Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting materials

Optimizing Short-Wave Infrared Photoluminescence Quantum Yield and Brightness of Er^{3+}, Yb^{3+} Co-Doped Yttrium Orthophosphate Phosphors for Tracer-Based Plastic Recycling

Nisrin Mohamed Bhiri[a], Herman Duim[b], Eduard Madirov[a], Justine Nyarige[a], Bryce S. Richards[a,c]*, Andrey Turshatov[a]*

[a] Institute of Microstructure Technology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

[b] Delmic BV, Oostsingel 209, 2612 HL Delft, The Netherlands

[c] Light Technology Institute, Karlsruhe Institute of Technology, Engesserstrasse 13, 76131 Karlsruhe, Germany

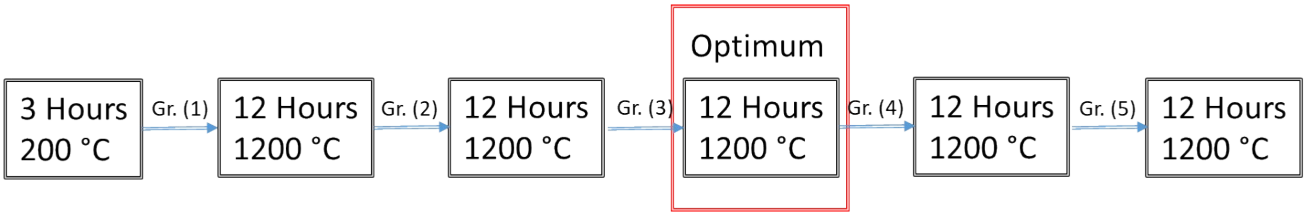

Figure S1. Flow chart of synthesis of YPO_4 samples: The mixture with precursors was manually grounded and preheated at 200 °C for 3 hours, then grounded again and heated at 1200 °C for variable time from 12 to 60 hours. Powders obtained after 12, 24, 36, 49 and 60 hours heating at 1200 °C were grounded again for subsequent structural analyses and optical measurements.

Table S1. Nominal and experimental (estimated using ICP-OES analysis) of the representative samples.

Sample		Er^{3+}, at%	Yb^{3+}, at%
YPO_4:2Er24Yb	Nominal	2.0	24.0
	Experimental	2.0	26.6
YPO_4:3Er24Yb	Nominal	3.0	24.0
	Experimental	2.9	23.2
YPO_4:4Er24Yb	Nominal	4.0	24.0
	Experimental	4.3	25.2

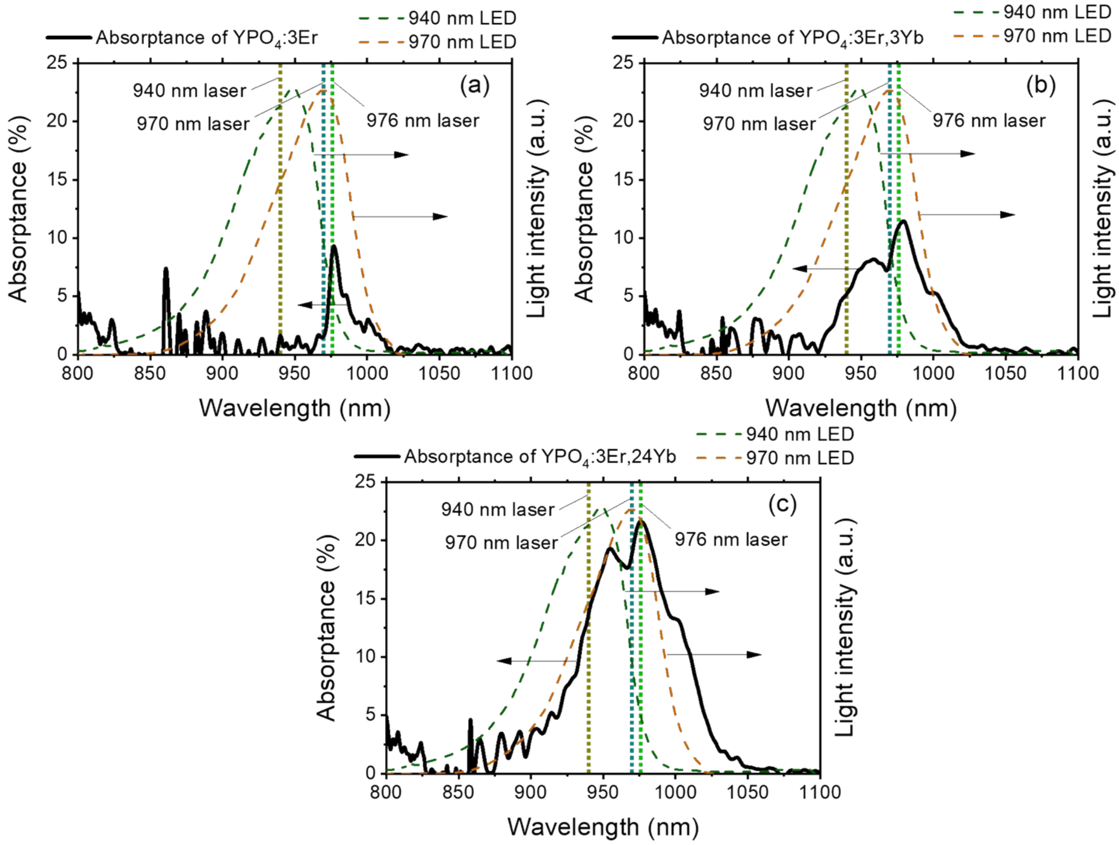

Figure S2. Absorptance (%) of (a) YPO_4:3Er, (b) YPO_4:3Er3Yb and (c) YPO_4:3Er24Yb samples. Each figure also shows the emission from two LEDs (940 and 970 nm) and three lasers (940, 970 and 976 nm shown as vertical lines). The absorbance data and spectra of the light sources were used to calculate the fraction of light that can be absorbed by these three tracers (Table S2) when one of these five light sources is applied.

Table S2. Fraction of light from different excitation sources absorbed by YPO_4:3Er, YPO_4:3Er3Yb and YPO_4:3Er24Yb samples, %.

Light source\Sample	3Er	3Er3Yb	3Er24Yb
940 nm laser	-	5.2	13.9
970 nm laser	1.5	8.1	18.9
976 nm laser	9.7	11.0	21.7
940 nm LED	0.6	4.0	10.3
970 nm LED	2.0	6.4	14.8

The results of Table S2 show that the highest fraction of absorbed light is always obtained using the 976 nm laser, reaching 21.7% for the YPO_4:3Er24Yb sample (with the highest Yb^{3+} concentration). Exposure to LEDs provides less absorbed photons - 10.3 and 14.8% for 940 nm LED and 970 nm LED respectively, which reduces the brightness of the YPO_4:3Er24Yb sample accordingly.

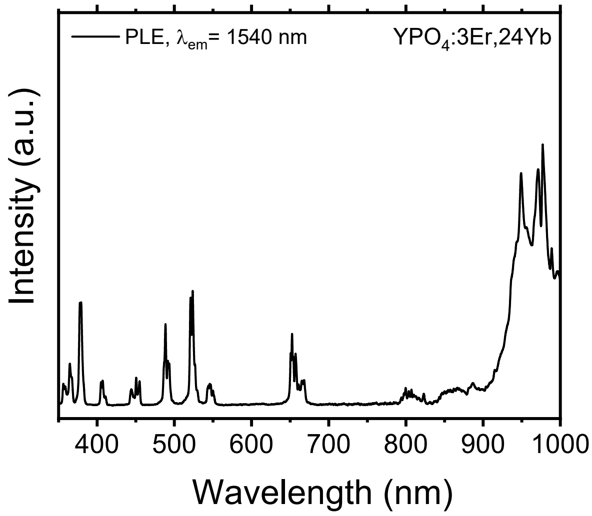

Figure S3. Photoluminescence excitation (PLE) spectrum of a representative sample YPO_4:3Er24Yb. Luminescence was detected at 1540 nm.

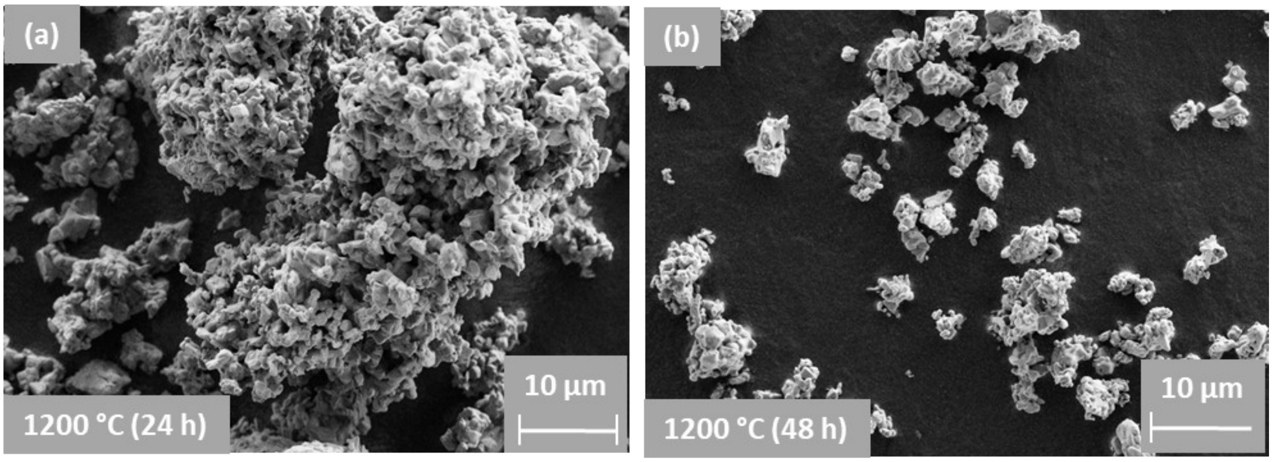

Figure S4. SEM images of YPO_4:3Er24Yb microcrystals obtained using calcination time of 24 hours (a) and 48 hours (b)

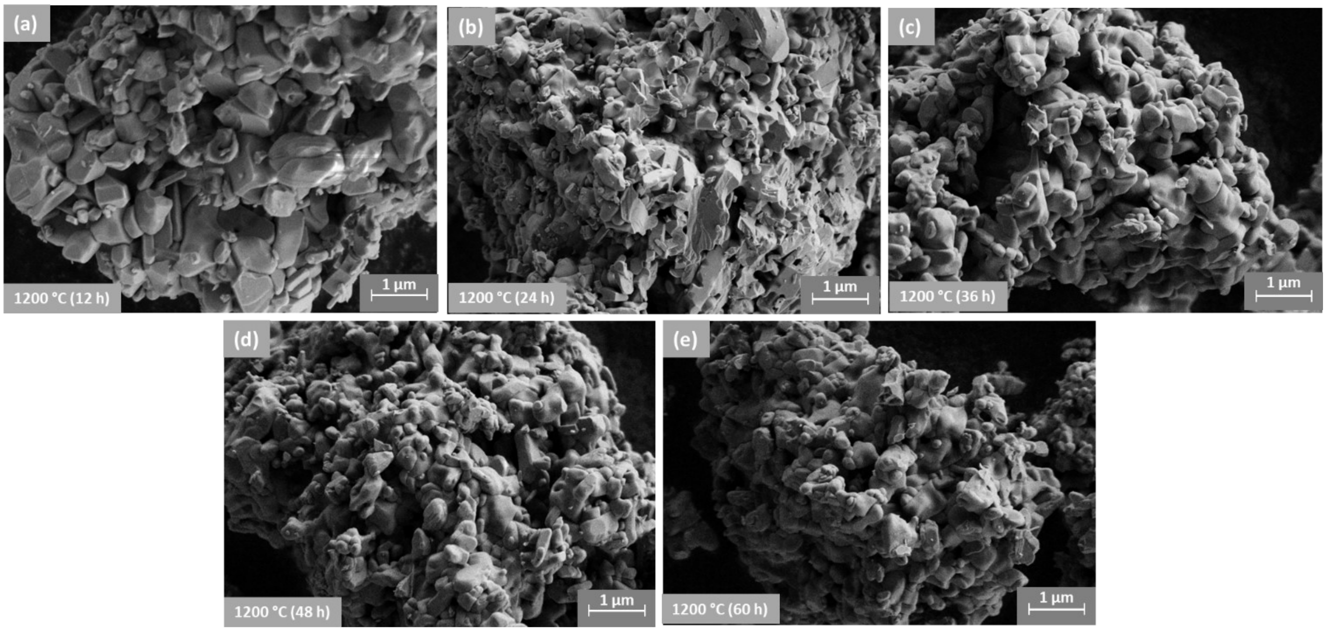

Figure S5. SEM images of YPO_4:3Er24Yb microcrystals obtained using calcination time of 12 hours (a), 24 hours (b), 36 hours (c), 48 hours (d) and 60 hours (e).

The crystallite size was calculated using the following equation of Debye-Scherer:

$$D_{sc} = \frac{K\lambda}{\beta\cos\theta}$$

Where D_{SC} is the average crystallite size, K is the shape factor (0.9), λ is the wavelength of Cu Kα radiation (1.5406 Å), β is the full width at half maximum (FWHM) of the diffraction peak in radians and θ is the diffraction Bragg angle of the most intense peak (200).

Table S3. Results calculation of average crystallite size using FWHM of the diffraction peak.

Calcination time (h)	FWHM	β	2θ	cos(θ)	D_{sc} (nm)
12	0.2113	0.00368	25.908	0.974	38.6
24	0.1754	0.00305	25.899	0.974	46.6
36	0.1567	0.00273	25.902	0.974	52.1
48	0.1662	0.00289	25.909	0.974	49.2
60	0.1674	0.00292	25.904	0.974	48.7

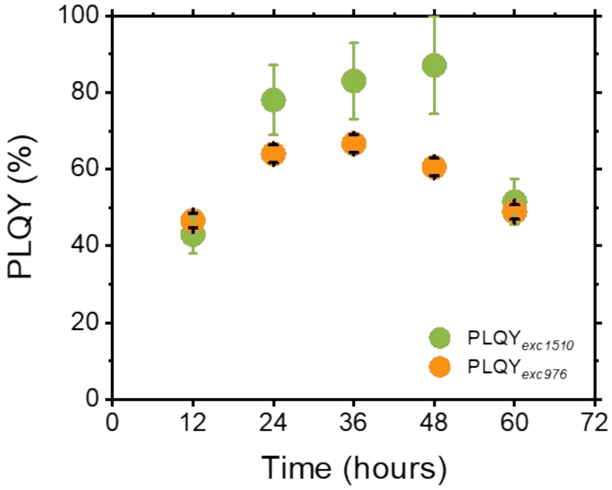

Figure S6. Dependence of PLQY of 1540 nm emission on calcination time (12 – 60 hours) for the YPO_4:3Er3Yb sample. Two excitation wavelengths were used: 1510 nm (PLQY^{exc1510}) and 976 nm (PLQY^{exc976}). Excitation intensity of 0.1 W/cm^2.

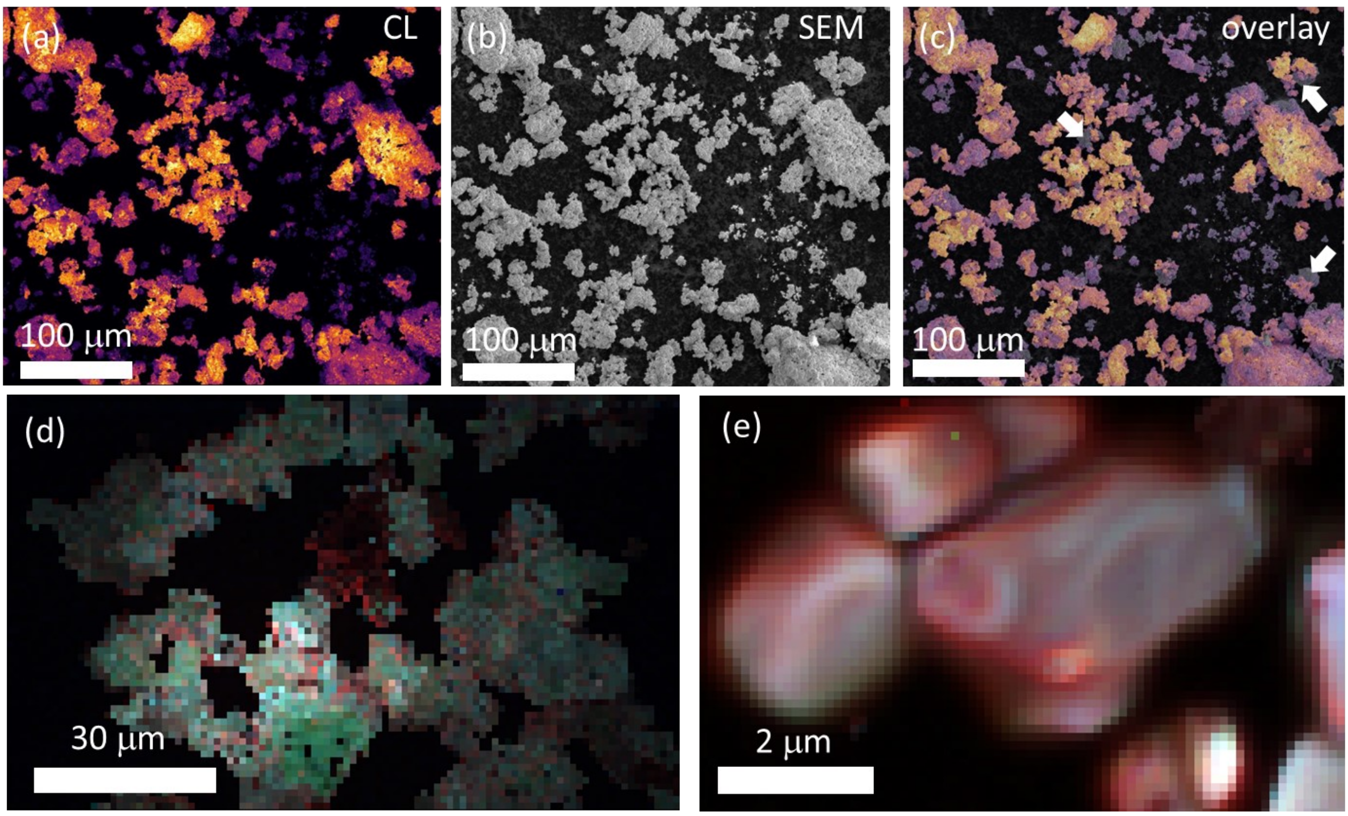

Figure S7. (a) cathodoluminescence image (CL integrated from 385 to 1100 nm); (b) SEM image; (c) overlay of (a) and (b); (d) and (e) are a pseudocolor overlay where arbitrary 420-440 nm (blue), 610-630 nm (green) and 980-1000 nm (red) channels.

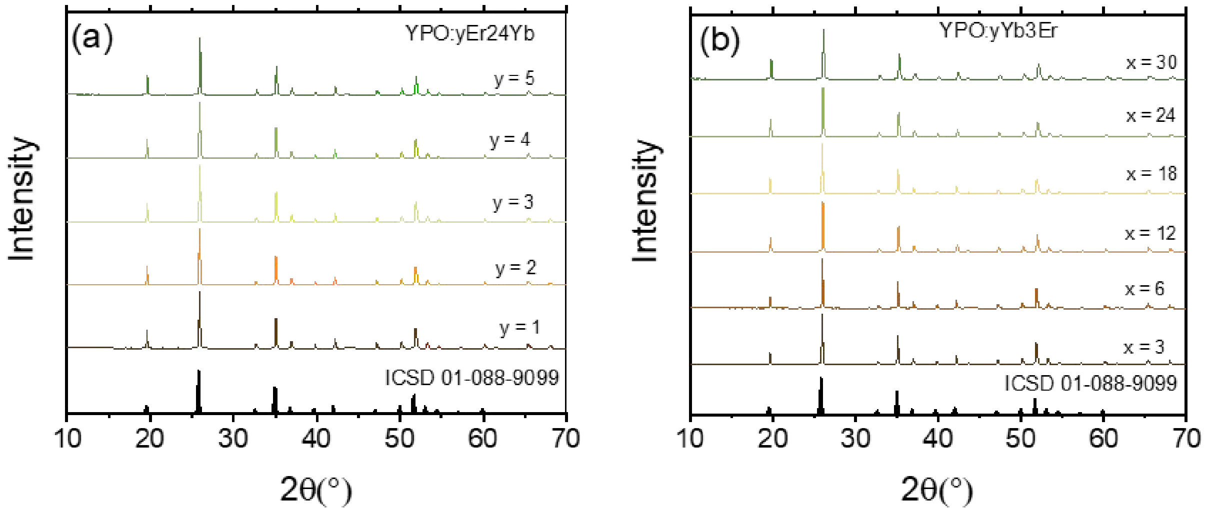

Figure S8. pXRD of (a) YPO_4:xEr24Yb and (b) YPO_4:yYb3Er series of samples synthesized using 36 hours calcination time at 1200 °C.

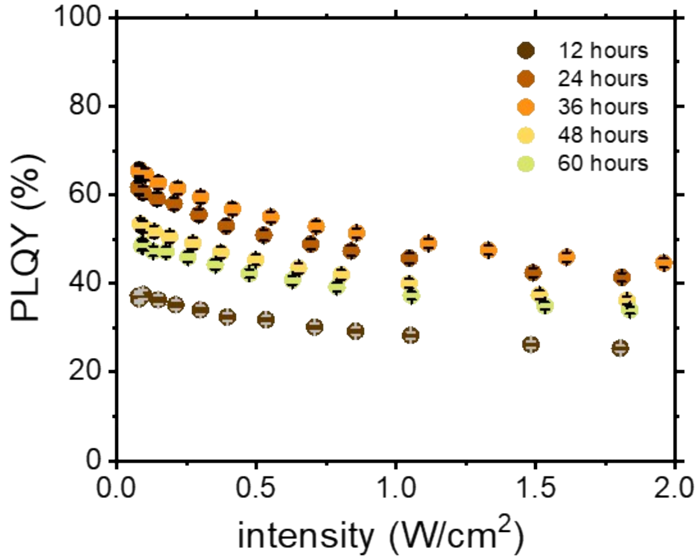

Figure S9. PLQY (excitation of 976 nm, integration range 1520 – 1650 nm) of YPO_4:3Er24Yb samples as a function of excitation intensity under excitation. The samples were synthesized using different calcination time (12, 24, 36, 48 and 60 hours) at 1200 °C.

Table S4. Temperature of the YPO_4: 3Yb3Er and YPO_4: 24Yb3Er samples under 940 nm excittaion with either 3 or 300 W/cm^2 intensity after 0, 30, 60 and 120 seconds of irradiation

Sample	YPO_4: 3Yb3Er		YPO_4: 24Yb3Er	
Intensity, W/cm^2	3 W/cm^2	300 W/cm^2	3 W/cm^2	300 W/cm^2
0 s	21.6	21.6	21.6	21.6
30 s	25.9	29.1	32.0	43.2
60 s	26.4	29.6	33.4	45.0
120 s	27.1	30.2	36.9	46.1

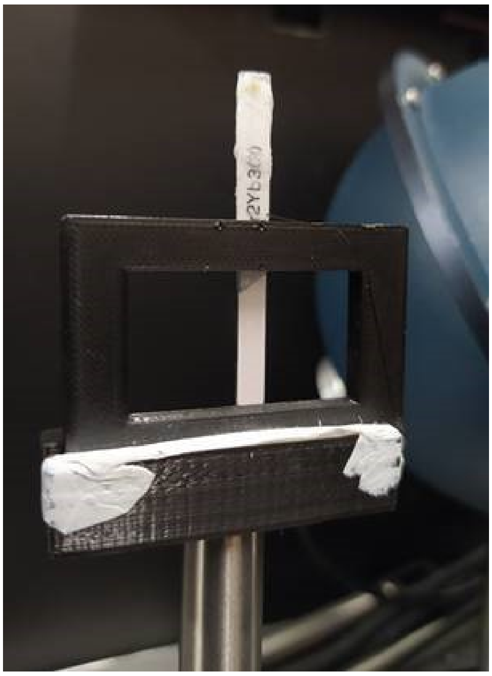

Figure S10. A sample: a rectangular glass capillary filled with powder of YPO_4 tracer. Similar samples were used in PLQY measurements.

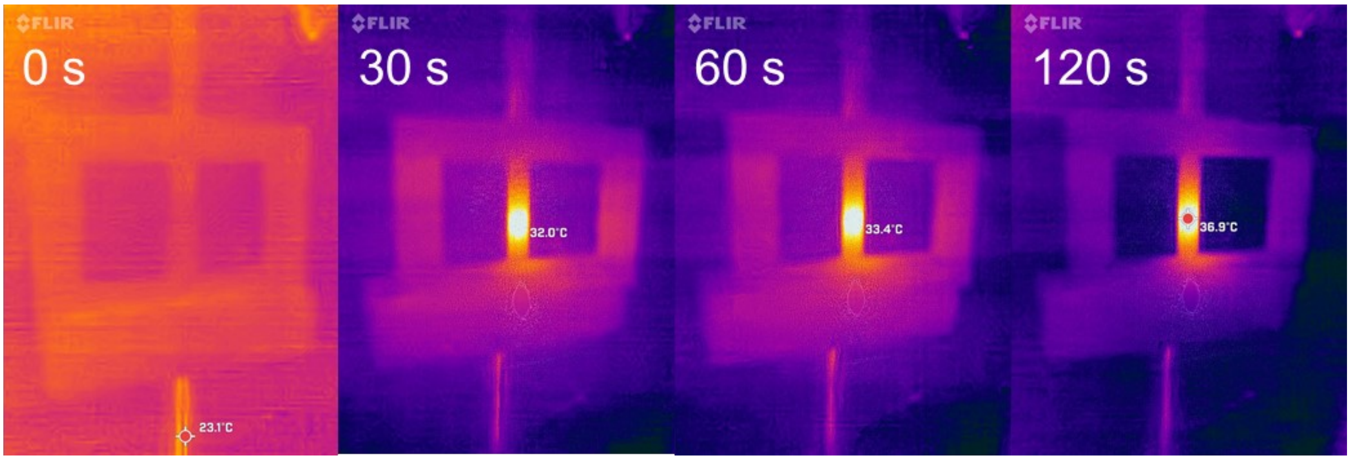

Figure S11. Thermal images of the YPO_4: 24Yb3Er sample under 940 nm, 3 W/cm^2 excitation after 0, 30, 60 and 120 s obtained with FLIR ONE PRO thermal camera. The figures also show the temperature of the hottest spot.

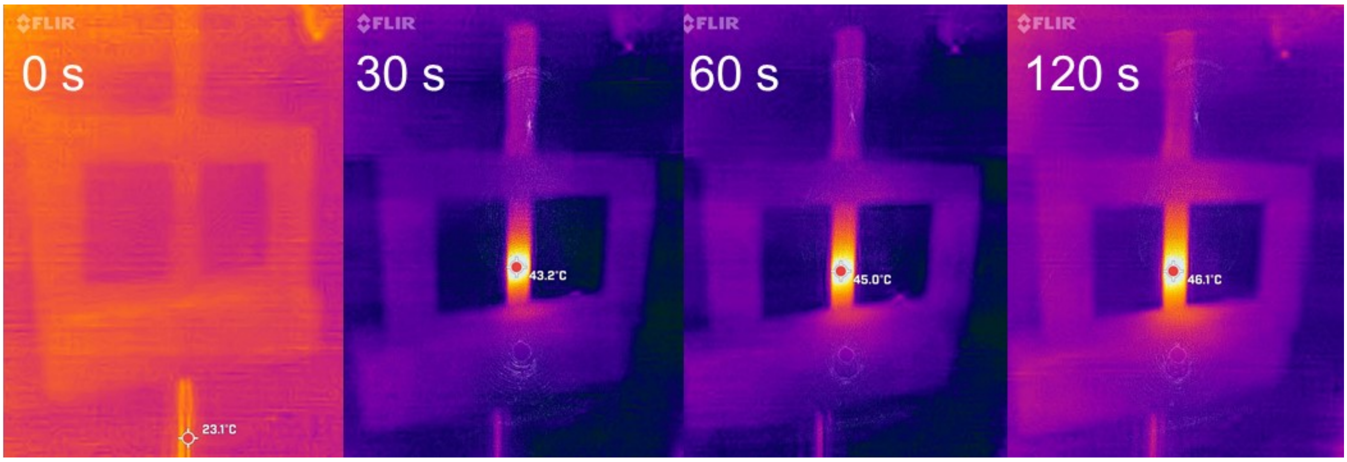

Figure S12. Thermal images of the YPO_4: 24Yb3Er sample under 940 nm, 300 W/cm^2 excitation after 0, 30, 60 and 120 s obtained with FLIR ONE PRO thermal camera. The figures also show the temperature of the hottest spot.

The error in the PLQY values is estimated according to Madirov *et al.* (https://doi.org/10.1002/adpr.202200187). According to this approach the PLQY error is mostly dependent on the absorbtance of the sample. Knowing the fraction of the absorbed excitation it is then possible to determine the relative error. Combining this with the PLQY value provides the absolute error which defines the error bar in the Figure 2d, Figure 4, Figure S3 and Figure S6.

It should also be noted that an experiment to test the repeatability of PLQY measurements was carried out using YPO_4:3Er24Yb phosphor with 976 nm excitation. In this experiment the PLQY of a sample was measured 4 times (each time the sample was taken out of the integrating sphere and put back in for measurement). Also 4 different samples (phosphors in a glass capillary) of the same phosphor (YPO_4:3Er24Yb) were characterized. As a result of the experiment we obtained a relative error of 3.4%, which agrees well with the value of 2.2% in Table S5-S11.

Table S5. Calculation of the error in the PLQY estimation for the series of YPO_4:3Er24Yb samples under 976 nm excitation

Calcination time, h	PLQY, %	Absorptance (976 nm), %	Relative error, %	Absolute error, %
12	37.5	43.9	2.6	1.0
24	61.8	46.4	2.4	1.5
30	65.7	48.3	2.2	1.4
48	53.5	44.8	2.5	1.4
60	48.8	46.8	2.3	1.1

Table S6. Calculation of the error in the PLQY estimation for the series of YPO_4:3Er24Yb samples under 1510 nm excitation

Calcination time, h	PLQY, %	Absorptance (1510 nm), %	Relative error, %	Absolute error, %
12	26.9	10.4	12.1	3.3
24	57.5	13.2	9.3	5.4
30	49.2	11.0	11.5	5.6
48	50.5	8.1	15.7	7.9
60	55.8	12.0	10.4	5.8

Table S7. Calculation of the error in the PLQY estimation for the series of YPO_4:3Er3Yb samples under 976 nm excitation

Calcination time, h	PLQY, %	Absorptance (976 nm), %	Relative error, %	Absolute error, %
12	46.7	27.0	4.1	1.9
24	64.0	31.6	3.6	2.3
30	66.7	33.6	3.5	2.3
48	60.6	30.3	3.8	2.3
60	48.9	30.0	3.8	1.9

Table S8. Calculation of the error in the PLQY estimation for the series of YPO_4:3Er3Yb samples under 1510 nm excitation

Calcination time, h	PLQY, %	Absorptance (976 nm), %	Relative error, %	Absolute error, %
12	43.0	10.8	11.7	5.1
24	78.0	10.8	11.7	9.1
30	83.0	10.6	12.0	9.9
48	87.1	8.6	14.6	12.7
60	51.5	10.9	11.5	5.9

Table S9. Calculation of the error in the PLQY estimation for the series of YPO_4:xEr24Yb samples under 976 nm excitation

Er^{3+}, at.%	PLQY, %	Absorptance (976 nm), %	Relative error, %	Absolute error, %
1	57.5	44.8	2.5	1.5
2	45.8	39.5	2.9	1.3
3	53.9	46.9	2.3	1.3
4	46.4	46.3	2.4	1.1
5	53.7	47.9	2.2	1.2

Table S10. Calculation of the error in the PLQY estimation for the series of YPO_4: yYb3Er samples under 976 nm excitation

Er^{3+}, at.%	PLQY, %	Absorptance (976 nm), %	Relative error, %	Absolute error, %
3	66.7	33.6	3.5	2.3
6	57.6	42.4	2.8	1.6
12	59.9	44.4	2.6	1.6
18	54.9	44.9	2.5	1.4
24	65.7	48.3	2.2	1.4
30	50.0	51.8	1.9	0.9

The relative error in the Brightness value is obtained by summing the relative errors of the PLQY and absorptance

Table S11. Calculation of the error in the Brightness estimation for the series of YPO_4: yYb3Er samples under 976 nm excitation

Er^{3+}, at.%	PLQY, %	Abs. (976 nm), %	Brightness	PLQY rel. error, %	Abs. rel error, %	Brightness rel. error, %	Brightness abs. error
3	66.7	33.6	0.22	3.49	0.02	3.51	0.01
6	57.6	42.4	0.24	2.76	0.02	2.78	0.01
12	59.9	44.4	0.27	2.59	0.01	2.60	0.01
18	54.9	44.9	0.25	2.54	0.01	2.55	0.01
24	65.7	48.3	0.32	2.20	0.01	2.21	0.01
30	50.0	51.8	0.26	1.85	0.01	1.86	<0.01