Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Elucidating the role of metal-ion co-doping towards boosting upconversion luminescence in gadolinium vanadate

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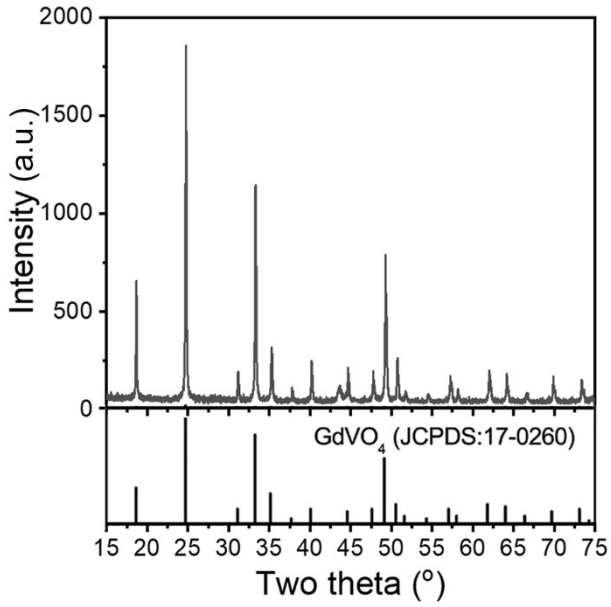

Figure S1: X-ray diffraction plots for $GdVO_4$:10Yb/2Er (reference: Co-ppt.; 850°C).

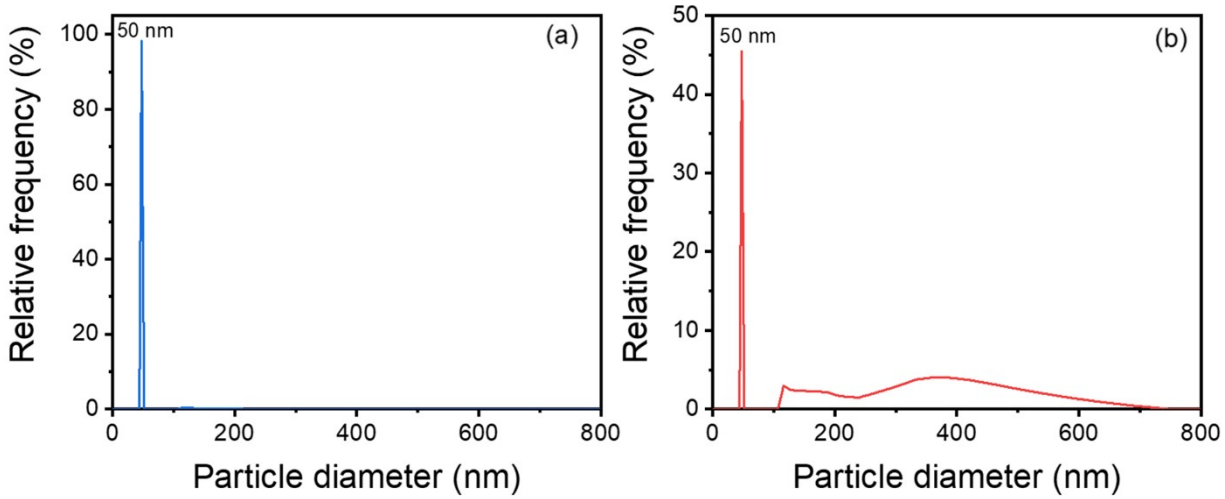

Figure S2: (a) Number and (b) volume weighted DLS particle size distribution for 10Yb/2Er.

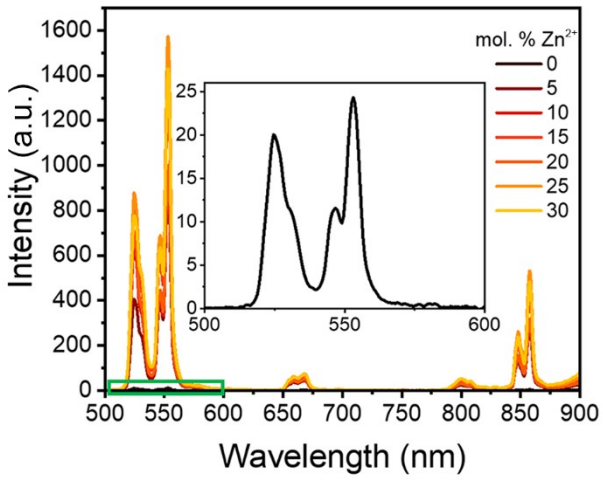

Figure S3: UC emission spectra of 10Yb/2Er/*x*Zn (*x* = 0-30 mol.%). Inset displays the corresponding emission spectrum for 10Yb/2Er for the highlighted section.

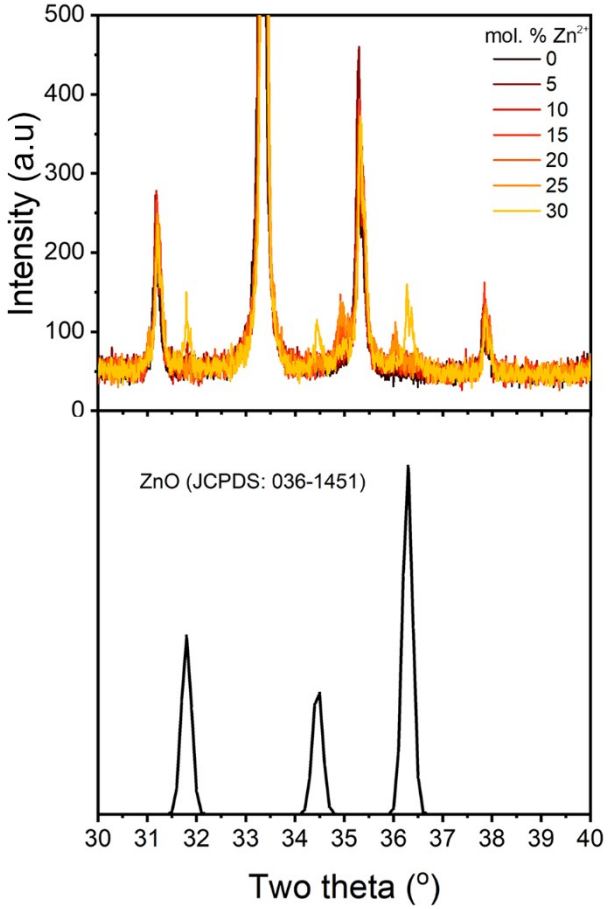

Figure S4: Selected-range XRD patterns for 10Yb/2Er/*x*Zn (*x* = 0-30) and the corresponding diffraction pattern for ZnO.

Table S1: Lattice parameters and corresponding cell volume for 10Yb/2Er/*x*Zn (*x* = 0-25 mol.%) series of samples calculated from Rietveld refinement of the X-ray diffraction data.

Sample	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Cell volume (Å^3)
10Yb/2Er (Ref.)	7.1926	7.1926	6.3392	90	90	90	327.952
10Yb/2Er/5Zn	7.1891	7.1891	6.3340	90	90	90	327.363
10Yb/2Er/10Zn	7.1860	7.1860	6.3315	90	90	90	326.946
10Yb/2Er/15Zn	7.1852	7.1852	6.3312	90	90	90	326.866
10Yb/2Er/20Zn	7.1850	7.1850	6.3313	90	90	90	326.843
10Yb/2Er/25Zn	7.1790	7.1790	6.3276	90	90	90	326.109

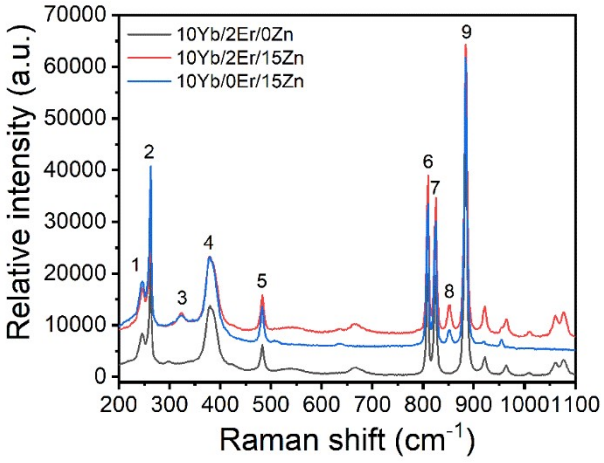

Figure S5: Raman spectra for 10Yb/*b*Er/*x*Zn (*b* = 0, 2; *x* = 0, 15).

Table S2: List and description of various Raman modes and other emission peaks observed for 10Yb/bEr/*x*Zn (b = 0, 2; *x* = 0, 15), as presented in Figure S5[1,2].

No.	Peak position (cm^{-1})	Symmetry	Description
1	246	E_g	GdO_8 stretching
2	263-264	$B_{1g/2g}$	$(Gd/Zn)O_8$ stretching
3	324	A_{1g}	O-V-O (Zn) bending
4	380	A_{1g}	ν_2 O-V-O (Gd) bending
5	483	B_{1g}	GO_8 stretching
-	664	-	Luminescence
6	810	E_g/B_{1g}	Symmetric O-V-O stretching
7	825	B_{1g}	ν_3 Symmetric O-V-O stretching
8	851	B_{1g}	Symmetric O-V-O stretching (Zn)
9	884	A_{1g}	ν_1 VO_4 asymmetric stretching
-	922	-	Luminescence
-	965	-	Luminescence
-	1059	-	Luminescence
-	1076	-	Luminescence

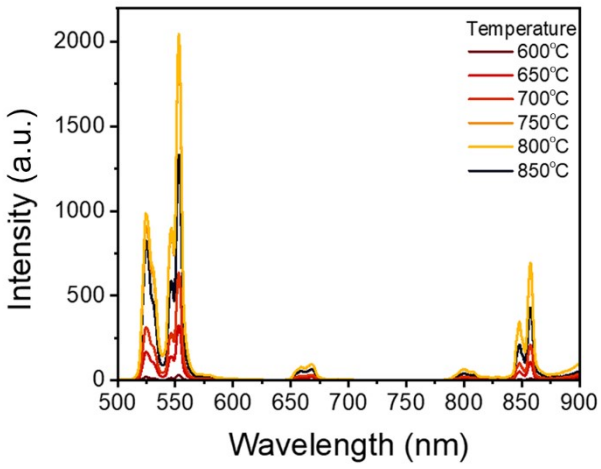

Figure S6: UC emission spectra of 10Yb/2Er/15Zn as a function of calcination temperature.

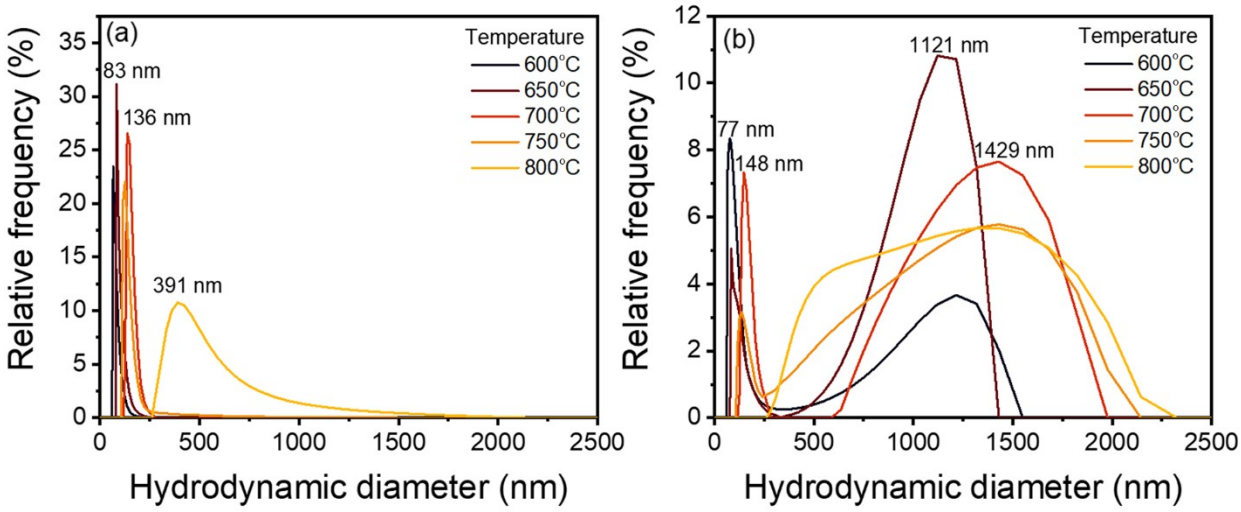

Figure S7 (a): Number-weighted and (b) volume weighted particle size distribution of 10Yb/2Er/15Zn as a function of calcination temperature.

Table S3: Key optical metrics for $GdVO_4$: 10 Yb^{3+}, 2 Er^{3+} (10Yb/2Er) and co-doped samples prepared in this study.

Sample	Absorption (abs.)	PLQY (%)	Cell volume ($Å^3$)	Crystallite size (nm)	Description
10Yb/2Er	0.33	0.003	327.952	56.06±1.66	Co-ppt. 850 °C
Effect of Zn doping					
10Yb/2Er/5Zn	0.24	0.13	327.363	69.52±2.96	Co-ppt., 850 °C
10Yb/2Er/10Zn	0.36	0.11	326.946	82.86±4.49	Co-ppt., 850 °C
10Yb/2Er/15Zn	0.29	0.18	326.866	81.62±4.41	Co-ppt., 850 °C
10Yb/2Er/20Zn	0.34	0.14	326.843	74.57±3.56	Co-ppt., 850 °C
10Yb/2Er/25Zn	0.34	0.20	326.109	78.65±3.42	Co-ppt., 850 °C
Effect of calcination temperature					
10Yb/2Er/15Zn	0.31	0.004	-	20.14±0.4	Co-ppt., 600 °C
10Yb/2Er/15Zn	0.38	0.03	-	45.83±0.77	Co-ppt., 650 °C
10Yb/2Er/15Zn	0.39	0.06	-	56.49±1.13	Co-ppt., 700 °C
10Yb/2Er/15Zn	0.48	0.14	-	91.59±5.48	Co-ppt., 750 °C
10Yb/2Er/15Zn	0.48	0.15	-	94.92±5.51	Co-ppt., 800 °C
Effect of Sc doping					
10Yb/2Er/5Sc	0.42	0.02	325.898	19.26±0.46	Co-ppt., 850 °C
10Yb/2Er/10Sc	0.29	0.06	325.315	57.14±1.55	Co-ppt., 850 °C
10Yb/2Er/15Sc	0.28	0.06	324.205	52.47±1.39	Co-ppt., 850 °C
10Yb/2Er/20Sc	0.29	0.06	321.875	43.13±1.16	Co-ppt., 850 °C
10Yb/2Er/25Sc	0.31	0.07	319.677	39.91±0.97	Co-ppt., 850 °C
Effect of calcination temperature (solid state)					
10Yb/2Er(ss)	0.29	0.09	-	62.26±2.99	Solid state, 850 °C
10Yb/2Er(ss)	0.31	0.13	-	69.52±2.77	Solid state, 950 °C
10Yb/2Er(ss)	0.32	0.15	-	71.15±2.89	Solid state, 1050 °C
10Yb/2Er(ss)	0.31	0.15	-	70.02±2.44	Solid state, 1150 °C

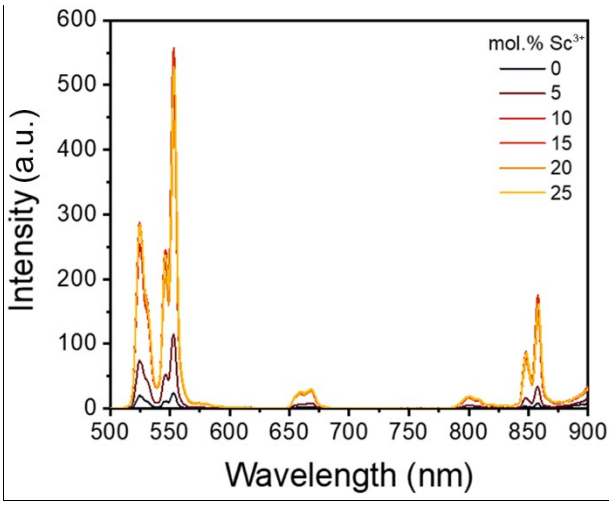

Figure S8: UC emission spectra of 10Yb/2Er/*x*Sc (*x* = 0-25 mol. %).

Table S4: Lattice parameters and corresponding cell volume for 10Yb/2Er/*x*Sc (*x* = 0-25 mol.%) series of samples calculated from Rietveld refinement of the X-ray diffraction data.

Sample	**a** (Å)	**b** (Å)	**c** (Å)	**α** (°)	**β** (°)	**γ** (°)	**Cell volume** (Å^3)
10Yb/2Er/5Sc	7.1756	7.1756	6.3295	90	90	90	325.898
10Yb/2Er/10Sc	7.1709	7.1709	6.3265	90	90	90	325.315
10Yb/2Er/15Sc	7.1616	7.1616	6.3212	90	90	90	324.205
10Yb/2Er/20Sc	7.1412	7.1412	6.3117	90	90	90	321.875
10Yb/2Er/25Sc	7.1222	7.1222	6.3021	90	90	90	319.677

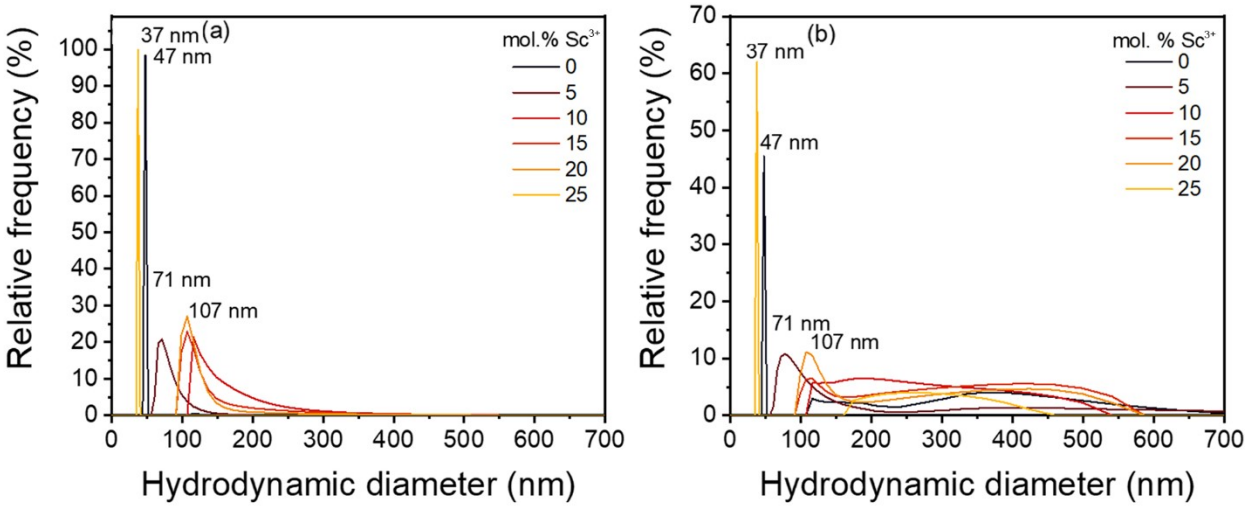

Figure S9: (a) Number-weighted and (b) volume-weighted particle size distribution of 10Yb/2Er/*x*Sc (*x* = 0-25).

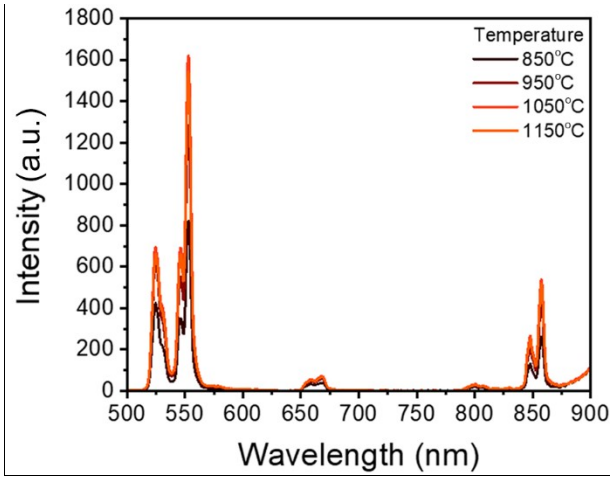

Figure S10: UC emission spectra of 10Yb/2Er(ss) as a function of calcination temperature.

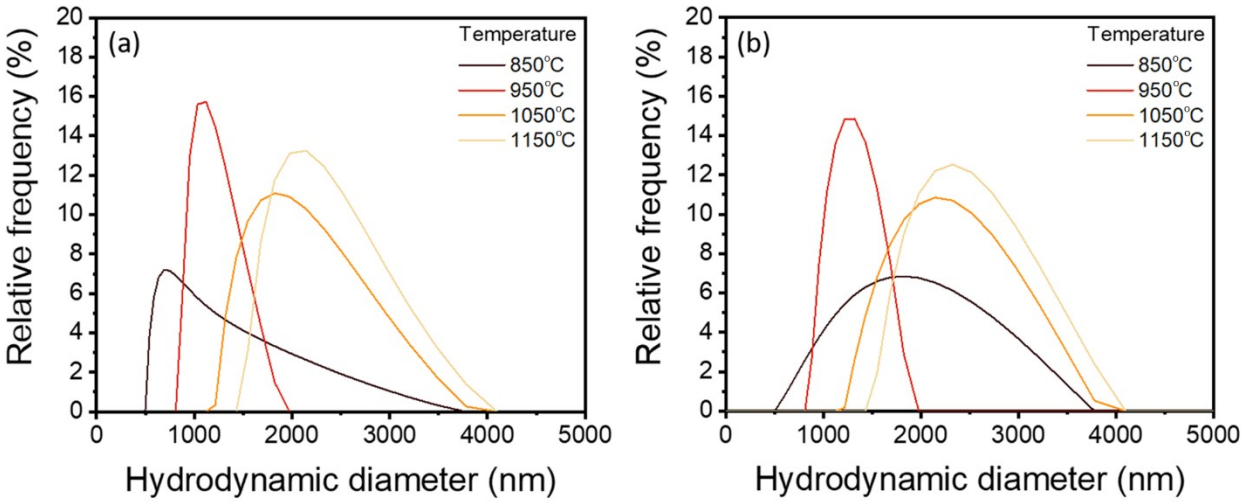

Figure S11: (a) Number-weighted and (b) volume weighted particle size distribution of 10Yb/2Er(*ss*) as a function of calcination temperature.

Table S5: Results from ICP-OES elemental composition analysis for all samples in this study.

		Gd	Yb	Er	V	Zn	Sc
Sample	**Values**	Mass %	Mass %	Mass %	Mass %	Mass %	Mass %
10Yb/2Er	Mean	48.60	6.02	1.17	17.79	-	-
	Std. dev.	0.20	0.02	0.01	0.03	-	-
	Error (±)	2.43	0.30	0.06	0.37	-	-
	Theoretical	50.51	6.32	1.22	18.59	-	-
10Yb/2Er/5Zn	Mean	47.10	6.46	1.23	18.42	1.17	-
	Std. dev.	0.20	0.03	0.01	0.05	0.01	-
	Error (±)	2.36	0.32	0.06	0.39	0.06	-
	Theoretical	48.45	6.42	1.24	18.91	1.21	-
10Yb/2Er/10Zn	Mean	45.30	6.57	1.25	18.51	2.43	-
	Std. dev.	0.20	0.03	0.01	0.06	0.01	-
	Error (±)	2.27	0.33	0.06	0.39	0.12	-
	Theoretical	46.32	6.54	1.26	19.24	2.47	-
10Yb/2Er/15Zn	Mean	43.60	6.69	1.28	18.57	3.73	-
	Std. dev.	0.10	0.02	0.01	0.03	0.01	-
	Error (±)	2.18	0.33	0.06	0.39	0.19	-
	Theoretical	44.12	6.65	1.29	19.58	3.77	-
10Yb/2Er/20Zn	Mean	42.10	6.86	1.31	18.40	5.11	-
	Std. dev.	0.20	0.04	0.01	0.05	0.01	-
	Error (±)	2.11	0.34	0.07	0.39	0.26	-
	Theoretical	41.84	6.77	1.31	19.93	5.12	-
10Yb/2Er/25Zn	Mean	39.60	7.00	1.29	18.33	7.16	-
	Std. dev.	0.10	0.02	0.01	0.03	0.03	-
	Error (±)	1.98	0.35	0.06	0.38	0.36	-
	Theoretical	39.47	6.89	1.33	20.29	6.51	-
10Yb/2Er/5Sc	Mean	46.90	6.26	1.26	18.31	-	0.81
	Std. dev.	0.10	0.02	0.01	0.03	-	0.00
	Error (±)	2.35	0.31	0.06	0.92	-	0.04

	Theoretical	48.64	6.45	1.25	18.98	-	0.84
10Yb/2Er/10Sc	Mean	45.10	6.44	1.27	18.72	-	1.69
	Std. dev.	0.10	0.03	0.01	0.05	-	0.03
	Error (±)	2.26	0.32	0.06	0.94	-	0.08
	Theoretical	46.68	6.59	1.27	19.39	-	1.71
10Yb/2Er/15Sc	Mean	43.30	6.49	1.25	18.85	-	2.72
	Std. dev.	0.10	0.03	0.01	0.07	-	0.01
	Error (±)	2.17	0.32	0.06	0.94	-	0.14
	Theoretical	44.64	6.73	1.30	19.81	-	2.62
10Yb/2Er/20Sc	Mean	41.40	6.87	1.32	19.16	-	3.53
	Std. dev.	0.10	0.03	0.01	0.07	-	0.01
	Error (±)	2.07	0.34	0.07	0.96	-	0.18
	Theoretical	42.52	6.88	1.33	20.25	-	3.58
10Yb/2Er/25Sc	Mean	38.90	7.06	1.36	19.29	-	4.54
	Std. dev.	0.20	0.05	0.01	0.11	-	0.02
	Error (±)	1.95	0.35	0.07	0.96	-	0.23
	Theoretical	40.29	7.04	1.36	20.72	-	4.57
10Yb/2Er(ss)	Mean	49.30	6.26	1.22	18.40	-	-
	Std. dev.	0.10	0.03	0.01	0.02	-	-
	Error (±)	2.47	0.31	0.06	0.92	-	-
	Theoretical	50.51	6.32	1.22	18.59	-	-

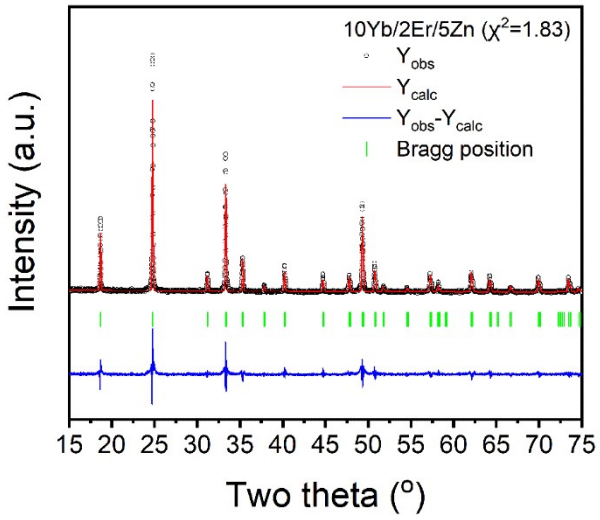

Figure S12: Rietveld refinement plots for 10Yb/2Er/5Zn. Black circles depict the experimental data (Y_{obs}), red continuous line the calculated plot in (Y_{calc}), green lines represent Bragg peaks, and the blue line depicts the difference ($Y_{obs} - Y_{calc}$).

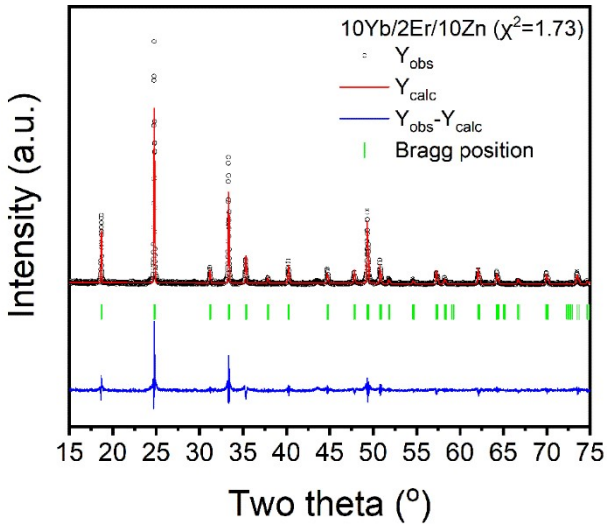

Figure S13: Rietveld refinement plots for 10Yb/2Er/10Zn. Black circles depict the experimental data (Y_{obs}), red continuous line the calculated plot in (Y_{calc}), green lines represent Bragg peaks, and the blue line depicts the difference ($Y_{obs} - Y_{calc}$).

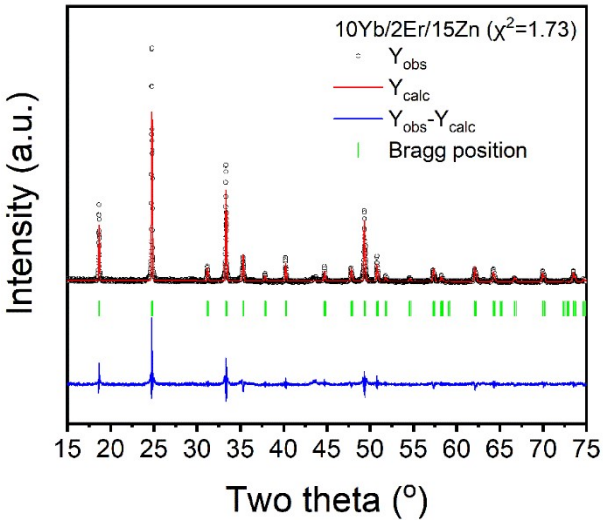

Figure S14: Rietveld refinement plots for 10Yb/2Er/15Zn. Black circles depict the experimental data (Y_{obs}), red continuous line the calculated plot in (Y_{calc}), green lines represent Bragg peaks, and the blue line depicts the difference ($Y_{obs} - Y_{calc}$).

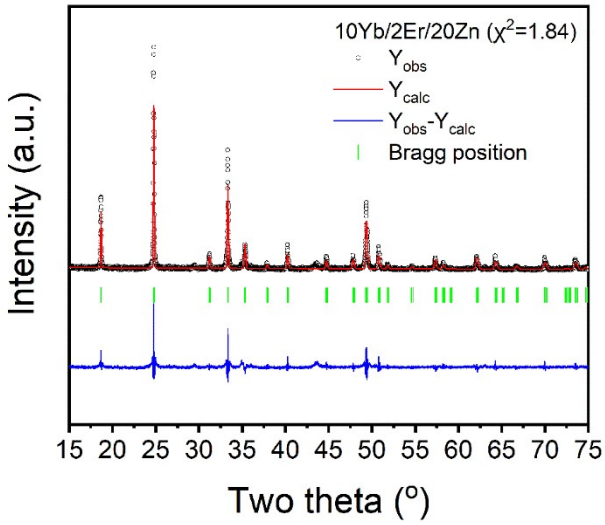

Figure S15: Rietveld refinement plots for 10Yb/2Er/20Zn. Black circles depict the experimental data (Y_{obs}), red continuous line the calculated plot in (Y_{calc}), green lines represent Bragg peaks, and the blue line depicts the difference ($Y_{obs} - Y_{calc}$).

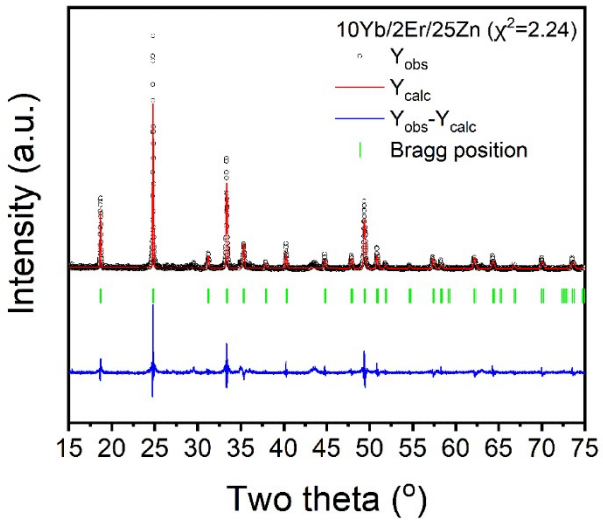

Figure S16: Rietveld refinement plots for 10Yb/2Er/25Zn. Black circles depict the experimental data (Y_{obs}), red continuous line the calculated plot in (Y_{calc}), green lines represent Bragg peaks, and the blue line depicts the difference ($Y_{obs} - Y_{calc}$).

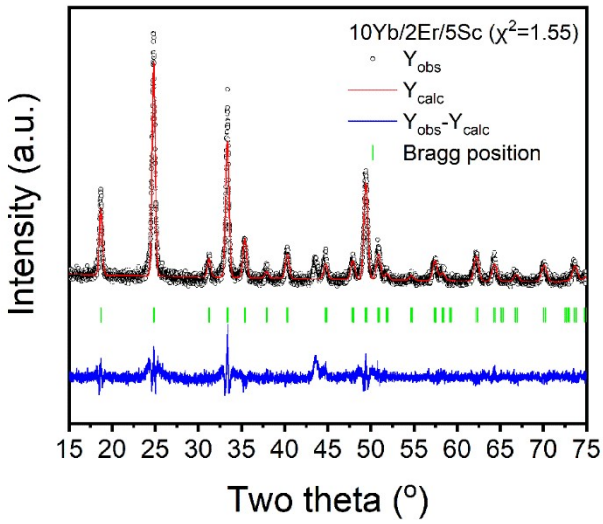

Figure S17: Rietveld refinement plots for 10Yb/2Er/5Sc. Black circles depict the experimental data (Y_{obs}), red continuous line the calculated plot in (Y_{calc}), green lines represent Bragg peaks, and the blue line depicts the difference ($Y_{obs} - Y_{calc}$).

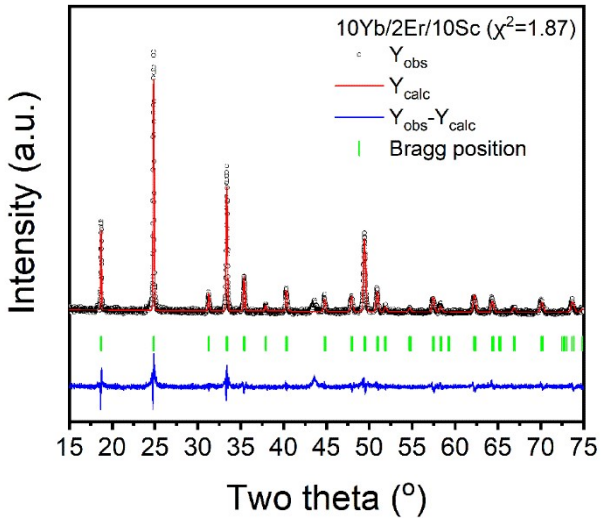

Figure S18: Rietveld refinement plots for 10Yb/2Er/10Sc. Black circles depict the experimental data (Y_{obs}), red continuous line the calculated plot in (Y_{calc}), green lines represent Bragg peaks, and the blue line depicts the difference ($Y_{obs} - Y_{calc}$).

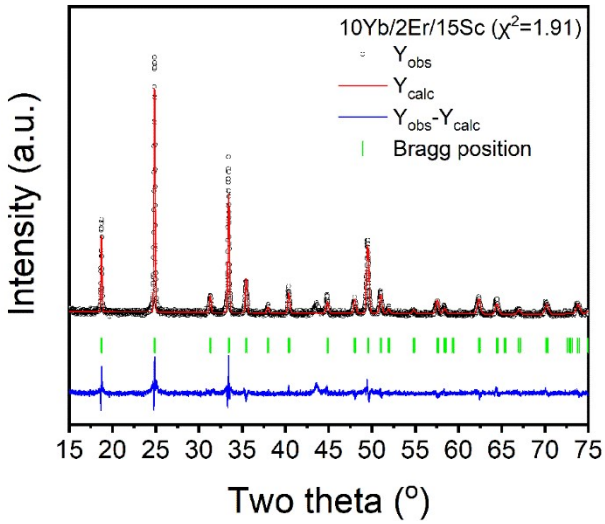

Figure S19: Rietveld refinement plots for 10Yb/2Er/15Sc. Black circles depict the experimental data (Y_{obs}), red continuous line the calculated plot in (Y_{calc}), green lines represent Bragg peaks, and the blue line depicts the difference ($Y_{obs} - Y_{calc}$).

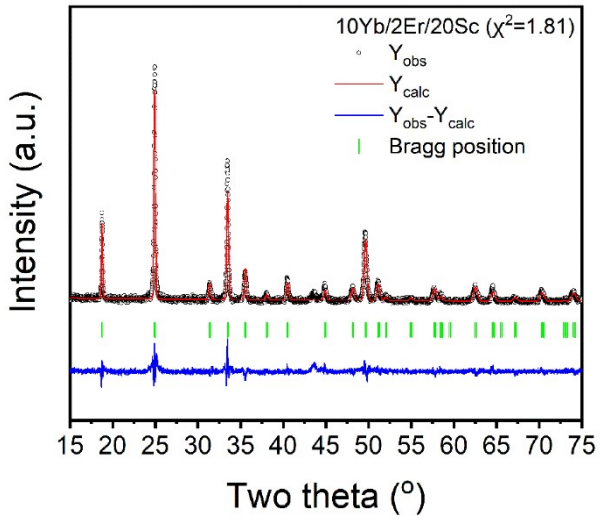

Figure S20: Rietveld refinement plots for 10Yb/2Er/20Sc. Black circles depict the experimental data (Y_{obs}), red continuous line the calculated plot in (Y_{calc}), green lines represent Bragg peaks, and the blue line depicts the difference ($Y_{obs} - Y_{calc}$).

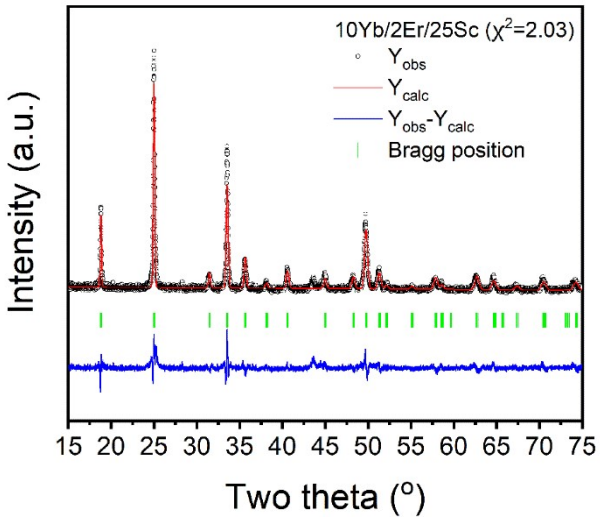

Figure S21: Rietveld refinement plots for 10Yb/2Er/25Sc. Black circles depict the experimental data (Y_{obs}), red continuous line the calculated plot in (Y_{calc}), green lines represent Bragg peaks, and the blue line depicts the difference ($Y_{obs} - Y_{calc}$).

References:

1 S. Rajkumar, E. Elanthamilan and J. P. Merlin, *J. Alloys Compd.*, 2021, **861**, 157939.

2 G. Lu, C. Li, W. Wang, Z. Wang, H. Xia and P. Zhao, *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.*, 2003, **98**, 156–160.