

Supplementary Information

Electronic and optical properties of Er-doped Y₂O₂S phosphors

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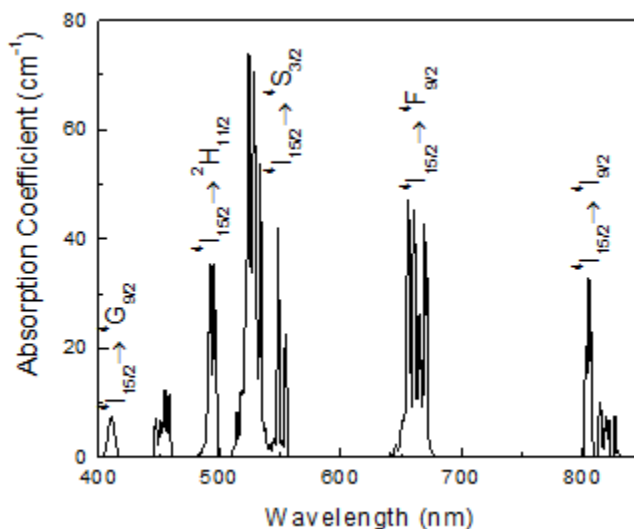


Figure S1. Absorption spectrum of Y₂O₂S:10%Er³⁺ in the range of 400 to 850 nm. Most of the other narrow bands in the absorption spectrum are corresponds to the f–f transition of Er³⁺ ions.

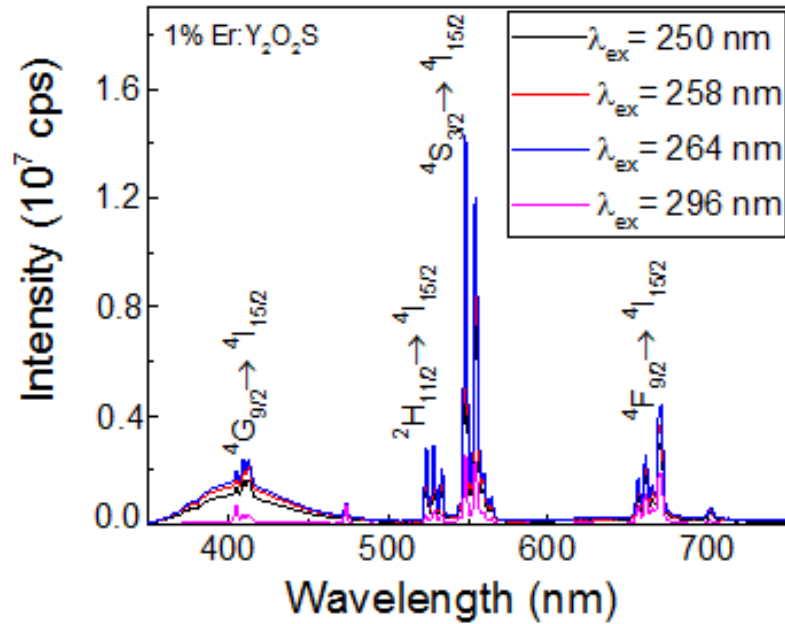


Figure S2. Emission spectra of $\text{Y}_2\text{O}_3\text{:1\%Er}^{3+}$ in the range of 350 to 850 nm under UV excitations.

At 296 nm excitation corresponding to CTB of $\text{Er}^{3+}\text{-S}^{2-}$, the broad emission at 410 nm is absent in the spectrum. Spectra also indicates that green emission intensity is much higher compared to those of red and UV, especially at lower Er doping. Furthermore, the green level was shown to decay faster than the red one (737 μs and 767 μs decay times, respectively). These results confirm that the green and red emitting levels are populated via the same route at lower Er doping concentration, which may be the tickling down of the excited state ion in the order.

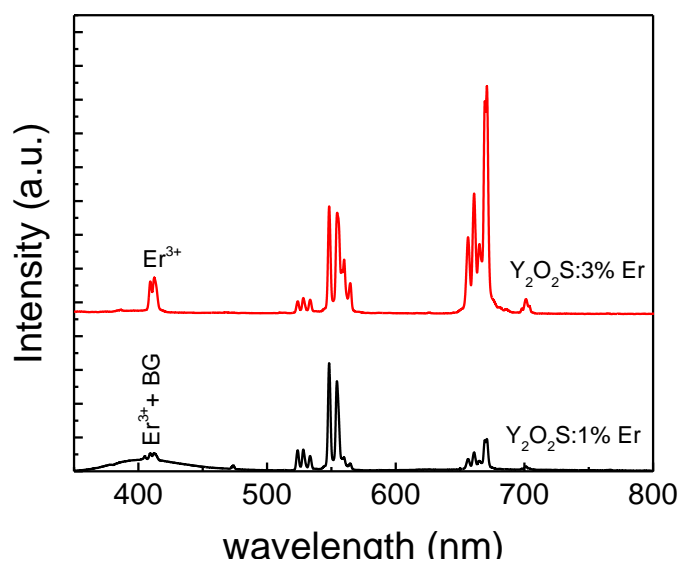


Figure S3. Downconversion (Stokes) emission spectra of the $\text{Y}_2\text{O}_2\text{S}:1\%\text{Er}^{3+}$ and $\text{Y}_2\text{O}_2\text{S}:3\%\text{Er}^{3+}$ phosphors under 250 nm excitation. The suppression of the bandgap related broad emission (350 to 500 nm) at or higher Er^{3+} doping (above 3%) could be clearly observed. This phenomenon confirms that the energy transfer from the $\text{Y}_2\text{O}_2\text{S}$ host to Er^{3+} dopants is nonradiative at higher Er^{3+} doping concentrations.

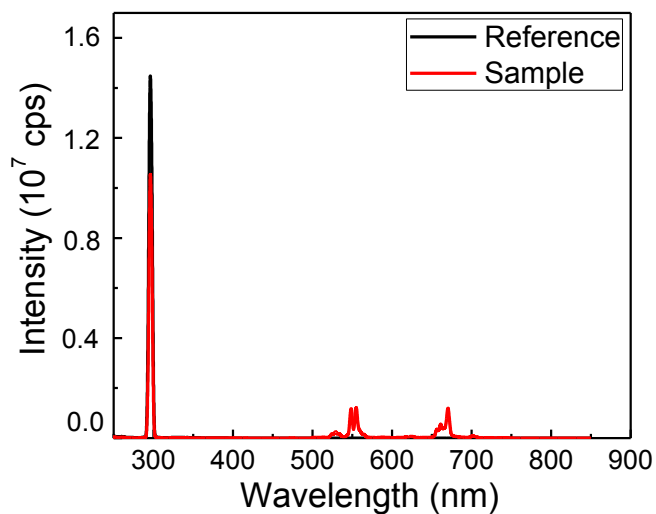


Figure S4. Representative fluorescence spectrum in the range of 500-750 nm were collected after diffuse reflectance from the samples relative to a non-absorbing standard (BenFlect) at the excitation wavelength range of 250-300 nm, specifically here at 296 nm, under the same condition using TE-cooled photo-multiplier tube (Hamamatsu, Model R928P).

For the absolute QY measurements, integrating sphere was employed in an Edinburgh Instruments FLS980 fluorometer. To be consistent with all experiments performed, the same sample weight (90 mg) and monochromator slit size (3 nm for both excitation and emission

monochromaters) were kept identical for all experiments, i.e. the same setup was used to compare fluorescence intensities between samples. Fluorescence spectra in the range of 500-750 nm were collected after diffuse reflectance from the samples relative to a non-absorbing standard (BenFlect) at the excitation wavelength range of 250-300 nm, specifically, 250, 258, 264, and 296 nm, under the same condition using TE-cooled photo-multiplier tube (Hamamatsu, Model R928P) as exemplified in Figure S3 under 296 nm excitation. The QY was measured by finding the ratio of the area under the emission spectra to the difference in corrected area under the diffuse reflectance of the excitation spectra for the sample and the reference as shown in equation below.

$$QY = \frac{NP_{emitted}}{NP_{absorbed}} = \frac{\int N_{em} d\lambda}{\int N_{abs} d\lambda} = \frac{A_{sample}}{A_{reference} - A_{sample}},$$

Including all the possible errors, such as reflectivity of the reference (< 3%), particle size effects (< 2%), and diffuse reflectance from the sample holder (< 3%), we estimated the error in the calculated QYs is about 10%. Similarly, we estimated the fluctuation of the excitation power is about 2%. The excitation power was measured to be 6 mW. Calculated QYs were tabulated in Table S1 below.

Table S1. Absolute downconversion (Stokes) QYs measured for selected Er³⁺ doping concentrations of the Y₂O₂S:x%Er³⁺ phosphors under 250 nm, 258 nm (above and at the host band gap edge), 264 nm (CTB band, Er³⁺-O²⁻), and 296 nm (CTB band Er³⁺-S²⁻) excitations.

λ_{ex} (nm)	Samples	Green (550 nm)	Red (667 nm)	Total (QY)%
250 nm	Y ₂ O ₂ S:10%Er	1.32 ± 0.13	7.71 ± 0.77	9.03 ± 0.9
	Y ₂ O ₂ S:7%Er	1.64 ± 0.16	2.99 ± 0.29	4.63 ± 0.46
	Y ₂ O ₂ S:1%Er	6.50 ± 0.65	2.79 ± 0.27	9.29 ± 0.92
258 nm	Y ₂ O ₂ S:10%Er	1.07 ± 0.10	7.53 ± 0.75	8.6 ± 0.86
	Y ₂ O ₂ S:7%Er	1.52 ± 0.15	2.73 ± 0.27	4.25 ± 0.42
	Y ₂ O ₂ S:1%Er	5.63 ± 0.56	2.42 ± 0.24	8.05 ± 0.80
264 nm	Y ₂ O ₂ S:10%Er	1.84 ± 0.18	5.32 ± 0.53	7.16 ± 0.71
	Y ₂ O ₂ S:7%Er	1.54 ± 0.15	2.73 ± 0.27	4.27 ± 0.42
	Y ₂ O ₂ S:1%Er	5.66 ± 0.56	2.38 ± 0.23	8.04 ± 0.80
296 nm	Y ₂ O ₂ S:10%Er	2.33 ± 0.23	7.02 ± 0.70	9.35 ± 0.93
	Y ₂ O ₂ S:7%Er	2.04 ± 0.20	4.00 ± 0.40	6.04 ± 0.60
	Y ₂ O ₂ S:1%Er	3.26 ± 0.32	2.89 ± 0.28	6.15 ± 0.61

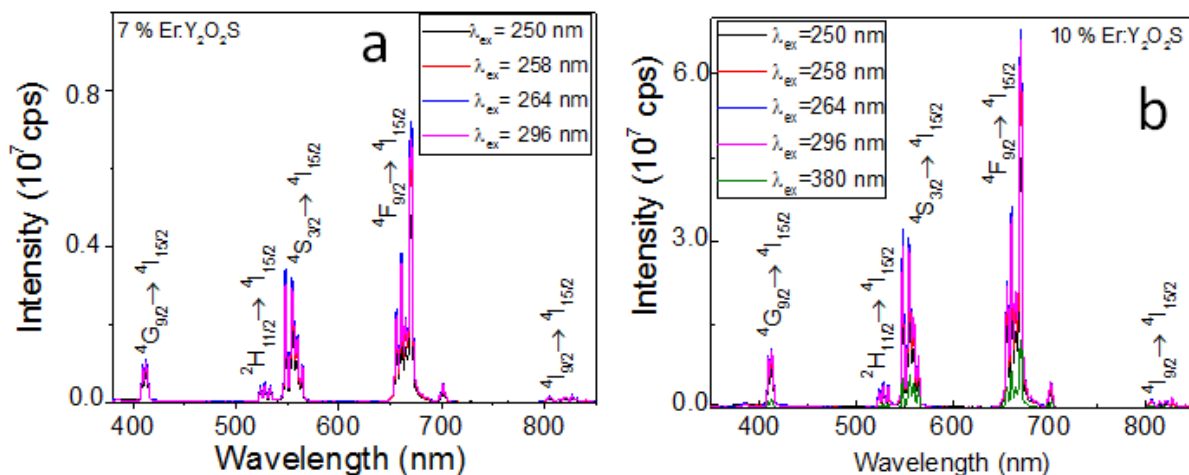


Figure S5. Emission spectra of $Y_2O_2S:x\%Er^{3+}$ ($x = 7$ and 10) in the range of 350 to 850 nm under UV excitations. However, at higher Er doping concentrations, red emission intensity is much higher compared to those of green and UV emissions. These results confirm that the green and red emitting levels are populated via the different route at higher Er doping concentration, which may be mostly dominated by the cross-relaxation between the Er^{3+} ions.

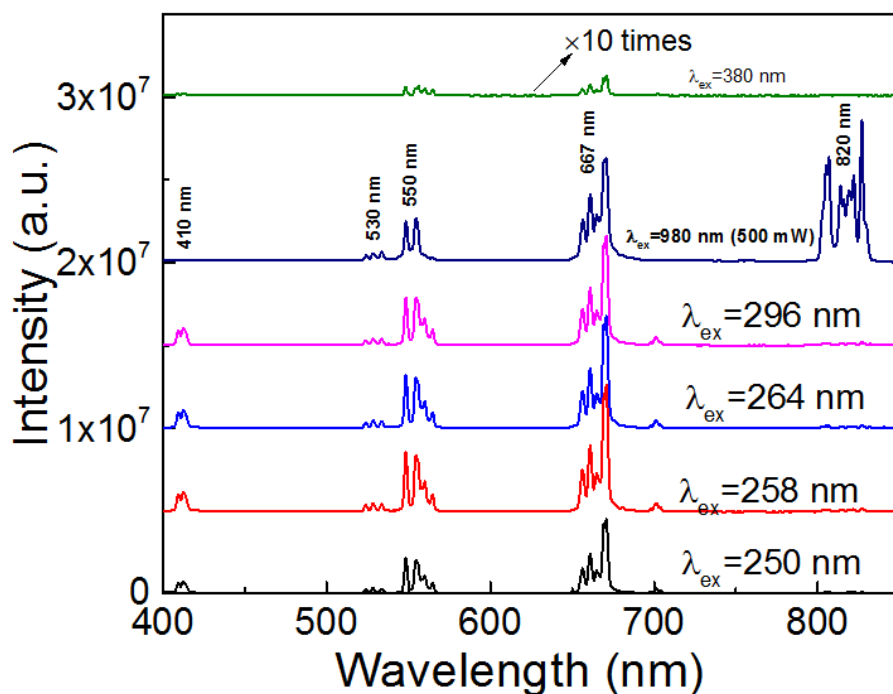


Figure S6. Emission spectra of the $Y_2O_2S:10\%Er^{3+}$ phosphor in the range of 350 to 850 nm under UV (250, 258, 264, and 296) and NIR (980 nm) excitations. At high Er doping concentrations, red emission intensity is much higher compared to that of green and UV emissions under 980 nm excitation based on this offset Y plot. This clearly shows that two different intermediate levels of Er^{3+} are involved in the UC mechanisms populating the green ($^4S_{3/2}$, $^2H_{11/2}$) and red ($^4F_{9/2}$) emitting levels of Er^{3+} . According to our experimental results, the population mechanism involved intermediate levels in the red energy level ($^4F_{9/2}$), which is $^4I_{13/2}$

via the Er^{3+} to Er^{3+} energy transfer. Note that the $^4\text{I}_{13/2}$ level is populated by nonradiative relaxation from the upper lying $^4\text{I}_{11/2}$ level as shown in energy level diagram (Figure 11). The lifetime of the $^4\text{I}_{13/2}$ level is much longer than that of others which makes the possibility of populating directly the red emitting level $^4\text{F}_{9/2}$ of Er^{3+} more favorable than populating the $^4\text{F}_{7/2}$ of Er^{3+} (i.e. populating the green emitting level of Er^{3+} from $^4\text{F}_{7/2} \rightarrow (^4\text{S}_{3/2}, ^2\text{H}_{11/2})$ energy transfer), and finally populate $^4\text{F}_{9/2}$ through the multiphonon relaxation. This also explains the high UC QY for red emission compared to QY for green emission observed in these materials when excited at 980 nm.

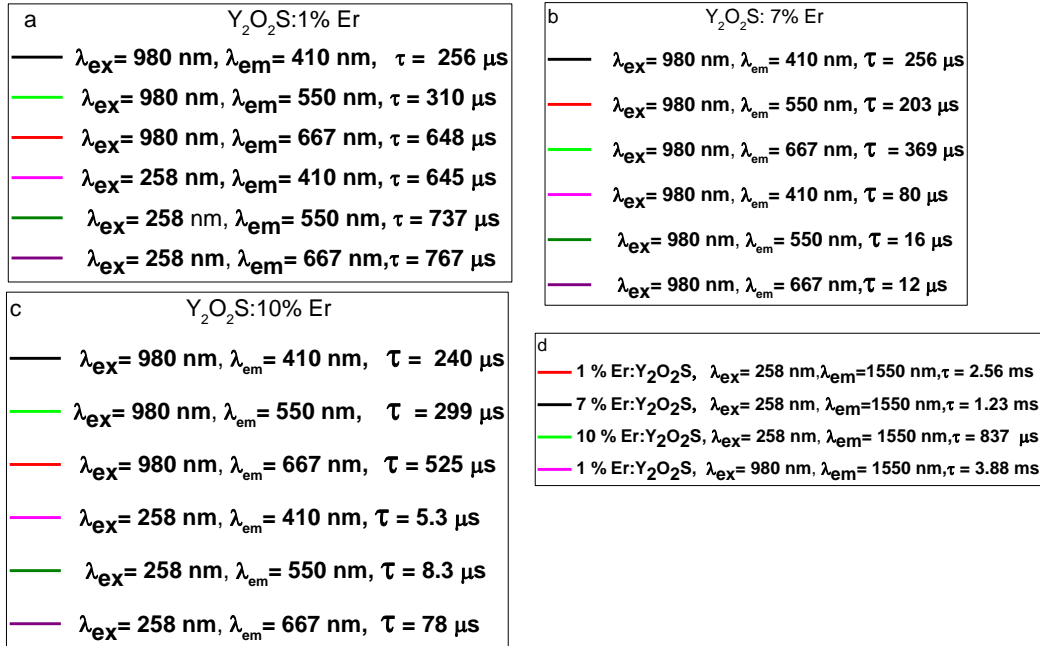


Figure S7. Fitted decay lifetimes of Er^{3+} excited states of (a) $\text{Y}_2\text{O}_2\text{S}:1\%\text{Er}^{3+}$, (b) $\text{Y}_2\text{O}_2\text{S}:7\%\text{Er}^{3+}$, and (c) $\text{Y}_2\text{O}_2\text{S}:10\%\text{Er}^{3+}$ after pulse excitations at 258 and 980 nm for UV (410 nm), green (550 nm) and red (667 nm) emissions, (d) $\text{Y}_2\text{O}_2\text{S}:x\%\text{Er}^{3+}$ ($x = 1, 7$ and 10) after pulse excitations at 258 and 980 nm for NIR (1550 nm) emission.

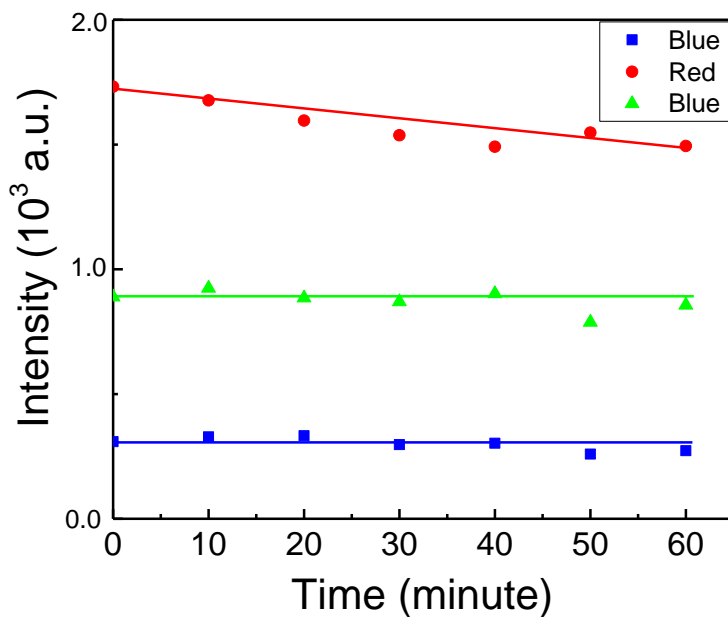


Figure S8. Variations of PL intensity over exposure time for blue, green and red emissions under X-ray excitation at tube voltage of 130 KV (5mA). Sample of the $Y_2O_2S:10\% Er^{3+}$ phosphor was irradiated for a total of 60 minutes in the same X-ray cabinet. Spectral data was collected every 10 minutes. The area of each emission peak was calculated and the resulting values were plotted vs. X-ray irradiation time to determine the photostability of the $Y_2O_2S:10\% Er^{3+}$ phosphor under X-ray irradiation.