tb_{0.09}Eu_{0.01})_3(OH)_7(C_7H_4O_5S)\cdot nH_2O$.

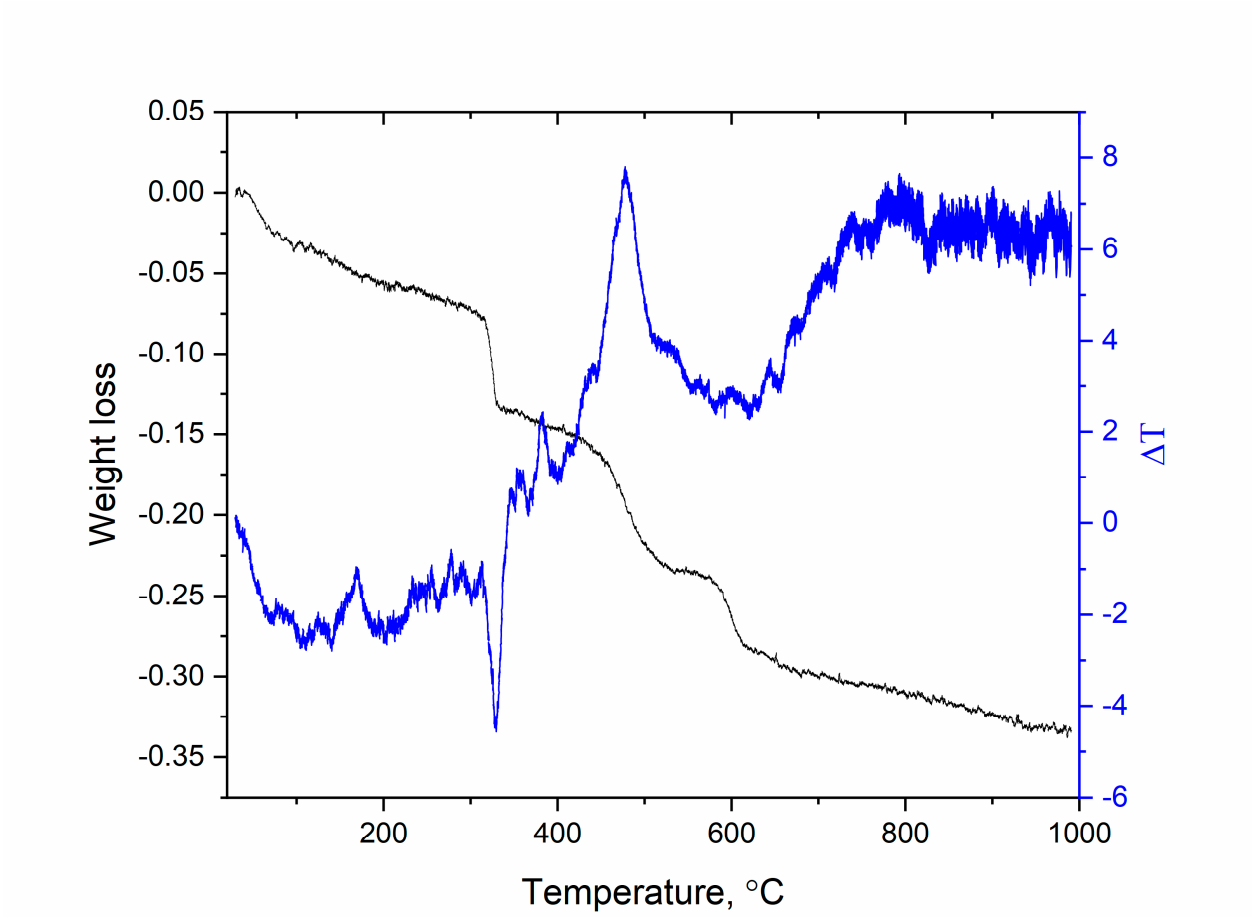

Figure S5. Thermal analysis data for $(Gd_{0.65}Tb_{0.33}Eu_{0.02})_3(OH)_7(C_7H_4O_5S)\cdot nH_2O$ sample obtained using the single-stage synthesis.

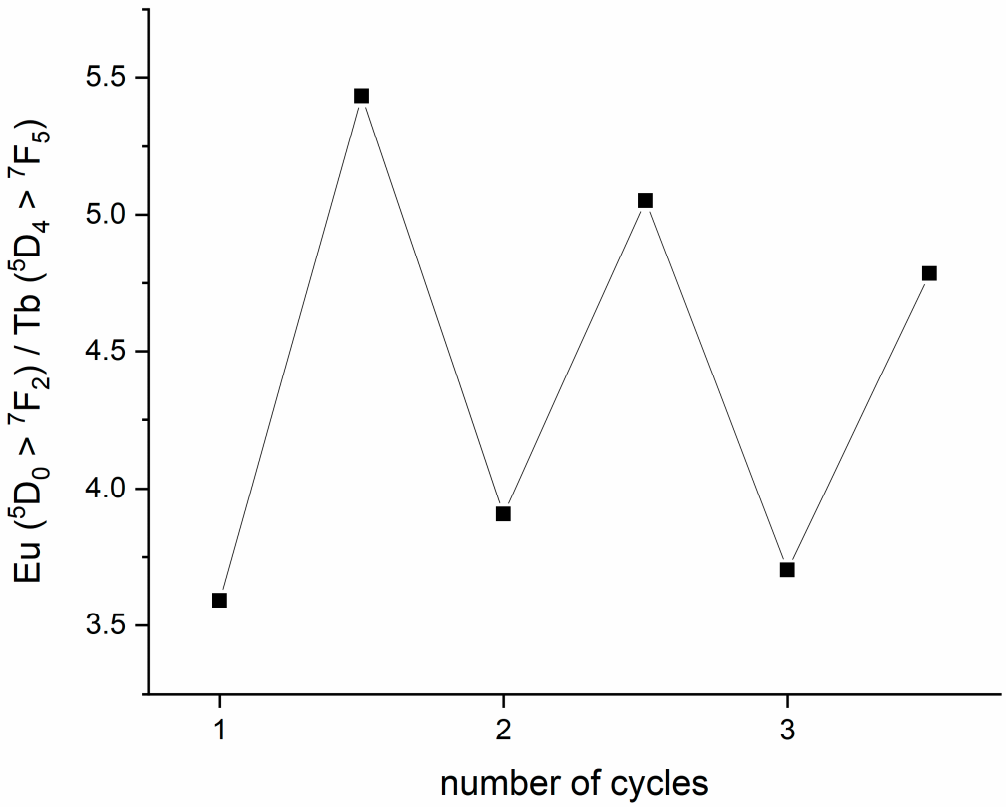

Figure S6. Changes in the intensity ratio Eu($^5D_0 \rightarrow {}^7F_2$)/Tb($^5D_4 \rightarrow {}^7F_5$) of europium and therbium luminescence bands for the $(Gd_{0.80}Tb_{0.05}Eu_{0.15})_3(OH)_7(C_7H_4O_5S)\cdot nH_2O$ sample during three heating-cooling cycles (25–90°C).