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


**Supplementary Information:**

Fig. S1 shows an absorption spectrum of a hydrothermal 0.2 at % $Tm^{3+}$ doped $K_2YbF_5$ crystal measured by an UV-VIS-NIR spectrophotometer Perkin-Elmer Lambda 9 with a resolution of 0.5 nm. It can be clearly seen the large and absorption peak corresponding to the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of $Yb^{3+}$ ions at around 980 nm, which are resonant with many commercial NIR continuous-wave laser diodes. On the other hand, due to the high absolute concentration of $Yb^{3+}$ ions in $K_2YbF_5$, namely about $8\times10^{21}$ at/$cm^3$, and low concentration quenching, the totality of $Yb^{3+}$ ions acts as an efficient collector of NIR photons the energy of which is transferred to an insignificant number of $Tm^{3+}$ ions, less than $1.6 \times10^{19}$, through energy migration over the $Yb^{3+}$-sublattice. By taking into account the zoomed details of the SEM images (see inset in Fig. S1), it can clearly be seen that there are laminar structures on the face of a $K_2YbF_5$ crystal, which points to the two-dimensional layer growth of the crystals under hydrothermal conditions causing their optical quality.

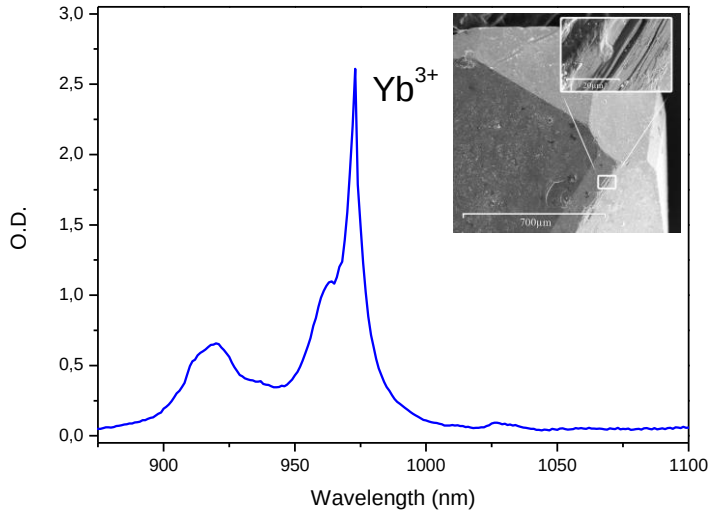


**Fig. S1.** Absorption spectra of a hydrothermal 0.2 at% $Tm^{3+}$-doped $K_2YbF_5$ crystal. Inset shows SEM images for the face of a $K_2YbF_5$ crystal.

Next, Fig. S2 illustrates the up-conversion mechanisms that give rise to the intense UV-VIS $Tm^{3+}$ emissions under 980 nm laser excitation of $Yb^{3+}$ ions in $K_2YbF_5$ crystals doped with $Tm^{3+}$. In that respect, it is well-known that RE ions are of the most promising suitable candidates for up-conversion generation due to their long lifetime excited states, narrow spectral lines and multiple emissions in the visible range (Ref. [1,2]). In particular, $Yb^{3+}$-$Tm^{3+}$ is a very efficient system for up-conversion energy transfer (ET), giving rise to UV-VIS light after NIR pumping. Energy donor $Yb^{3+}$ ions act as sensitizer antennas for energy acceptor $Tm^{3+}$ ions, due to large absorption cross-section at 980 nm ($^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition), and subsequently highly efficient non-resonant ET from the $Yb^{3+}$:$^2F_{5/2}$ state to the $Tm^{3+}$:$^3H_5$ state, followed by additional excited-state absorption mechanisms to higher energy levels, yielding to intense UV and blue up-conversion emissions.

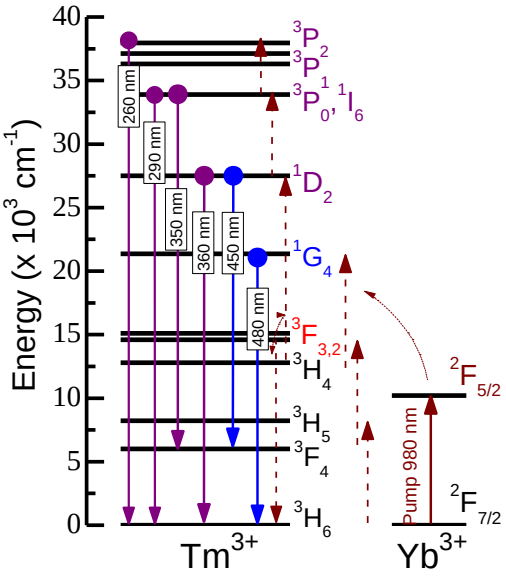


**Fig. S2.** Energy level diagrams of $Yb^{3+}$ and $Tm^{3+}$ ions along with the scheme of up-conversion mechanisms.

Finally in Fig. S3, we present a luminescence quantum efficiency estimation of UC processes for a 0.1 at% $Tm^{3+}$-doped $K_2YbF_5$ crystal under continuous-wave laser diode at 980 nm with a power up to 300 mW focused with a 4X micro-objective lens. It should be mentioned that an accurate determination of the absolute quantum efficiency of UC processes presently constitutes a controversial matter, which is reflected in that fact that many reviews of potential

materials (e.g., Ref. [2,17]) often disregard some critical discussion or calculation of up-conversion quantum yield. Alternatively, a simple quantitative method has been proposed by Suyver et al. (Ref. [26]) and hereafter it has been used by many other authors to characterize UC luminescent materials. Within this formalism, the intensity of the up-conversion emission is characterized in terms of a comparative band area evaluation of the UC spectra, where the actual photon flux is determined on emission spectra, so as to determine the number of up-converted photons relative to the total number of NIR excitation photons absorbed by the material. Here a very similar way to analyze the UC emission spectra of a 0.1 at % $Tm^{3+}$ doped $K_2YbF_5$ crystal is used. Additionally, in this area calculation, the number of photons emitted in each up-conversion band corresponding to 2-, 3-, 4 and 5-photon up-conversion processes is multiplied by factor of 2, 3, 4 and 5 respectively, which is also depicted in Fig. S3 in order to appreciate the fact that in these UC processes, absorption of multiple infrared (980nm) photons are involved. Within this scheme, we have calculated a relatively high value of around 36% for this crystal, representing in this case the fraction of the total UC photons emitted from the sample which overlaps the absorbance wavelength range of the photo-initiator (see Fig. S1), and therefore, contribute to the photo-polymerization and ensuing curing process of the photo-sensible resins.

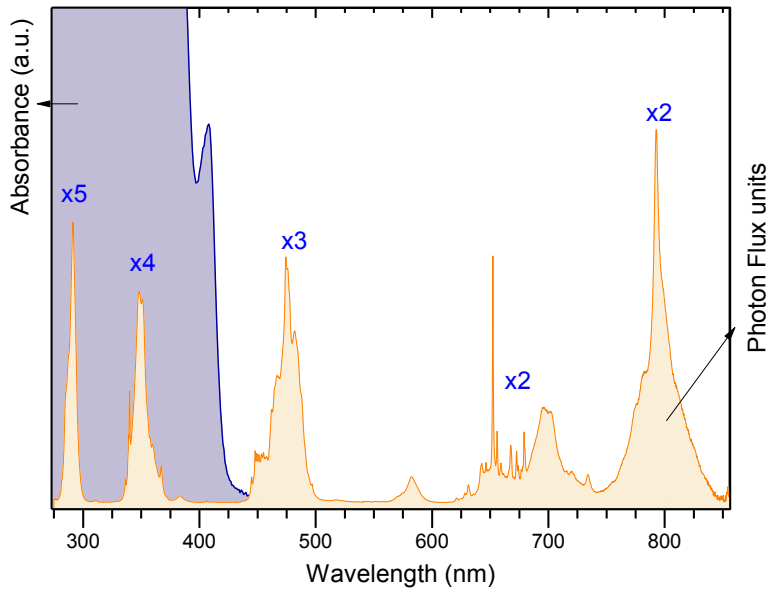


**Fig. S3.** Up-conversion UV-VIS emission spectrum of a 0.1 at % $Tm^{3+}$-doped $K_2YbF_5$ crystal under 980 nm excitation for 300 mW pump power in photon flux units and absorption spectrum of UV-sensible photoinitiator Irgacure-819®