Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

$Tb(HSO_4)(SO_4)$ – A Green Emitting Hydrogensulfate Sulfate with Second Harmonic Generation Response

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Table S1: Wyckoff symbol, atomic coordinates *x; y; z* and equivalent isotropic displacement parameters U_{eq} for $Tb(HSO_4)(SO_4)$ (corresponding standard deviations given in parentheses)

Atom	Wyckoff symbol	*x*	*y*	*z*	U_{eq}
Tb01	2*a*	0.35019(4)	0.74999(7)	0.63157(4)	0.00544(8)
S1	2*a*	0.7801(2)	0.70420(19)	0.4304(2)	0.0062(3)
S2	2*a*	0.2397(2)	0.5805(2)	0.1047(2)	0.0067(3)
O11	2*a*	0.9877(6)	0.7299(13)	0.5621(7)	0.0106(11)
O12	2*a*	0.6845(8)	0.9008(7)	0.3641(8)	0.0140(11)
O13	2*a*	0.7803(7)	0.5722(7)	0.2560(7)	0.0094(9)
O14	2*a*	0.6455(7)	0.5907(7)	0.5396(7)	0.0092(9)
O21	2*a*	0.2410(7)	0.7037(6)	0.2819(7)	0.0116(11)
O22	2*a*	0.3179(8)	0.6908(7)	-0.0441(7)	0.0134(11)
O23	2*a*	0.3500(8)	0.3905(7)	0.1617(7)	0.0132(10)
O24	2*a*	0.0144(13)	0.5299(9)	-0.0008(14)	0.0107(13)
H1	2*a*	-0.055(11)	0.542(12)	0.102(11)	0.016

Table S2: Anisotropic displacement parameters U_{ij} in Å^2 for $Tb(HSO_4)(SO_4)$ (corresponding standard deviations given in parentheses)

Atom	U11	U22	U33	U23	U13	U12
Tb01	0.00601(12)	0.00483(12)	0.00575(12)	-0.0006(2)	0.00201(8)	-0.0005(2)
S1	0.0056(7)	0.0048(9)	0.0090(7)	-0.0003(5)	0.0031(6)	-0.0002(5)
S2	0.0064(7)	0.0079(7)	0.0059(7)	0.0005(6)	0.0018(6)	0.0000(6)
O11	0.0053(18)	0.011(3)	0.015(2)	0.000(3)	0.0002(15)	-0.003(2)
O12	0.014(3)	0.005(2)	0.023(3)	0.000(2)	0.004(2)	0.0038(18)
O13	0.010(2)	0.009(2)	0.010(2)	-0.0013(18)	0.0035(19)	-0.0019(17)
O14	0.009(2)	0.009(2)	0.012(2)	-0.0007(18)	0.0062(19)	0.0012(17)
O21	0.016(2)	0.011(3)	0.007(2)	-0.0035(16)	0.0012(18)	0.0012(17)
O22	0.016(3)	0.018(3)	0.007(2)	0.0041(17)	0.0054(19)	-0.0031(17)
O23	0.014(3)	0.012(2)	0.013(3)	0.0011(19)	0.003(2)	0.0048(19)
O24	0.007(3)	0.015(4)	0.011(2)	0.002(3)	0.0034(19)	0.000(3)

Table S3: ECon derived by MAPLE-calculations for Tb atoms in $Tb(HSO_4)(SO_4)$

Atom	*x*	*y*	*z*	Distance / pm	EcoN (1)	Econ(3)
Central atom						
Tb1	0.3502	0.1721	0.6316			
Ligand						
O22	0.3179	0.1129	0.9559	230.32	1.154	1.161
O12	0.3155	-0.1772	0.6359	231.571	1.122	1.129
O23	0.65	0.3125	0.8383	232.307	1.103	1.11
O21	0.241	0.1258	0.2819	232.539	1.097	1.104
O11	-0.0123	0.1521	0.5621	234.045	1.058	1.065
O14	0.6455	0.0128	0.5396	244.356	0.801	0.808
O13	0.2197	0.4942	0.744	248.678	0.699	0.706
O14	0.3545	0.5128	0.4604	253.396	0.595	0.601
Next Ligand						
O12	0.6845	0.3228	0.3641	335.86	0.001	0.001

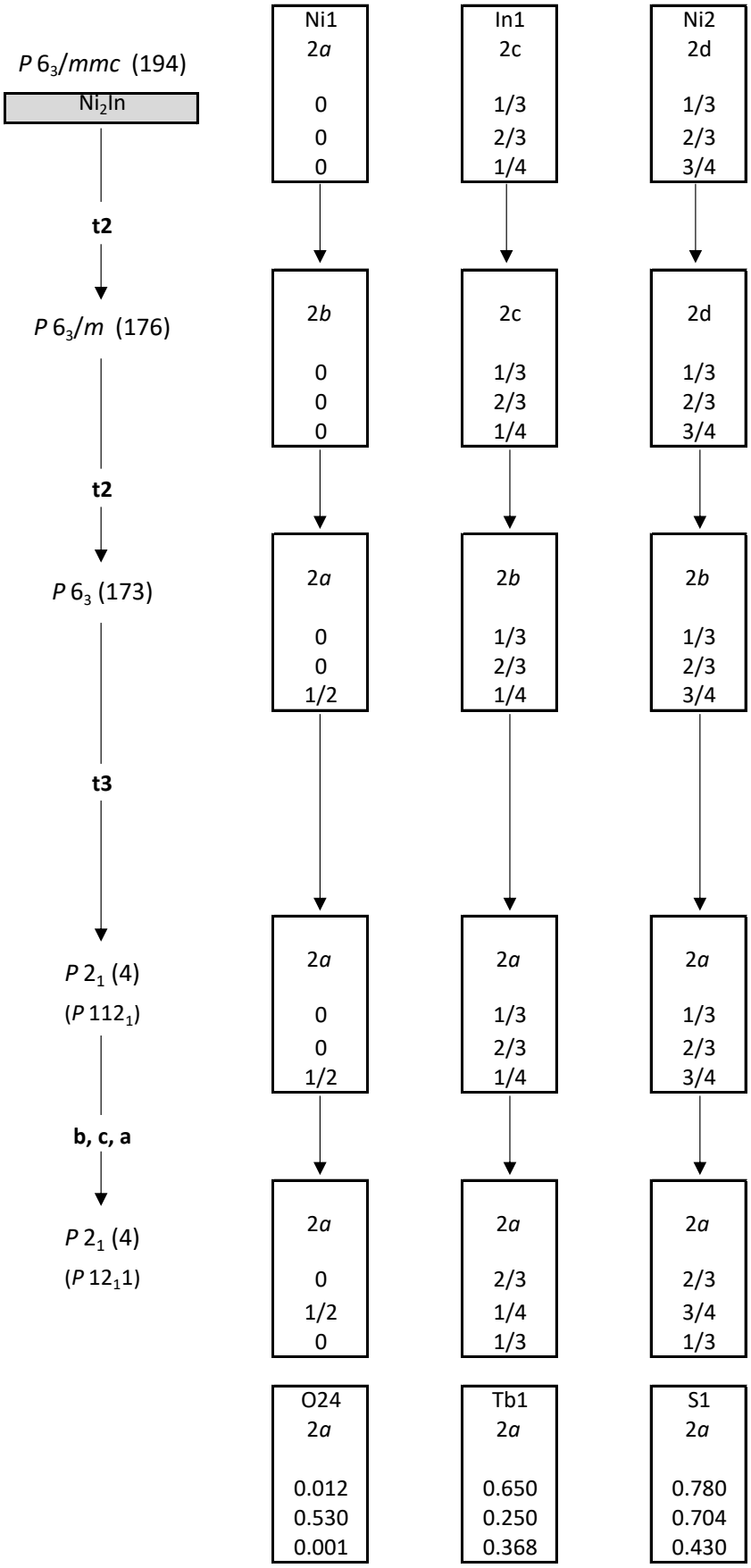

Figure S1: Group-subgroup relation scheme between Ni_2In and O (protonated oxygen atom from the hydrogensulfate anion), S (sulfur from the sulfate anion) and Tb in $Tb(HSO_4)(SO_4)$.

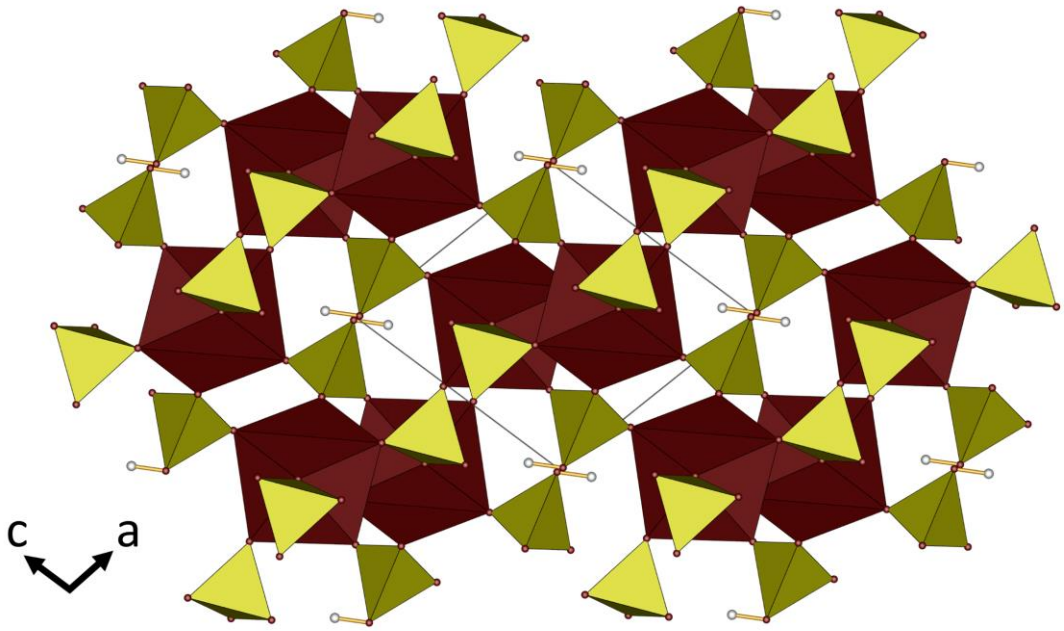

Figure S2: 3D network formed by $Tb(HSO_4)_{3/3}(SO_4)_{4/4}$ units viewed along [010].

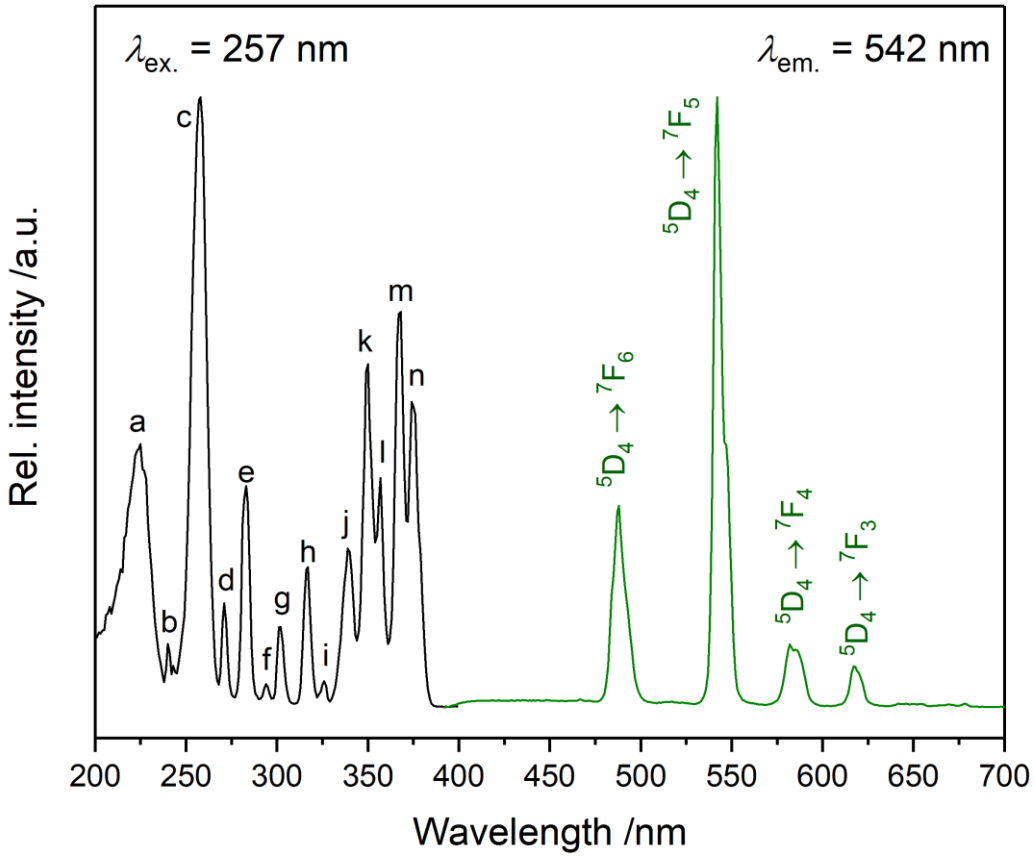

Figure S3: Corrected excitation (black) and emission (green) spectra of $Tb(HSO_4)(SO_4)$; the assignment of the excitation spectrum is listed in table S4

Table S4: Assignment of the excitation bands in $Tb(HSO_4)(SO_4)$ according to Carnall[1]

Band	Transition $^7F_6 \rightarrow$	Wavelength /nm
a	5*d*	224
b	$^5K_7$	240
c	5*d*	258
d	$^5I_7$	271
e	$^5I_8$	283
f	$^5H_5$	294
g	$^5H_6$	302
h	$^5H_7$	317
i	$^5D_1$	326
j	$^5L_7 + {}^5L_8$	339
k	$^5L_9$	350
l	$^5G_5$	357
m	$^5L_{10}$	368
n	$^5G_6$	374

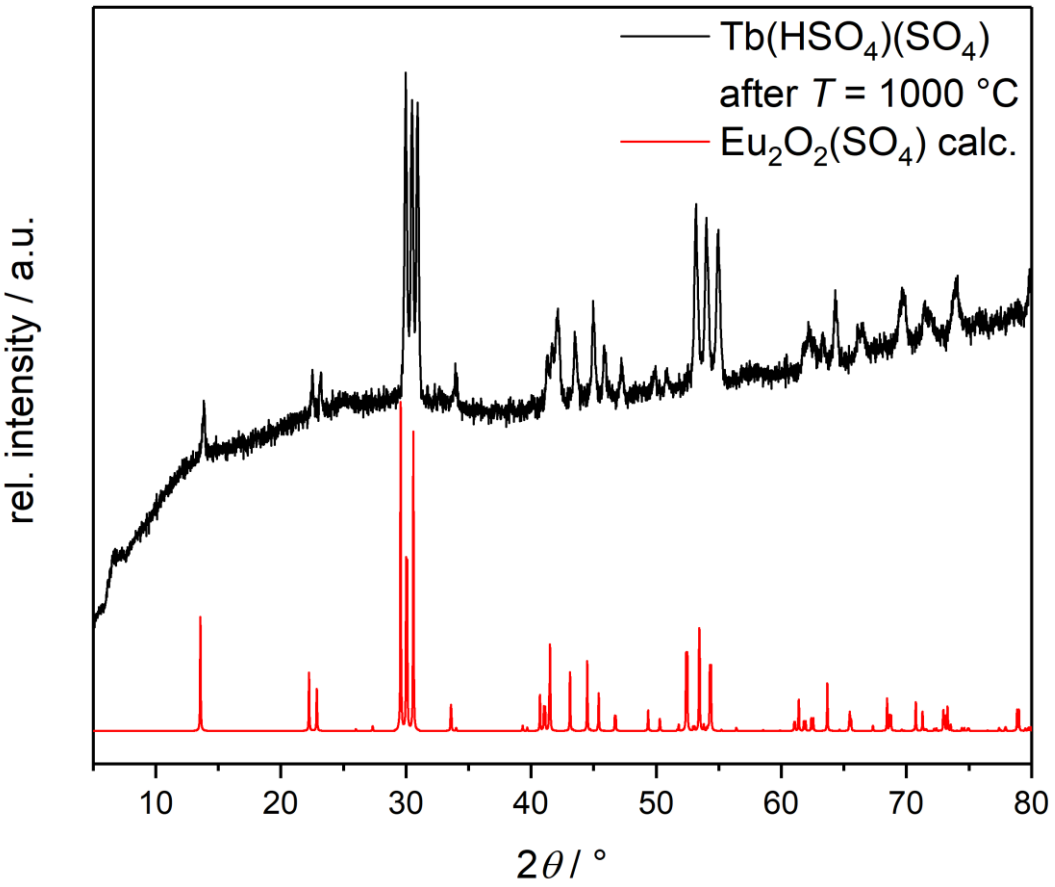

Figure S4: PXRD of a sample of $Tb(HSO_4)(SO_4)$ after thermogravimetric analysis to 1000 °C in comparison to the calculated pattern of $Eu_2O_2(SO_4)$.[2]

References

1 W. T. Carnall, P. R. Fields and K. Rajnak, *J. Chem. Phys.*, 1968, **49**, 4447–4449.

2 I. Hartenbach and T. Schleid, *Z. Anorg. Allg. Chem.*, 2002, **628**, 2171.