Supporting information

Color Tunable Upconversion in Er\textsuperscript{3+}/Yb\textsuperscript{3+} Co-doped KLaF\textsubscript{4} Nanophosphors by Incorporation of Tm\textsuperscript{3+} Ions for Biological Applications

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**Supplementary Table S1:** Calculated structural Parameters of un-doped and 0 to 5% Tm$^{3+}$ codoped KLaF$_4$: 1%Er$^{3+}$/ 20%Yb$^{3+}$ nanocrystals from XRD data.

| Sample   | Lattice constant $a$ [Å] | $d_{hkl}$ [Å] | Lattice strain ($\varepsilon$ or $n$) $\times 10^{-2}$ | Particle size (nm) |
|----------|--------------------------|---------------|---------------------------------|-------------------|
| Undoped  | 5.93                     | 3.422         | 1.05                            | 7.79              |
| 0% Tm$^{3+}$ | 5.92                     | 3.420         | 1.57                            | 7.53              |
| 1% Tm$^{3+}$ | 5.83                     | 3.368         | 1.67                            | 6.57              |
| 2% Tm$^{3+}$ | 5.82                     | 3.365         | 3.00                            | 6.41              |
| 3% Tm$^{3+}$ | 5.81                     | 3.352         | 3.38                            | 6.02              |
| 4% Tm$^{3+}$ | 5.80                     | 3.349         | 4.20                            | 6.00              |
| 5% Tm$^{3+}$ | 5.75                     | 3.325         | -3.23                           | 5.52              |

**Supplementary Table S2:** The effective phonon energies obtained from Raman Spectra.

| Sample   | Phonon Energy (cm$^{-1}$) |
|----------|---------------------------|
| undoped  | 316                       |
| 0:1:20   | 318                       |
| 1:0:20   | 324                       |
| 1:1:20   | 337                       |
| 1:2:20   | 351                       |
| 1:3:20   | 358                       |
| 1:4:20   | 362                       |
| 1:5:20   | 367                       |
Supplementary Figure S1: Excitation Power dependent Upconversion PL spectra of (a) 1%Er$^{3+}$/20%Yb$^{3+}$ (b)1%Tm$^{3+}$/20%Yb$^{3+}$ (c)1%Er$^{3+}$/1%Tm$^{3+}$/20%Yb$^{3+}$ codoped KLaF$_4$ samples. Excited with 980nm CW diode laser at various powers, as shown.

Supplementary Table S3: Slope (n) values at two pump powers of Figure 6.

| Emission band | KLaF$_4$:Er$^{3+}$/Yb$^{3+}$ | KLaF$_4$:Tm$^{3+}$/Yb$^{3+}$ | KLaF$_4$:Er$^{3+}$/Tm$^{3+}$/Yb$^{3+}$ |
|---------------|-------------------------------|-------------------------------|----------------------------------|
|               | low power | High power | low power | High power | low power | High power |
| 450 nm        |           |            | 3.35±0.09  | 0.59±0.21  |           |            |
| 472 nm        |           |            | 2.46±0.08  | 0.41±0.03  | 2.94±0.08  | 1.52±0.16  |
| 545 nm        | 1.24±0.03 | 0.18±0.07  |           |            | 2.0±0.06  | 1.07±0.18  |
| 654 nm        | 2.05±0.04 | 0.45±0.09  | 2.53±0.07  | 0.82±0.25  | 1.92±0.06  | 0.84±0.12  |

Lattice strain calculation

The lattice strain was calculated using the Williamson-Hall expression

$$\frac{\beta \cos \theta}{\lambda} = \frac{1}{D} + \frac{\varepsilon \sin \theta}{\lambda}$$

(1)
Where, $\beta$ defines full width at half maxima, $D$ (nm) is the crystallite size. The micro strain ($\varepsilon$ or $n$) is the slope of the linear graph of $\beta \cos \theta / \lambda$ vs $\sin \theta / \lambda$.

**Band gap evaluation:** The band gap ($E_g$) of synthesized materials was calculated using the Kubelka-Munk function and Tauc relationship for the direct band gap.

$$[F(R_\infty)h\nu] = C_1(h\nu - E_g)^m$$  \hspace{1cm} (2)

Where, $m=1/2$ for direct band gap and $m=2$ for indirect band gap, $F(R_\infty)$ defines Kubelka-Munk function and evaluated from the relationship

$$F(R_\infty) = \frac{K}{S} = \frac{(1 - R_\infty)^2}{2R_\infty}$$  \hspace{1cm} (3)

Where K and S indicate absorption and scattering coefficients and $R_\infty$ is the ratio of reflectance of sample and reflectance of non-absorbing standard sample BaSO$_4$.

**Rate Equations:**
In this paper, we have utilised a theoretical model$^4$ to better understand the inter-ionic ET and EBT processes in tri-doped KLaF$_4$ host lattice. In all the tri-doped samples, the concentration ratio of Er$^{3+}$ to Yb$^{3+}$ is fixed at 1:20 and Tm$^{3+}$ content varies from 0 to 5 mol%. Therefore, it is reasonable to predict that ET from Yb$^{3+}$ to Er$^{3+}$ (or Tm$^{3+}$) due to the much larger cross section (~15 times) of Yb$^{3+}$ is the main source of population for blue, green and red emissions at 980 nm excitation. The rate equations are expressed as follows:

$$\frac{dN_1}{dt} = w_b N_4 N_{Yb0} + w_{21} N_2 - w_{11} N_{Yb1} N_1 - A_1 N_1$$  \hspace{1cm} (4)

$$\frac{dN_2}{dt} = w_0 N_0 N_{Yb1} + w_{22} N_2 - w_{12} N_2 - w_{21} N_{Yb2} N_{Yb1} - w_{44} N_2 N_{Yb2} - A_2 N_2$$  \hspace{1cm} (5)
\[
\frac{dN_2}{dt} = w_3 N_4 N_{0'} - w_{2/2} N_{2'} 
\]
\[
\frac{dN_3}{dt} = w_1 N_4 N_{Yb1} + w_{43} N_4 + w_4 N_2 N_{1'} - A_3 N_3 
\]
\[
\frac{dN_4}{dt} = w_2 N_2 N_{Yb1} - w_{43} N_4 - w_3 N_4 N_{0'} - w_b N_4 N_{Yb0} - A_4 N_4 
\]
\[
\frac{dN_{Yb1}}{dt} = \rho \sigma N_{Yb0} + w_b N_4 N_{Yb0} - \sum_i w_i N_i N_{Yb1} - A_{Yb1} N_{Yb1} 
\]

Where \( \sigma \) is absorption cross section of \( ^2F_{5/2} \) state of \( \text{Yb}^{3+} \), \( \rho \) is pump rate (\( \rho \propto P, P \) is incident pump power). \( N_i \) (\( i = 0, 1, 2, 3, 4 \)), \( N_{2'}, N_{0'}, N_{1'}, N_{Yb0} \) and \( N_{Yb1} \) are the population densities of \( \text{Er}^{3+} \) \( ^4I_{15/2}, ^4I_{13/2}, ^4I_{11/2}, ^4F_{9/2}, ^2H_{11/2} / ^4S_{3/2} / ^4F_{7/2}, ^4I_{9/2} \) states (thermally coupled \( ^2H_{11/2}, ^4S_{3/2} \) and \( ^4F_{7/2} \) states are treated as one), \( \text{Tm}^{3+} \) \( ^3H_6, ^3F_4, ^3\text{Yb}^{3+} \) \( ^2F_{7/2} \) and \( ^2F_{5/2} \) levels respectively. \( w_i \) (\( i = 0, 1, 2, 3, 4 \)) and \( w_b \) are the energy transfer rates corresponding to ET1: \( ^2F_{5/2}(\text{Yb}^{3+}) + ^4I_{15/2}(\text{Er}^{3+}) \rightarrow ^2F_{7/2}(\text{Yb}^{3+}) + ^4I_{11/2}(\text{Er}^{3+}) \), ET2: \( ^2F_{5/2}(\text{Yb}^{3+}) + ^4I_{13/2}(\text{Er}^{3+}) \rightarrow ^2F_{7/2}(\text{Yb}^{3+}) + ^4F_{9/2}(\text{Er}^{3+}) \), ET3: \( ^2F_{5/2}(\text{Yb}^{3+}) + ^4I_{11/2}(\text{Er}^{3+}) \rightarrow ^2F_{7/2}(\text{Yb}^{3+}) + ^4F_{7/2}(\text{Er}^{3+}) \), ET4: \( ^4S_{3/2}(\text{Er}^{3+}) + ^3H_6(\text{Tm}^{3+}) \rightarrow ^4I_{9/2}(\text{Er}^{3+}) + ^3F_4(\text{Tm}^{3+}) \), ET5: \( ^3F_4(\text{Tm}^{3+}) + ^4I_{11/2}(\text{Er}^{3+}) \rightarrow ^3H_6(\text{Tm}^{3+}) + ^4F_{9/2}(\text{Er}^{3+}) \) and EBT from \( \text{Er}^{3+} \) to \( \text{Yb}^{3+} \): \( ^2H_{11/2} / ^4S_{3/2}(\text{Er}^{3+}) + ^2F_{7/2}(\text{Yb}^{3+}) = ^4I_{13/2} \) (\( \text{Er}^{3+} \)) + \( ^2F_{5/2} \) (\( \text{Yb}^{3+} \)) followed by ET2, respectively. \( w_{21}, w_{2/2} \) and \( w_{43} \) are non-radiative (NR) rates from \( ^4I_{11/2} \rightarrow ^4I_{13/2}, ^4I_{9/2} \rightarrow ^4I_{11/2} \) and \( ^4F_{7/2} \rightarrow ^4F_{9/2} \) of \( \text{Er}^{3+} \) ions, respectively. \( A_i \) (\( i = 1, 2, 3, 4 \)) and \( A_{Yb1} \) are the radiative rates of the \( \text{Er}^{3+} \) \( ^4I_{13/2}, ^4I_{11/2}, ^4F_{9/2}, ^2H_{11/2} / ^4S_{3/2} / ^4F_{7/2} \) and \( \text{Yb}^{3+} \) \( ^2F_{5/2} \), respectively.

At low pump powers, the depletion mechanism of \( ^4I_{11/2} \) state takes place through ET3 process. In this condition, we can neglect the corresponding ET3 term from equation 5. At high \( \text{Yb}^{3+} \) content, many radiative and non-radiative processes are omitted, for examples: CR process.
between Er$^{3+}$ ions, EBT process from Er$^{3+}$ to Yb$^{3+}$, NR processes and so on. The rate equations at study state are as follows:

\begin{align}
  w_{21}N_2 - w_1N_1N_{Yb1} &= 0 \\ 
  w_0N_0N_{Yb1} - w_{21}N_2 - w_4N_2N_1 &= 0 \\ 
  w_3N_4N_{0r} - w_{2/2}N_{2r} &= 0 \\ 
  w_1N_1N_{Yb1} + w_{43}N_4 + w_4N_2N_1 + A_3N_3 &= 0 \\ 
  w_2N_2N_{Yb1} - w_{43}N_4 - w_3N_4N_{0r} - A_4N_4 &= 0
\end{align}

(10) \hspace{1cm} (11) \hspace{1cm} (12) \hspace{1cm} (13) \hspace{1cm} (14)

\[ N_{Yb1} = \frac{\rho\sigma N_{Yb0}}{\sum_i w_i N_i - A_{Yb1}} \propto P \]

(15)

By solving above equations $N_3$ and $N_4$ can be expressed as

\[ N_4 = \frac{w_0w_2N_0N_{Yb1}^2}{[(w_{21} + N_{1'w_4})(N_0'w_3 + A_4 + w_{43})]} \propto P^2 \]

(16)

\[ N_3 = \frac{w_0N_0N_{Yb1}}{A_3} + \frac{w_0w_2w_{43}N_0N_{Yb1}^2}{A_3[(w_{21} + N_{1'w_4})(N_0'w_3 + A_4 + w_{43})]} \propto aP^1 + bP^2 \]

(17)

Red to green ratio

\[ \frac{N_3}{N_4} = \frac{(w_{21} + N_{1'w_4})(N_0'w_3 + A_4 + w_{43}) + w_2w_{43}N_{Yb1}}{A_3w_2N_{Yb1}} \propto P^{-1} \]

(18)

Equations (16) and (17) indicate that both green and red emitting manifolds $N_4 \propto P^2$ and $N_3 \propto P^2$ $(a \approx 0)$ have quadratic dependence on the pump power. Which are in good agreement with the
experimental results \((n_{\text{red}} = 1.92 \text{ and } n_{\text{green}} = 2.0)\) presented in figure 6 and table S3. As can be seen from equation (18), red to green ratio has inverse proportional relationship with pump power. At high pump power, ET2 and ET3 are much more efficient processes over linear decay of \(4_{13/2} \text{ and } 4_{11/2}\) states. Therefore many radiative and non-radiative processes can be neglected in equation 5. We have

\[
N_4 = \frac{w_0 N_0 N_{Yb1}}{(N_{o} w_3 + A_4 + W_{43})} \propto P^1
\]  

(19)

\[
N_3 = \frac{w_0 N_0 (w_{21} + N_4 w_4)}{w_2 A_3} + \frac{w_0 w_{43} N_0 N_{Yb1}}{A_3 [(N_{o} w_3 + A_4 + W_{43})]} \propto P^1
\]  

(20)

As can be seen from equations (19) and (20), at high pump power, both green and red emissions \(N_4 \propto P^1\) and \(N_3 \propto P^1\) become a single photon absorption process. This shows good agreement with results shown in figure 6 and table S3. Finally, we summarize the key findings on the basis of power dependence measurements: first, at low pump power in tri-doped KLaF\(_4\) host lattice, two photon upconversion processes is needed for green and red emitting manifolds while at high pump power, the population of \(2H_{11/2}/4S_{3/2}\) and \(4F_{9/2}\) states become independent of pump power. The saturation effect leads reduction in power dependence of red and green emissions from \(P^2\) to \(P^1\) respectively. The experimental results presented in figure 6 and listed in table S3 agree well with theoretical considerations and explains abnormal dependence on pump power.

The temporal evolutions of blue \((1G_4 - 3H_6)\), green \((2H_{11/2}/4S_{3/2} - 4I_{15/2})\) and red \((4F_{9/2} - 4I_{15/2})\) emitting levels measured for doped samples under 980 nm pulsed laser excitation have been done figure S2 (a-d). The calculated life times for blue, green and red emitting levels are shown in figure S2 (e). The ET efficiency between Er\(^{3+}\) and Tm\(^{3+}\) ions is further estimated\(^3\) from the experimentally measured radiative lifetimes of the Er\(^{3+}\): \(2H_{11/2}/4S_{3/2}, 4F_{9/2}\) and Tm\(^{3+}\): \(1G_4\) states S7
from the equation \( \eta = 1 - \left( \frac{\tau}{\tau_0} \right) \). Where \( \tau_0 \) and \( \tau \) are the lifetimes of the sample without and with Tm\(^{3+} \) content, respectively.
(b) $^2\text{H}_{11/2}$ $\rightarrow ^4\text{I}_{15/2}$ (545 nm)

Intensity (a.u.)

| $x$ | $\tau$ (ms) |
|-----|-------------|
| 0   | 0.155      |
| 1   | 0.142      |
| 2   | 0.136      |
| 3   | 0.131      |
| 4   | 0.148      |
| 5   |            |

(c) $^4\text{S}_{3/2}$ $\rightarrow ^4\text{I}_{15/2}$ (554 nm)

Intensity (arb. units)

| $x$ | $\tau$ (ms) |
|-----|-------------|
| 0   | 0.238      |
| 1   | 0.228      |
| 2   | 0.154      |
| 3   | 0.151      |
| 4   | 0.143      |
| 5   | 0.137      |
Supplementary Figure. S2: UC emission decay curves of x.0 wt.% Tm$^{3+}$ (x = 0 to 5) co-doped KLaF$_4$: 1%Er$^{3+}$/20%Yb$^{3+}$ nanophosphors (a), (b), (c), (d) (e) Concentration dependence of calculated lifetimes and (f) energy transfer efficiency versus Tm$^{3+}$ ions concentration for blue, green and red emissions. The data point (●) is for 1%Tm$^{3+}$/20%Yb$^{3+}$ doping at 472 nm.
The main findings from the life time measurements are: (1) the red and blue emitting levels have longer life time than the green emitting level. It means the red Er\(^{3+}:4{F}_{9/2}\) and blue Tm\(^{3+}:1{G}_{4}\) states populate in longer time than the green Er\(^{3+}:2{H}_{11/2}/4{S}_{3/2}\) state. The red emission can be attributed to the CR process: 
\[
4{S}_{3/2}\ (\text{Er}^{3+}) \rightarrow 4{I}_{9/2}\ (\text{Er}^{3+}) \rightarrow 4{I}_{11/2}\ (\text{Er}^{3+}) \rightarrow 3{F}_{4}\ (\text{Tm}^{3+}) \rightarrow 4{F}_{9/2}\ (\text{Er}^{3+})
\]
between Er\(^{3+}\) and Tm\(^{3+}\) while green emission does not require this additional time due to the absence of CR process. (2) In the tri-doped sample KLaF\(_{4}:1\%\text{Er}^{3+}/1\%\text{Tm}^{3+}/20\%\text{Yb}^{3+}\), the decay lifetimes of the Er\(^{3+}:2{H}_{11/2}/4{S}_{3/2}, 4{F}_{9/2}\) levels are shorter than the co-doped KLaF\(_{4}:1\%\text{Er}^{3+}/20\%\text{Yb}^{3+}\) sample. While the life time of Tm\(^{3+}:1{G}_{4}\) level does not change significantly from the co-doped KLaF\(_{4}:1\%\text{Tm}^{3+}/20\%\text{Yb}^{3+}\) sample. It can be explained that the energy transfer between Er\(^{3+}\) and Tm\(^{3+}\) are not processed through higher states (1{G}_{4}, 1{D}_{2}) of Tm\(^{3+}\) dopant. (3) The lifetime of blue, red and green emissions decreases while ET efficiency \(\eta\) increases systematically with the increase of Tm\(^{3+}\) ions doping as shown in figure S2. On increasing concentration of Tm\(^{3+}\) content, lifetime of green emitting level decrease more quickly in comparison to red emitting level. This observation once again supports the existence of the proposed CR process between Er\(^{3+}\) and Tm\(^{3+}\).

The down conversion (DC) spectra for all doped samples have been recorded under 405 nm, 60 mW diode laser excitation figure S3. Unlike the upconversion , the down conversion spectra contain a broad green emission in the range 462-730 nm, corresponding to the transitions Er\(^{3+}:2{H}_{11/2}/4{S}_{3/2} - 4{I}_{15/2}, 4{F}_{0/2} - 4{I}_{15/2} + \text{ Tm}^{3+}: 1{D}_{2} - 3{F}_{4} 1{G}_{4} - 3{H}_{6}, 3{F}_{3,2} - 3{H}_{6}. The intensity of this overlapping peak increased monotonically with the increase of Tm\(^{3+}\) content. Such an enhancement is expected due to depopulation of Tm\(^{3+}:3{F}_{4}\) state by direct radiation. The down conversion measurements and log (Integrated intensity) vs. log (pump power) curves for 1\%Er\(^{3+}/1\%\text{Tm}^{3+}/20\%\text{Yb}^{3+}\) doped host lattice measured after excitation of 405 nm is shown in
The slope value \( n = 1.15 \) depicts that down conversion process involves single photon absorption process.

**Supplementary Figure. S3:** Down-conversion emission spectra of KLaF\(_4\): 1\%Er\(^{3+}\) / (0-5) %Tm\(^{3+}\) / 20\%Yb\(^{3+}\) samples with ~ 60 mW 405nm diode laser.

**Supplementary Figure. S4:** Down-conversion emission spectra of 1\%Er\(^{3+}\)/1\%Tm\(^{3+}\)/20\%Yb\(^{3+}\) doped KLaF\(_4\) samples excited at various powers along with integrated intensity vs excitation laser power plot for 553nm emission line. Th excitation is from 405 nm CW diode laser.
Supplementary Figure S5: Upconversion emission spectra of (a) 1%Er³⁺/20%Yb³⁺ (b) 1%Tm³⁺/20%Yb³⁺ (c) 1%Er³⁺/1%Tm³⁺/20%Yb³⁺ (d) 1%Er³⁺/2%Tm³⁺/20%Yb³⁺ excited at various excitation wavelengths, spanning 690-1040nm. The average power is fixed at 30mW.
Supplementary Figure S6: Comparison of UC-PLE with diffused reflectance spectra (black color).

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