

Supporting information

Up-conversion luminophore with high quantum yield and brightness based on $\text{BaF}_2\text{:Yb}^{3+},\text{Er}^{3+}$ single crystals

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Raman spectrum

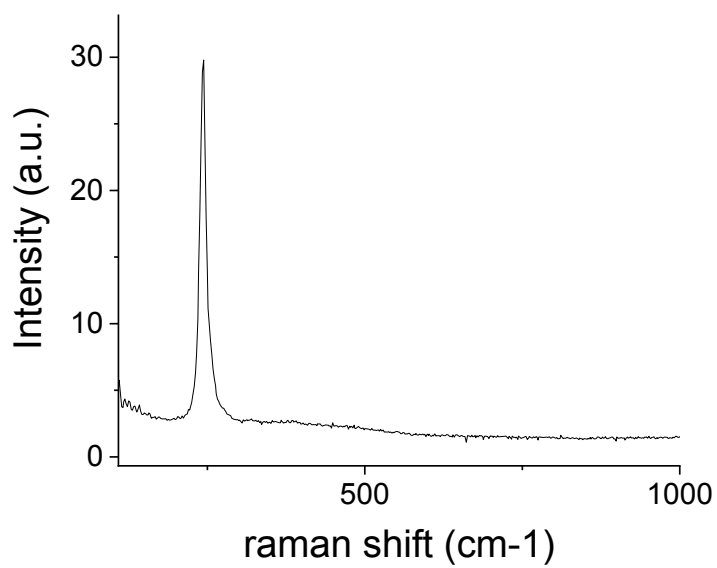


Figure S1. Raman spectrum of the undoped BaF₂ sample under 785 nm laser.

The Raman spectrum of the undoped BaF₂ sample contains a single peak at 240 cm⁻¹, which is expected maximum phonon energy of the BaF₂ matrix.

Doping concentrations, lattice constants and refractive indexes

Table S1. Nominal concentration in molar %, concentrations of the doping ions based on WDXRF and ions per cm³, unit cell parameters and refractive indexes (measured at 1520 nm) of the BaF₂ doped with Er³⁺, Yb³⁺.

Sample name	Er		Yb		a, Å	n
	mol.,%	N, 10 ²⁰ cm ⁻³	mol.,%	N, 10 ²⁰ cm ⁻³		
Er2Yb2	1,96	3.42	1,69	2.91	6.1785(2)	1.472
Er2Yb3	2.00	3.44	2.59	4.40	6.1645(4)	1.473
Er2Yb5	1.73	2.98	3.93	6.70	6.1588(8)	1.474
Er2Yb7	1.72	2.94	5.58	9.47	6.1442(9)	1.475
Er2Yb10	1.76	2.99	9.40	15.83	6.118(1)	1.475
Er2Yb15	1.86	3.15	11.98	20.06	6.100(2)	1.475
Er3Yb3	2.50	4.35	2.15	3.71	6.1664(4)	1.475
Er5Yb3	4.09	7.10	2.16	3.72	6.1560(6)	1.478
Er10Yb3	8.14	13.83	2.08	3.50	6.1320(8)	1.488
Er15Yb3	12.82	21.67	2.40	4.01	6.0961(7)	1.495

The unit cell parameter (a) was calculated based equation for cubic crystal system: $1/d^2 = (h^2 + k^2 + l^2)/a^2$, where h, k, l are Miller index and d is interplanar distance. The interplanar distance was calculated by the Wolfe-Bragg equation: $n\lambda = 2d\sin\Theta$. n is diffraction order and in our case is equal 1. λ is wavelength of CuK α radiation 1.54051 Å. Θ is angle of scanning. The calculation was carried out by the least square method. The error of calculation (ΔQ) was less 10. $\Delta Q = 10^4/d_{\text{theoretical}}^2 - 10^4/d_{\text{experimental}}^2$

Energy level diagram I

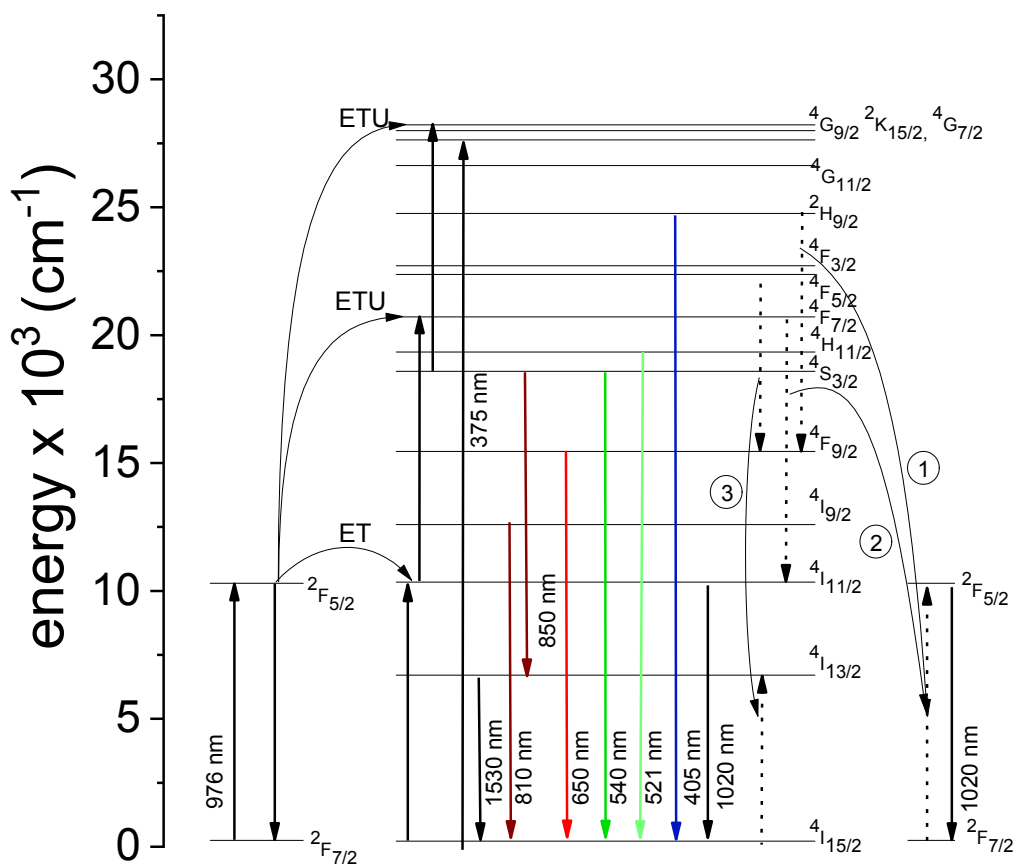


Figure S2. Energy level diagram of the Er^{3+} and Yb^{3+} ions as well as energy migration pathways under 375 nm excitation

The figure shows position of the observed emission bands on the Er^{3+} and Yb^{3+} ions (solid lines) and some resonant non-radiative transitions (dotted lines).

Energy level diagram II

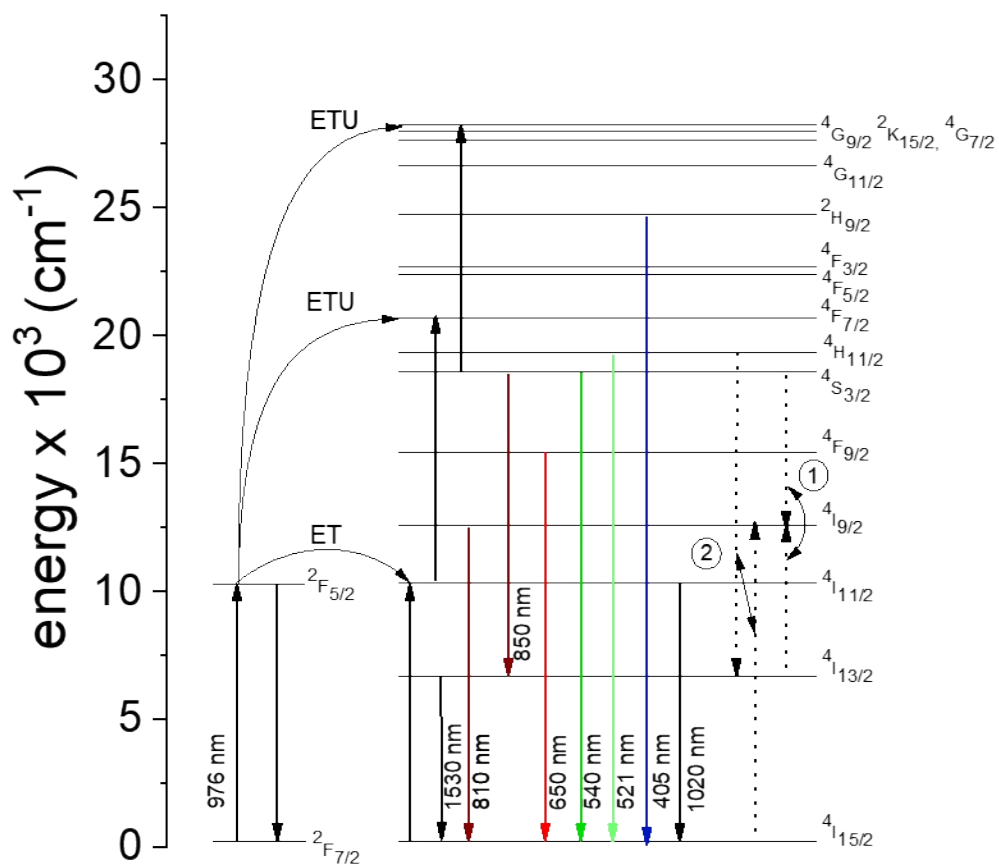


Figure S3. Energy level diagram of the Er^{3+} and Yb^{3+} ions as well as energy migration pathways under 976 nm excitation

Excitation spectra monitored at 660 nm.

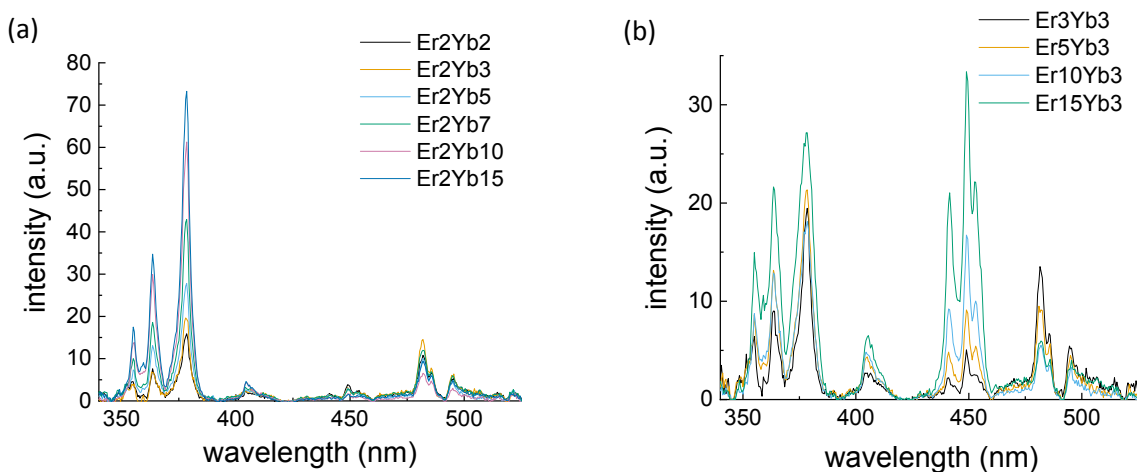


Figure S4. Excitation spectra detected at 660 nm ($^4F_{9/2} - ^4I_{15/2}$ transition of the Er^{3+} ions).

The increase in intensity of the excitation bands at wavelengths shorter than 400 nm at higher Yb^{3+} concentration is observed (Figure S4a). This suggests that $^4F_{9/2}$ can be populated *via* the $^2H_{9/2} \rightarrow ^4F_{9/2}$ transition in Er^{3+} resonant with the $\text{Yb}^{3+}: ^2F_{7/2} \rightarrow ^2F_{5/2}$ transition. The probability of this process is rising at higher Yb^{3+} concentrations. Almost negligible band around 450 nm in the samples with high Yb^{3+} concentration proves the existence of the transition from $^4F_{5/2}$ to $^4F_{3/2}$ and its resonance with the $^2F_{7/2} \rightarrow ^2F_{5/2}$ transition in the Yb^{3+} ions.

The growth of Er^{3+} concentration (Figure S4b) leads to the small rise in excitation bands with wavelengths shorter than 400 nm and strong increase in 450 nm excitation bands. The high intensity of the excitation band at 450 nm in the samples with high Er^{3+} concentration explicitly indicates the efficient non-radiative energy transfer (cross-relaxation) from higher $^4F_{5/2}$ and $^4F_{3/2}$ states to the lower $^4F_{9/2}$ state. These transitions (presented on energy level diagram in Figure S2) can be resonant with $\text{Er}^{3+}: ^4I_{15/2} \rightarrow ^4I_{13/2}$ transition. All of the proposed energy migration pathways are in line with the assumptions made in the discussion of the emission spectra and luminescence decay times.

Luminescence decay curves under 375nm and 976 nm excitation

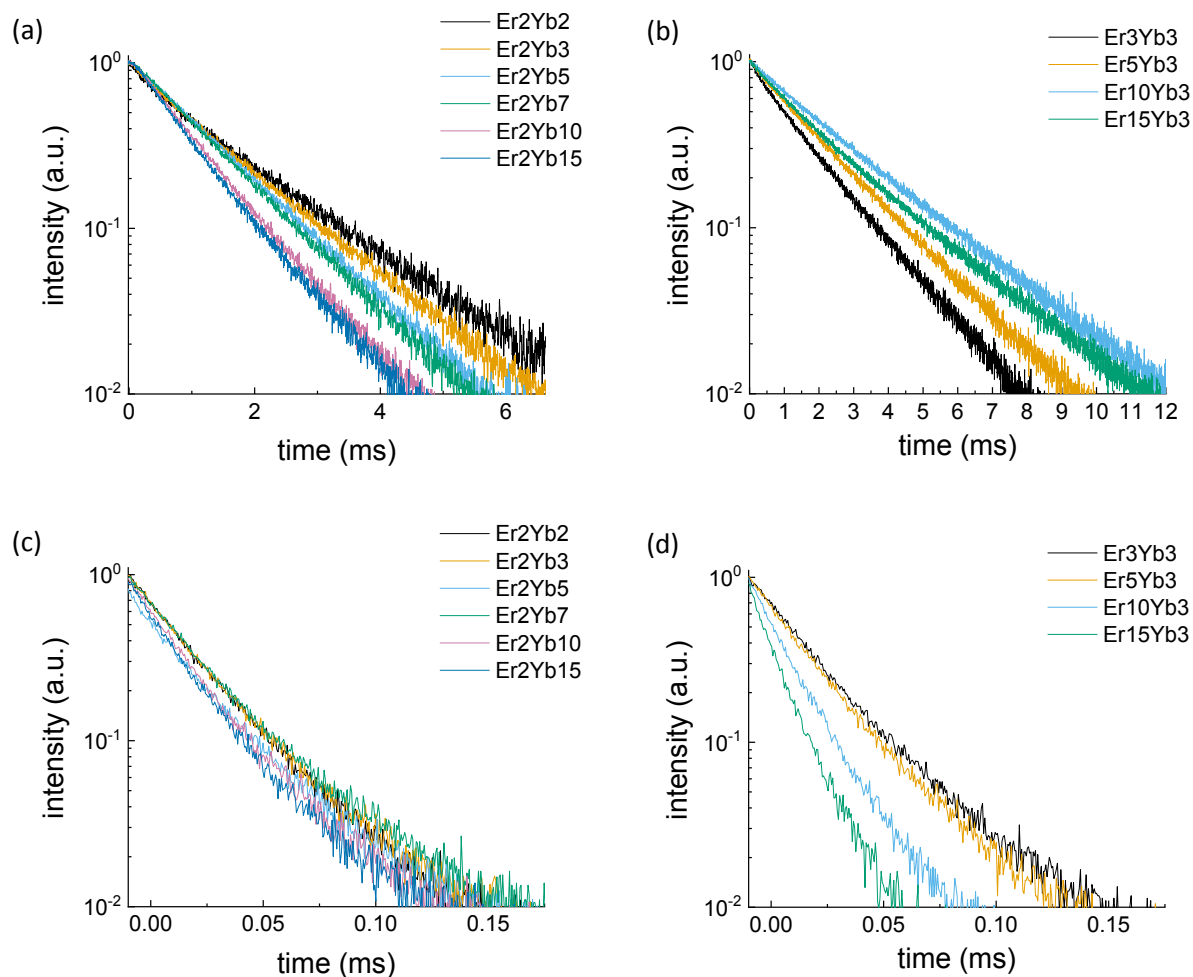


Figure S5. Luminescence decay curves monitored at 407 nm ($^2H_{9/2} - ^4I_{15/2}$ transition of the Er^{3+} ions). a), b) – 976 nm excitation, c), d) – 375 nm excitation

The luminescence lifetime under 375 nm excitation is significantly shorter. Under both excitation sources the decay curves can be fitted with a single exponent decay.

Luminescence decay curves under 375nm and 976 nm excitation

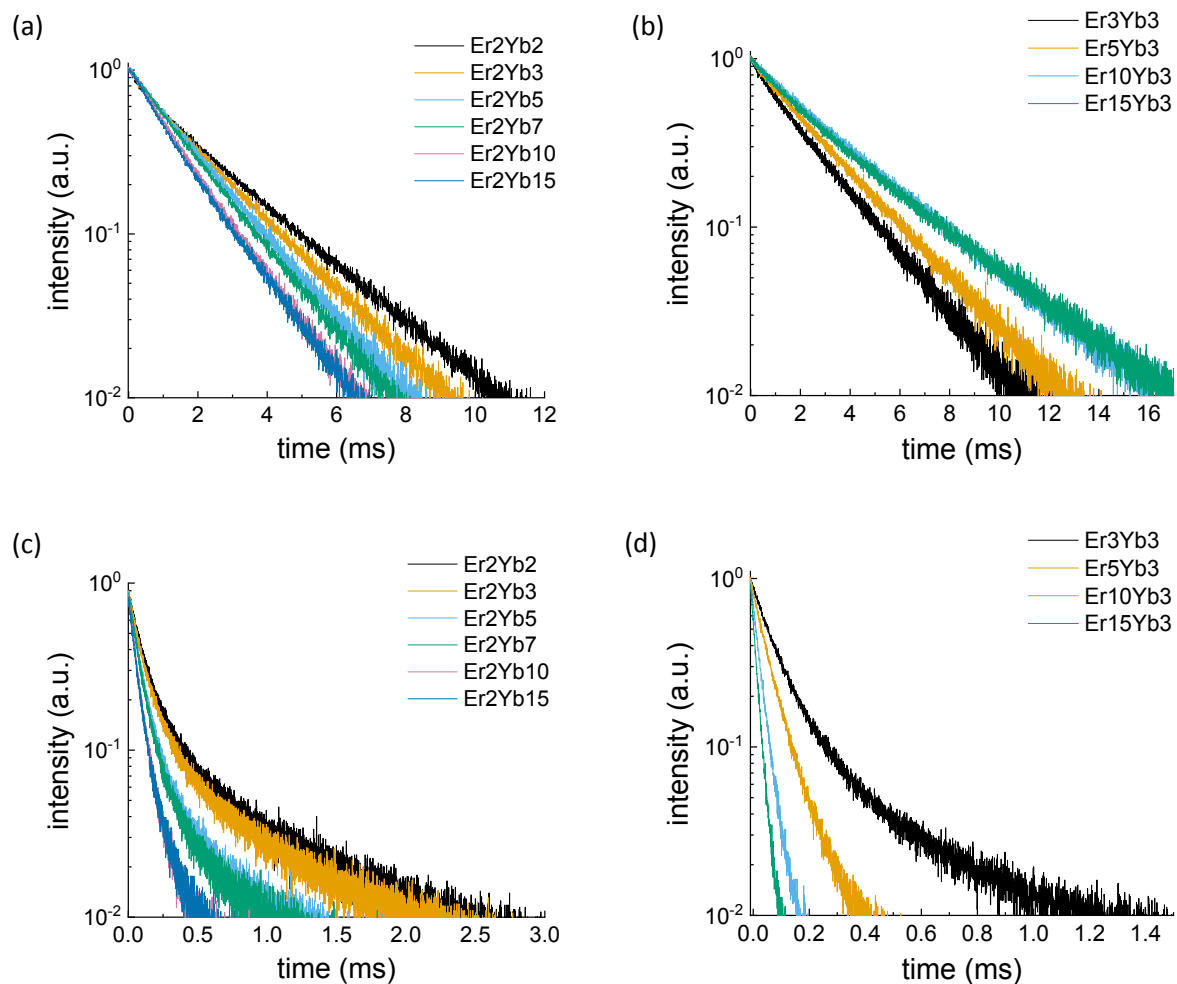


Figure S6. Luminescence decay curves monitored at 540 nm ($^4S_{3/2} - ^4I_{15/2}$ transition of the Er^{3+} ions). a), b) – 976 nm excitation, c), d) – 375 nm excitation

The decay curves obtained under 375 nm excitation exhibit non-single exponential behaviour, whereas luminescence decay under 976 nm is single exponential.

Luminescence decay curves under 375nm and 976 nm excitation

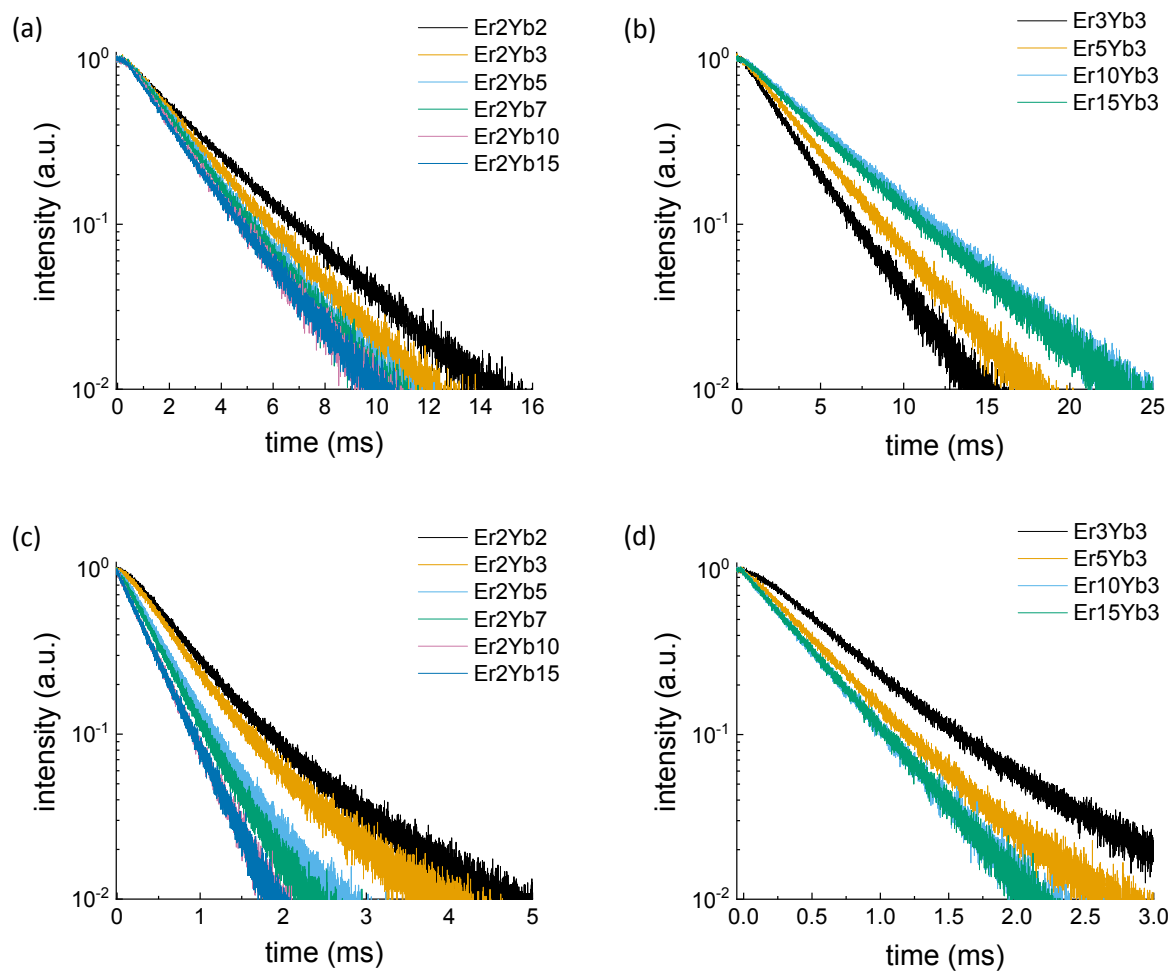


Figure S7. Luminescence decay curves monitored at 660 nm ($^4\text{F}_{9/2} - ^4\text{I}_{15/2}$ transition of the Er^{3+} ions). a), b) – 976 nm excitation, c), d) – 375 nm excitation

The decay curves of the samples with low doping concentrations obtained under 375 nm excitation exhibit non-single exponential behaviour. With the increase in doping concentration the curves become single exponential. Luminescence decay under 976 nm is single exponential.

Luminescence decay curves under 375nm and 976 nm excitation

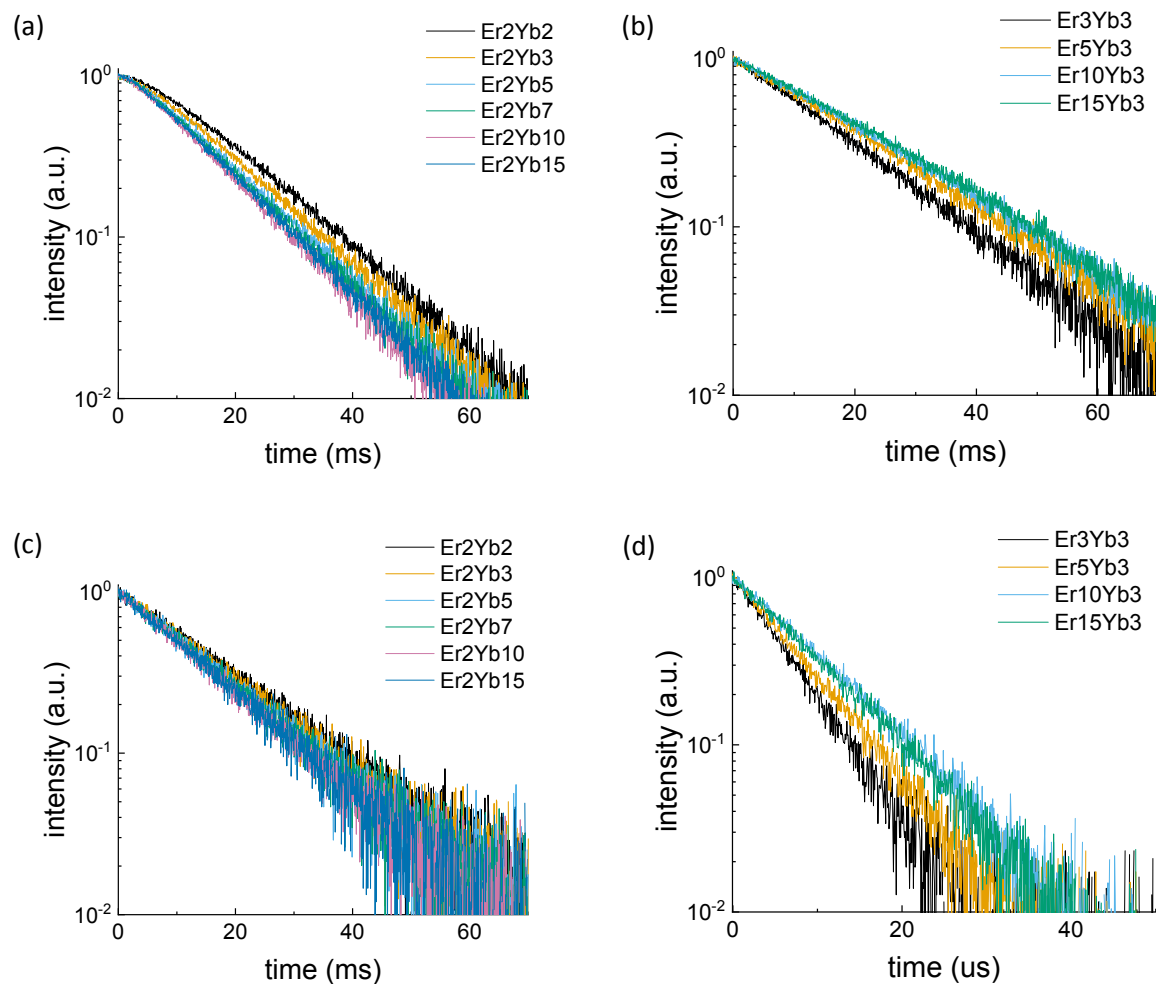


Figure S8. Luminescence decay curves monitored at 990 nm (transition from $\{\text{Er}^{3+}:^4\text{I}_{11/2} \& \text{Yb}^{3+}:^2\text{F}_{7/2}\}$ manifold. a), b) – 976 nm excitation, c), d) – 375 nm excitation.

The decay obtained under 375 nm and 976 nm excitation are almost indistinguishable in case of every sample.

Table S2. Luminescence decay times of $^4S_{3/2} \rightarrow ^4I_{15/2}$, and $^4F_{9/2} \rightarrow ^4I_{15/2}$ transitions of the Er^{3+} ions as well as $\{Er^{3+}:^4I_{11/2} \& Yb^{3+}:^2F_{7/2}\}$ manifold under 375 nm and 976 nm excitation, ms

	$Er^{3+}:^4S_{3/2} \rightarrow ^4I_{15/2}$ (540 nm)		$Er^{3+}:^4F_{9/2} \rightarrow ^4I_{15/2}$ (660 nm)		$\{Er^{3+}:^4I_{11/2} \rightarrow ^4I_{15/2}$ $Yb^{3+}:^2F_{5/2} \rightarrow ^2F_{7/2}\}$ (990 nm)	
	375	976	375	976	375	976
Er2Yb2	0.30	2.35	0.77	2.86	6.12	5.39
Er2Yb3	0.26	2.02	0.68	2.39	5.17	4.50
Er2Yb5	0.15	1.73	0.52	2.11	4.49	4.06
Er2Yb7	0.16	1.62	0.47	2.05	4.92	3.72
Er2Yb10	0.08	1.40	0.40	1.94	4.02	3.03
Er2Yb15	0.08	1.40	0.40	1.95	4.12	3.42
Er3Yb3	0.20	2.36	0.68	2.93	6.08	5.23
Er5Yb3	0.07	2.72	0.53	3.60	7.22	6.12
Er10Yb3	0.07	3.45	0.46	4.91	9.50	8.01
Er15Yb3	0.02	3.46	0.46	4.63	9.12	8.62
Er2Yb0						14.55
Er3Yb0						10.73
Er5Yb0						7.41
Er0Yb2						2.77
Er0Yb3						2.44
Er0Yb5						0.77

Decay times in single-doped BaF₂ crystals.

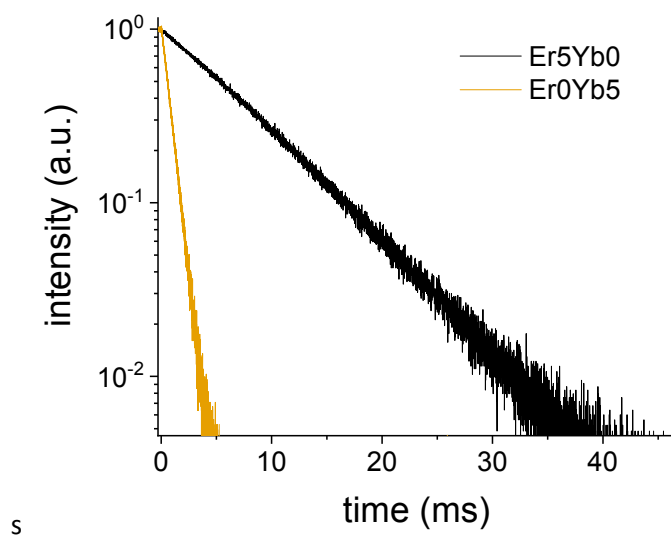


Figure S9. Luminescence decay curves monitored at 990 nm ($^4I_{11/2} - ^4I_{15/2}$ transition single-doped with Er³⁺ (5mol.%) BaF₂ crystal and $^2F_{5/2} - ^2F_{7/2}$ transition in single-doped with Yb³⁺ (5 mol. %) BaF₂ crystal. Excitation - 976 nm.

Table S3. ϕ_{UC} of several weak Er^{3+} emission bands in the 400 – 900 nm range under 976 nm excitation

	$Er^{3+}: {}^2H_{11/2} - {}^4I_{15/2}$ (521 nm)	$Er^{3+}: {}^4I_{9/2} - {}^4I_{15/2}$ (800 nm)	$Er^{3+}: {}^4S_{3/2} - {}^4I_{13/2}$ (850 nm)
Er2 Yb 2	<0.01	<0.01	0.01
Er 2 Yb 3	<0.01	<0.01	0.01
Er 2 Yb 5	<0.01	<0.01	0.01
Er 2 Yb 7	<0.01	<0.01	0.01
Er 2 Yb 10	<0.01	<0.01	0.01
Er 2 Yb 15	<0.01	<0.01	0.01
Er 3 Yb 3	<0.01	<0.01	0.01
Er 5 Yb 3	<0.01	<0.01	0.01
Er 10 Yb 3	0	<0.01	0.01
Er 15 Yb 3	0	<0.01	<0.01

The ϕ_{UC} under 976 nm excitation with power density of 490 W/cm² lowers with the increase of doping ion concentration. For the samples with high doping concentration of Er^{3+} ions the ϕ_{UC} of the ${}^2H_{11/2} - {}^4I_{15/2}$ transition is lower than signal/noise ratio and considered to be 0.

Table S4. ϕ_{DS} values of several Er^{3+} emission bands in the 405 – 850 nm range under 375 nm excitation

	405 nm	521 nm	540 nm	650 nm	800 nm	850 nm
	$^2\text{H}_{9/2} - ^4\text{I}_{15/2}$	$^2\text{H}_{11/2} - ^4\text{I}_{15/2}$	$^4\text{S}_{3/2} - ^4\text{I}_{15/2}$	$^4\text{F}_{9/2} - ^4\text{I}_{15/2}$	$^4\text{I}_{9/2} - ^4\text{I}_{15/2}$	$^4\text{S}_{3/2} - ^4\text{I}_{13/2}$
Er2 Yb 2	<0.01	<0.01	0.04	0.10	<0.01	0.03
Er 2 Yb 3	<0.01	0	0.02	0.06	<0.01	0.02
Er 2 Yb 5	<0.01	0	0.03	0.07	<0.01	0.02
Er 2 Yb 7	<0.01	0	0.03	0.06	<0.01	0.02
Er 2 Yb 10	<0.01	0	0.02	0.09	<0.01	0.01
Er 2 Yb 15	<0.01	0	0.01	0.08	<0.01	0.01
Er 3 Yb 3	<0.01	0	0.03	0.05	<0.01	0.02
Er 5 Yb 3	<0.01	0	0.02	0.03	<0.01	0.02
Er 10 Yb 3	0	0	0.01	0.02	<0.01	0.01
Er 15 Yb 3	0	0	<0.01	0.02	<0.01	<0.01

The indicator of crystal temperature at excitation with different intensity.

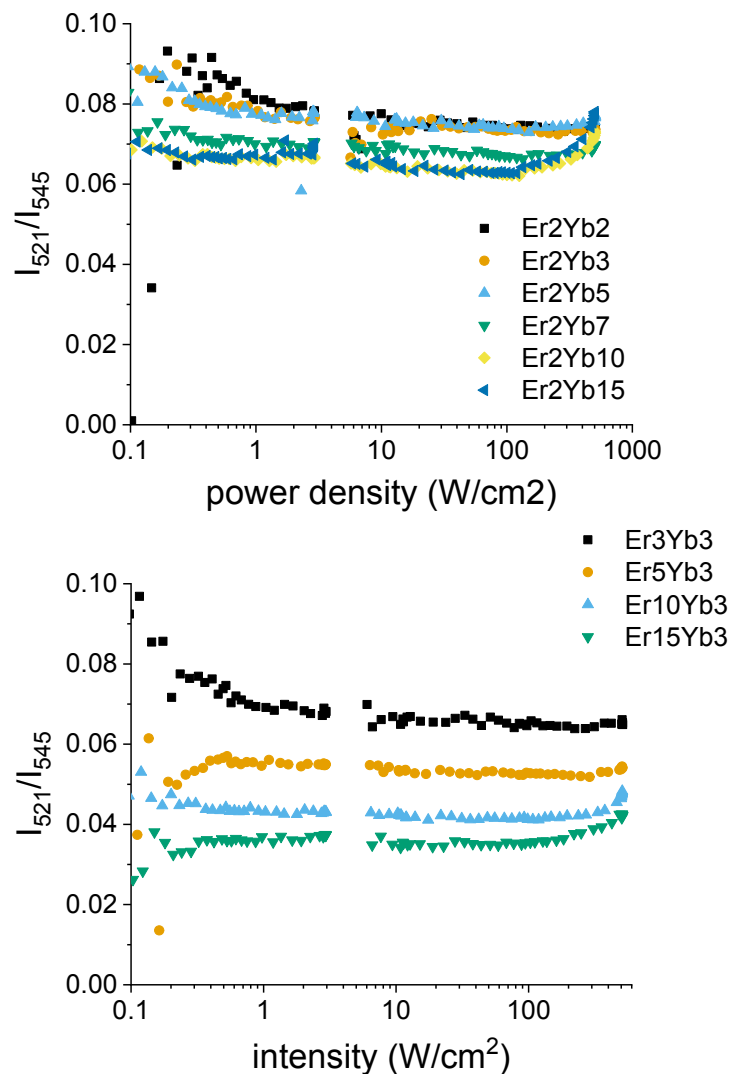


Figure S10. Ratio of the $^2H_{11/2} - ^4I_{15/2}$ (521 nm) and $^4S_{3/2} - ^4I_{15/2}$ (545 nm) emission bands of the Er^{3+} ion under 976 nm CW excitation.

The ratio of the $^2H_{11/2} - ^4I_{15/2}$ (521 nm) and $^4S_{3/2} - ^4I_{15/2}$ (545 nm) emission bands of the Er^{3+} ion is known to be indicative of the sample temperature [1]. This figure is meant to show that even at higher excitation power densities the temperature does not significantly deviate from the room temperature.

Critical Power density

Table S5. Critical power density of Er^{3+} : $^4\text{S}_{3/2} - ^4\text{I}_{15/2}$ emission band, W/cm^2

540 nm	
	$^4\text{S}_{3/2} - ^4\text{I}_{15/2}$
Er 2 Yb 10	1.0 ± 0.1
Er 2 Yb 15	1.1 ± 0.2
Er 10 Yb 3	2.1 ± 0.1
Er 15 Yb 3	1.2 ± 0.1

Table S6. ϕ_{DS} under direct excitation of the $^4\text{S}_{3/2}$, $^4\text{F}_{9/2}$ and $^4\text{I}_{13/2}$ levels of Er^{3+} ions.

	$^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$	$^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$	$^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$
Excitation wavelength, nm	522	652	1530
Er2Yb2	0.04	0.24	1.00
Er2Yb3	0.04	0.22	0.68
Er2Yb5	0.03	0.26	0.62
Er2Yb10	0.03	0.24	0.50
Er2Yb15	0.03	0.25	0.64
Er3Yb3	0.03	0.21	0.74
Er5Yb3	0.02	0.21	0.89
Er10Yb3	0.02	0.19	0.94
Er15Yb3	0.01	0.15	0.51

Down-shifting photoluminescence quantum yield (ϕ_{DS}).

Table S7. ϕ_{DS} of several Er^{3+} emission bands under 522 nm excitation

	650 nm	800 nm	850 nm
	$^4\text{F}_{9/2} - ^4\text{I}_{15/2}$	$^4\text{I}_{9/2} - ^4\text{I}_{15/2}$	$^4\text{S}_{3/2} - ^4\text{I}_{13/2}$
Er2 Yb 2	0.09	<0.01	0.02
Er 2 Yb 3	0.07	<0.01	0.02
Er 2 Yb 5	0.05	<0.01	0.02
Er 2 Yb 10	0.01	<0.01	0.02
Er 2 Yb 15	0.01	<0.01	0.02
Er 3 Yb 3	0.06	<0.01	0.02
Er 5 Yb 3	0.02	<0.01	0.01
Er 10 Yb 3	<0.01	<0.01	0.01
Er 15 Yb 3	<0.01	<0.01	<0.01

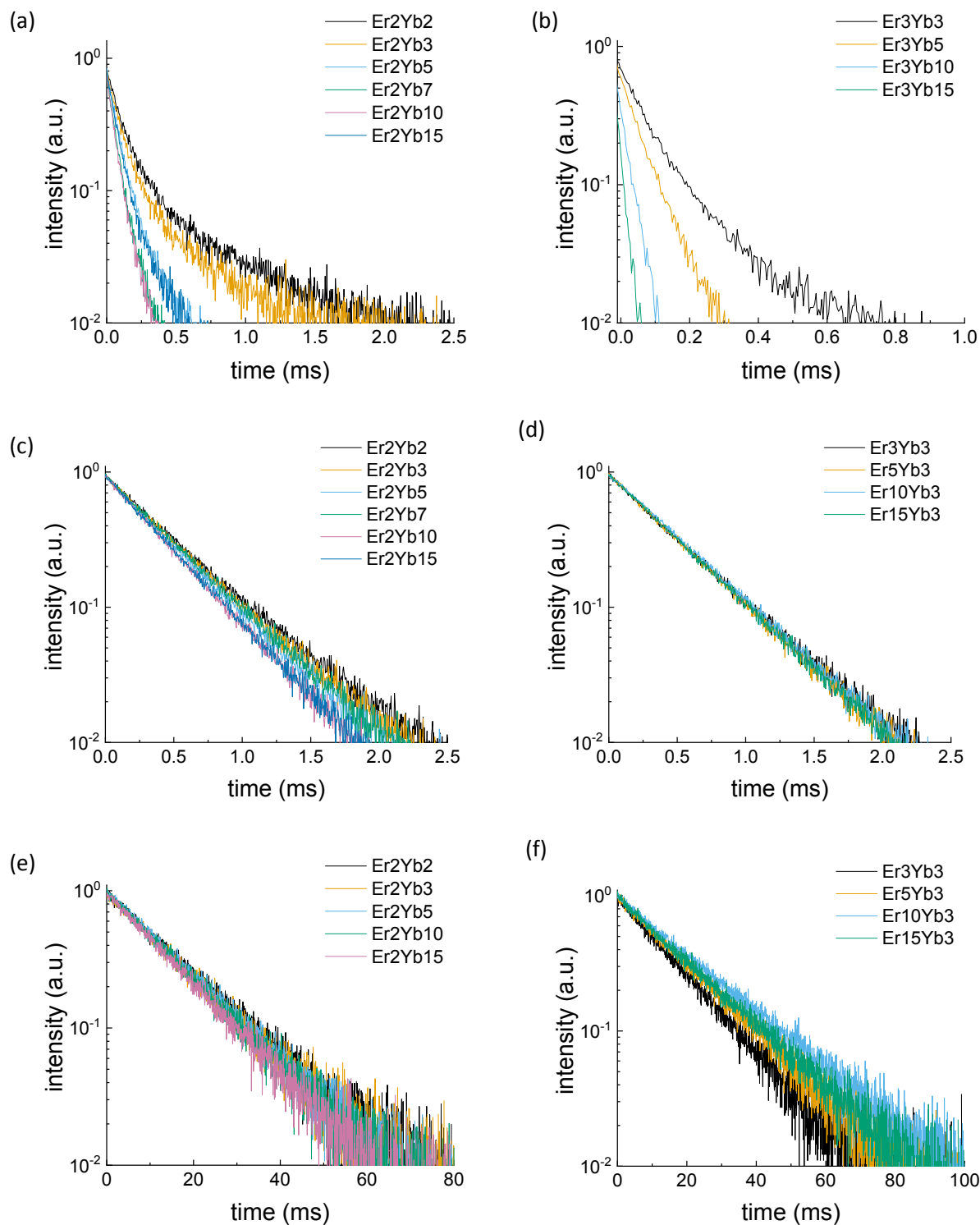


Figure S11. Luminescence decay curves of the a), b) $4S_{3/2} \rightarrow 4I_{15/2}$ transition upon 522 nm excitation; c), d) $4F_{9/2} \rightarrow 4I_{15/2}$ transition upon 652 nm excitation; e), f) $4I_{13/2} \rightarrow 4I_{15/2}$ transition upon 1550 nm excitation

Judd-Ofelt analysis

Absorption cross-section values calculated based on the absorption spectra (Figure 2) as well as concentration values from the elemental analysis. Due to the cubic symmetry of the BaF₂ lattice it is possible to use unpolarized spectra, which strongly simplifies the calculations. The absorption cross-sections allow calculating the line strengths via the use of eqn (5):

$$S_{meas} = \frac{3hc(2J+1)n}{3\pi^3\lambda_{mean}} \left[\frac{9}{(n^2+2)^2} \right] \int \sigma(\lambda) d\lambda \quad (5)$$

Where J is the total angular momentum quantum number of the initial state ($J = 15/2$ for Er³⁺ ion), n is the refractive index, λ_{mean} is the mean wavelength of the corresponding absorption band, $\int \sigma(\lambda) d\lambda$ is the integrated absorption cross-section. These values are then compared to the theoretically obtained ones via the eqn (6):

$$S_{JJ'}^{ed} = \sum_{t=2,4,6} \Omega_t | \langle (S,L),J || U^t || (S',L'),J' \rangle |^2$$

$$S_{JJ'}^{md} = \sum_{t=2,4,6} | \langle (S,L),J || L + 2S || (S',L'),J' \rangle |^2 \quad (6)$$

where Ω_2 , Ω_4 and Ω_6 are the Judd-Ofelt intensity parameters and $\langle U^t \rangle$ are the doubly reduced matrix elements of rank t ($t = 2, 4$ and 6), taken from the work by Carnall et al [2].

Table S8. Judd-Ofelt parameters, $\times 10^{20} \text{ cm}^2$

	Ω_2	Ω_4	Ω_6
Er2 Yb 2	0.95	0.49	1.45
Er 2 Yb 3	1.01	0.50	1.54
Er 2 Yb 5	1.18	0.74	1.94
Er 2 Yb 10	1.31	0.71	2.12
Er 2 Yb 15	1.32	0.60	2.16
Er 3 Yb 3	1.07	0.58	1.71
Er 5 Yb 3	1.04	0.70	1.88
Er 10 Yb 3	1.06	0.80	2.44
Er 15 Yb 3	0.94	0.63	2.36

An application of least-squares fitting between experimental and theoretical strengths provides Judd-Ofelt (Ω_2 , Ω_4 and Ω_6) parameters (Table S8). Thereafter these parameters are used to obtain probabilities of the spontaneous transition between two levels as eqn (7):

$$A(J \rightarrow J') = \frac{32\pi^3 c \alpha_f n^2}{3(2J+1)\lambda_{mean}^3} \left(\frac{(n^2+2)^2}{9n} S_{JJ'}^{ed} + S_{JJ'}^{md} \right) \quad (7)$$

where α_f is the fine structure constant.

Table S9. Comparison of the radiative lifetimes (τ_r) of the Er^{3+} emission bands obtained via Judd – Ofelt approach and decay lifetimes obtained experimentally (τ), ms. β is the branching ratio of the corresponding transition.

	τ_r , ms	β	τ , ms	ϕ_{DS}^{calc}
Er2Yb2				
$^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$	1.13	0.67	0.21	0.13
$^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$	2.25	0.89	0.47	0.19
$^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$	12.11	1.00	14.97	>1
Er2Yb3				
$^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$	1.06	0.67	0.16	0.10
$^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$	2.15	0.89	0.45	0.19
$^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$	11.69	1.00	14.29	>1
Er2Yb5				
$^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$	0.84	0.67	0.10	0.08
$^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$	1.63	0.90	0.43	0.24
$^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$	10.04	1.00	14.38	>1
Er2Yb10				
$^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$	0.77	0.67	0.07	0.06
$^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$	1.55	0.89	0.39	0.22
$^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$	9.46	1.00	13.80	>1
Er2Yb15				
$^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$	0.76	0.67	0.07	0.06
$^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$	1.59	0.89	0.40	0.23
$^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$	9.38	1.00	13.24	>1
Er3Yb3				

$^4S_{3/2} \rightarrow ^4I_{15/2}$	0.95	0.67	0.11	0.08
$^4F_{9/2} \rightarrow ^4I_{15/2}$	1.91	0.89	0.47	0.22
$^4I_{13/2} \rightarrow ^4I_{15/2}$	10.91	1.00	15.38	>1
Er5Yb3				
$^4S_{3/2} \rightarrow ^4I_{15/2}$	0.87	0.67	0.06	0.05
$^4F_{9/2} \rightarrow ^4I_{15/2}$	1.69	0.90	0.45	0.24
$^4I_{13/2} \rightarrow ^4I_{15/2}$	10.24	1.00	17.60	>1
Er10Yb3				
$^4S_{3/2} \rightarrow ^4I_{15/2}$	0.67	0.67	0.03	0.03
$^4F_{9/2} \rightarrow ^4I_{15/2}$	1.35	0.89	0.43	0.28
$^4I_{13/2} \rightarrow ^4I_{15/2}$	8.58	1.00	17.19	>1
Er15Yb3				
$^4S_{3/2} \rightarrow ^4I_{15/2}$	0.69	0.67	0.02	0.02
$^4F_{9/2} \rightarrow ^4I_{15/2}$	1.47	0.89	0.45	0.27
$^4I_{13/2} \rightarrow ^4I_{15/2}$	8.83	1.00	18.20	>1

References

- [1] Joseph, Reetu E., et al. "A method for correcting the excitation power density dependence of upconversion emission due to laser-induced heating." *Optical materials* 82 (2018): 65-70.
- [2] Carnall, W. T., et al. "A systematic analysis of the spectra of the lanthanides doped into single crystal LaF₃." *The Journal of Chemical Physics* 90.7 (1989): 3443-3457.