Electronic Supplementary Information

Multi-photon upconversion luminescence from Ca_xYF_{3+2x} host by doping Yb^{3+}/Er^{3+} or Yb^{3+}/Tm^{3+} †

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Experimental details

Materials. Rare earth oxides Y_2O_3 (99.99%), Yb_2O_3 (99.99%), Er_2O_3 (99.99%), and $Ca(OH)_2$ (95%) were purchased from Sinopharm Chemical Reagent Company and used as received.

Synthesis of the Upconversion(UC) materials. Rare earth nitrates $Y(NO_3)_3$, $Yb(NO_3)_3$, $Er(NO_3)_3$, and $Tm(NO_3)_3$ were prepared by dissolving the rare earth oxides in nitric acid. The UC materials were prepared by hydrothermal synthesis strategy. Rare earth nitrate ($RE(NO_3)_3$, RE: 78 mol% Y, 20 mol% Yb, 2 mol% Er) aqueous solution were mixed together at 60-70 ^{o}C under agitation. 0.2 g CTAB, proper amount of $Ca(OH)_2$ and 1 ml octanol were mixed in water solution under thorough stirring, then this mixture was dropwisely added to the rare earth nitrate solution. A homogeneous microemulsion might be formed, 4 ml 1.0 mol/l NH_4F solution was dropwisely added. After vigorous stirring at room temperature for 30 min, the colloidal solution was transferred into a 30 ml teflon-lined autoclave, sealed and heated at 180 ^{o}C for 8 h. The system was allowed to cool naturally to room

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temperature, and the products were deposited at the bottom of the vessel. The precipitates were separated by centrifugation, washed with water and ethanol for several times and dried at 140 ^{o}C for 1 h. The final product was obtained after calcination of the precipitates at 400 ^{o}C for 1 h.

0.5 mol% Tm^{3+} doped samples were prepared by the same procedure, except for changing the 2 mol% Er^{3+} to 0.5 mol% Tm^{3+}.

Samples of YF_3: $Yb_{0.20}Er_{0.02}$ and CaF_2: $Yb_{0.20}Er_{0.02}$ were also synthesized by the similar procedure.

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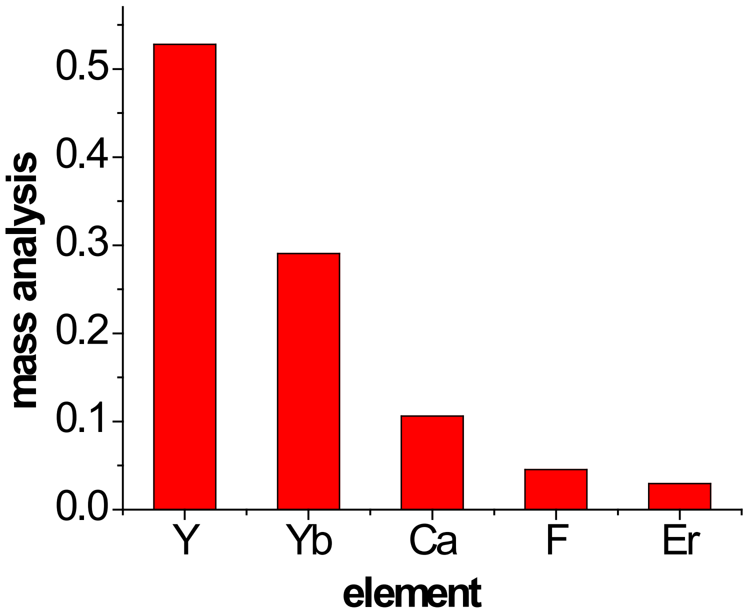
Figure S1-S14:



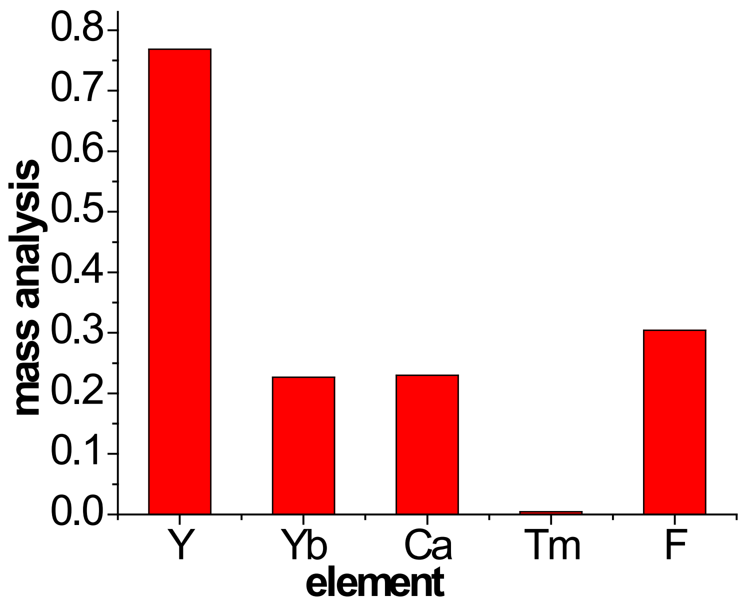


Figure S1. The XRF data for $Ca_{0.34}Y_{0.76}Yb_{0.22}Er_{0.02}F_{3.68}$ and $Ca_{0.23}Y_{0.769}Yb_{0.226}Tm_{0.005}F_{3.46}$ respectively

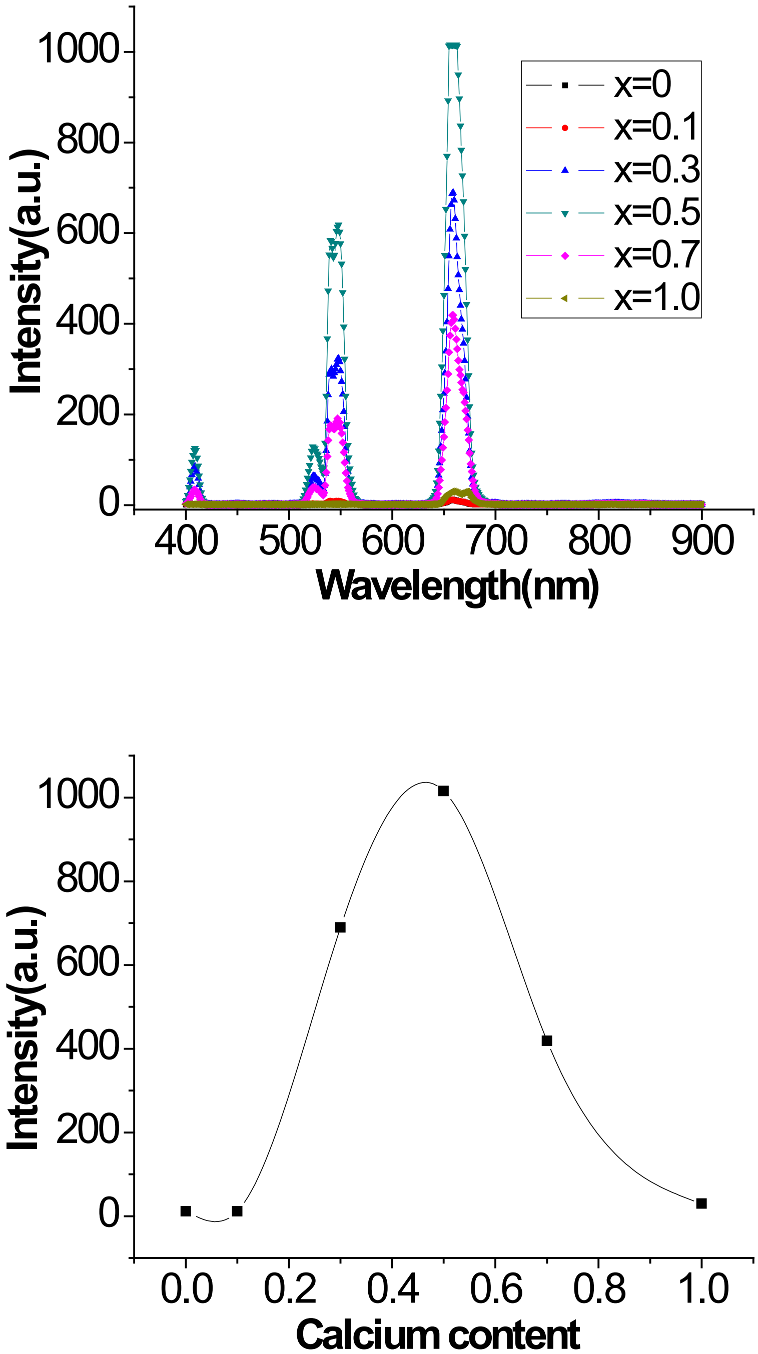


Figure S2. UC luminescence spectra (top) and the luminescent intensities of $Ca_xY_{0.76}Yb_{0.22}Er_{0.02}F_{3+2x}$ with the different designed x values (down).

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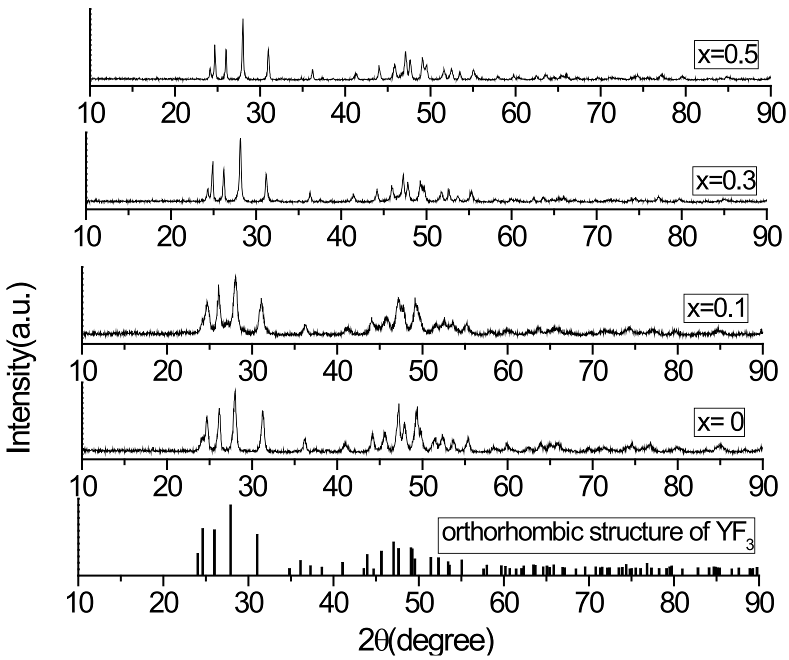

Figure S3. The XRD patterns of $Ca_xY_{0.76}Yb_{0.22}Er_{0.02}F_{3+2x}$ microcrystals with the designed x values of 0, 0.1, 0.3, 0.5 respectively

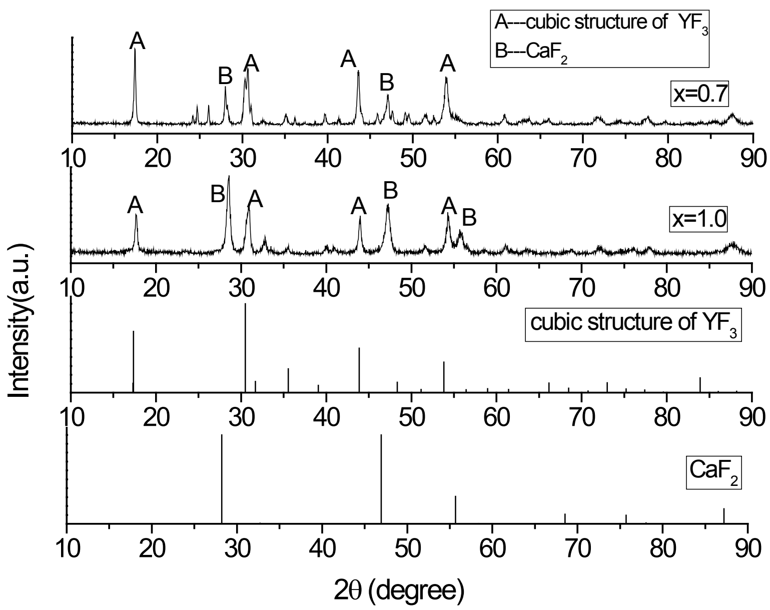

Figure S4. The XRD patterns of $Ca_xY_{0.76}Yb_{0.22}Er_{0.02}F_{3+2x}$ microcrystals with the designed x values of 0.7, 1.0 respectively

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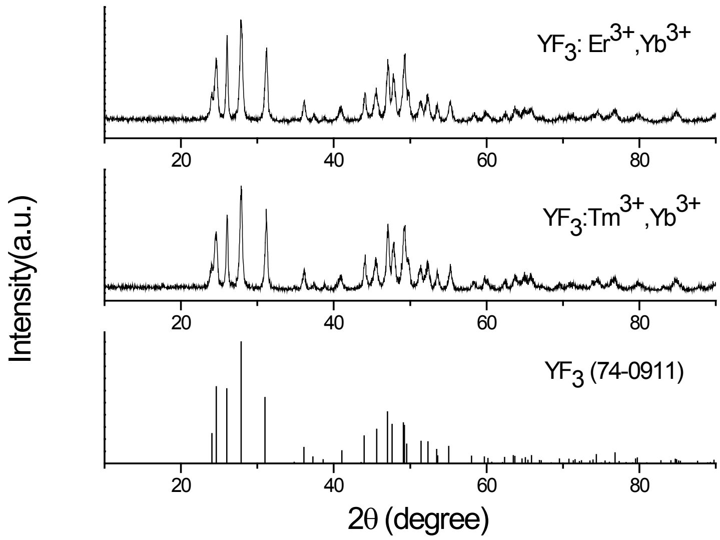

Figure S5. The XRD patterns for YF_3:$Yb_{0.20}Er_{0.02}$ and YF_3:$Yb_{0.20}Tm_{0.005}$ microcrystals respectively

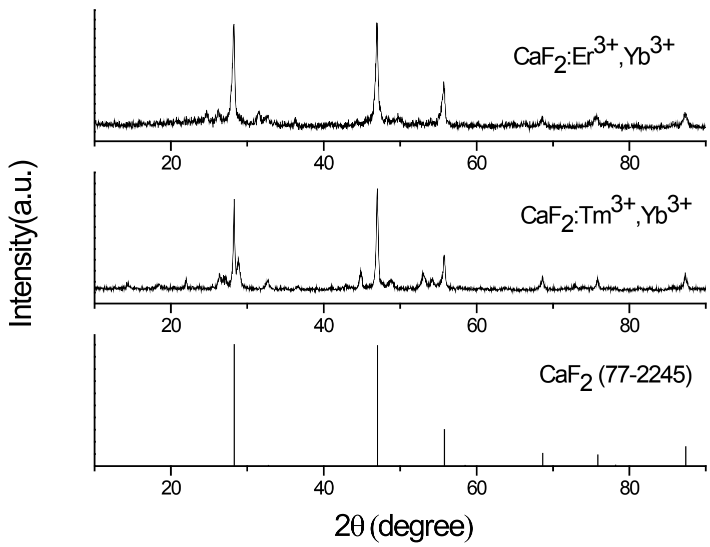

Figure S6. The XRD patterns for CaF_2:$Yb_{0.20}Er_{0.02}$ and CaF_2:$Yb_{0.20}Tm_{0.005}$ microcrystals respectively

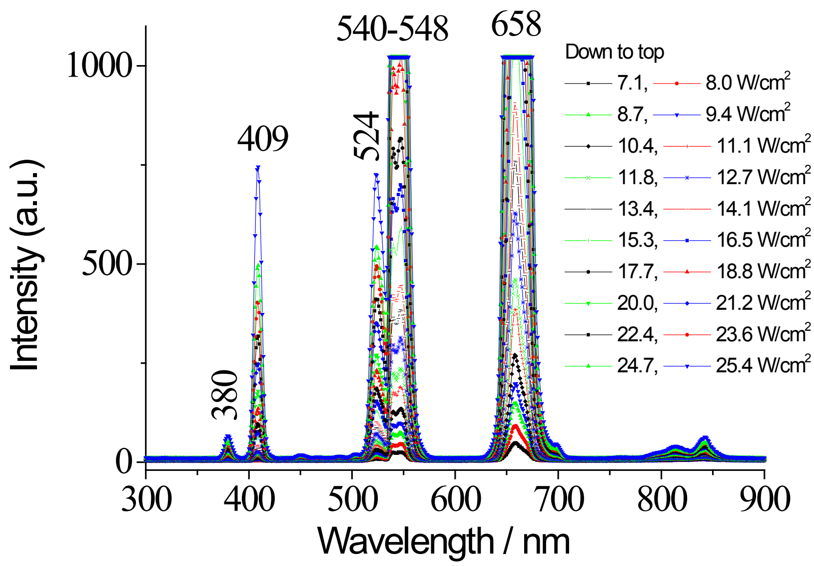

Figure S7. UC emission spectra of $Ca_{0.34}Y_{0.76}Yb_{0.22}Er_{0.02}F_{3.68}$ under different excitation power density (7.1 ~ 25.4 W·cm^{-2}).

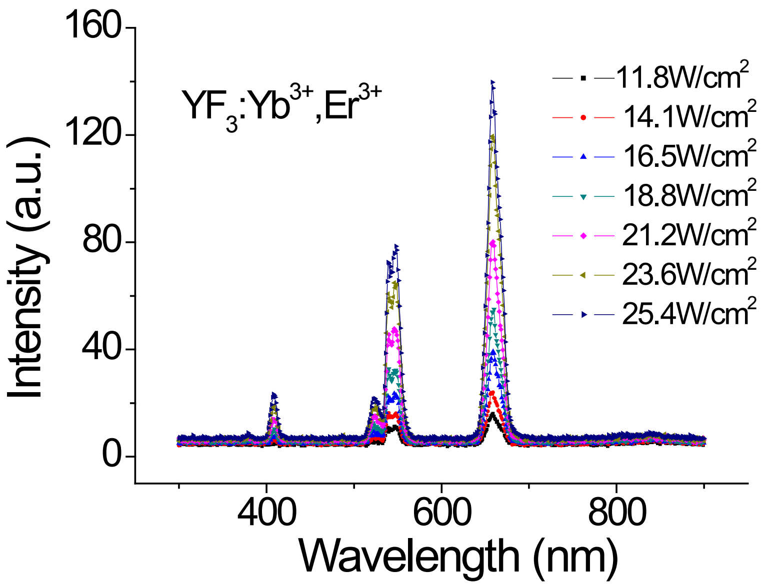

Figure S8. UC emission spectra of YF_3: $Yb_{0.20}Er_{0.02}$ under different excitation power density (11.8 ~ 25.4 W·cm^{-2}).

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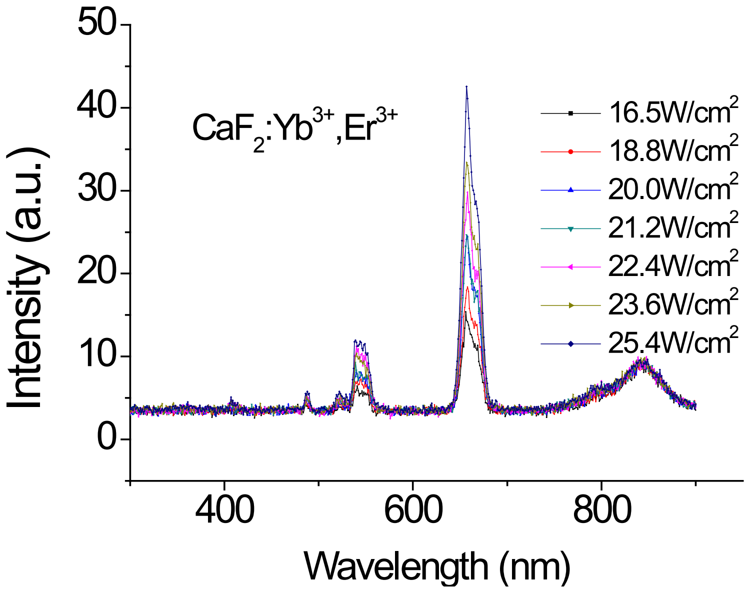

Figure S9. UC emission spectra of CaF_2: $Yb_{0.20}Er_{0.02}$ under different excitation power density (16.5 ~ 25.4 W·cm^{-2}).

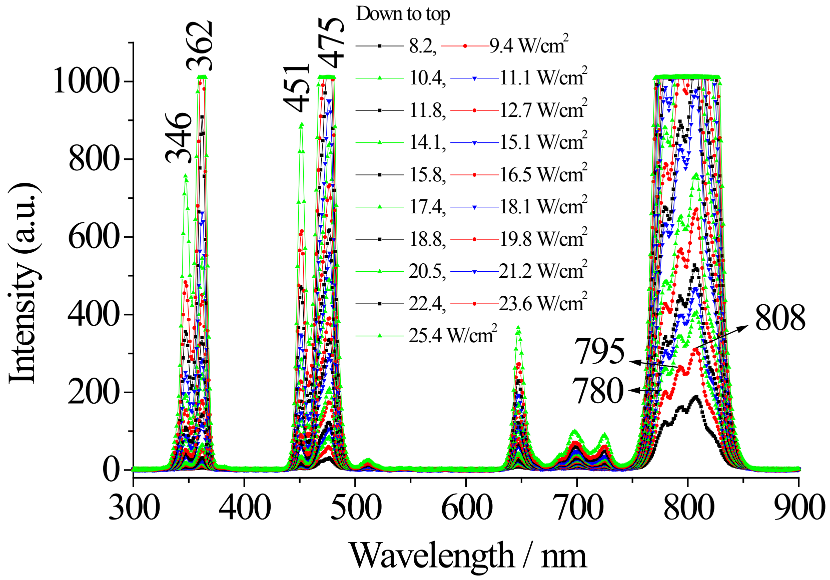

Figure S10. UC emission spectra of $Ca_{0.236}Y_{0.769}Yb_{0.226}Tm_{0.005}F_{3.472}$ under different excitation power density (8.2 ~ 25.4 W·cm^{-2}).

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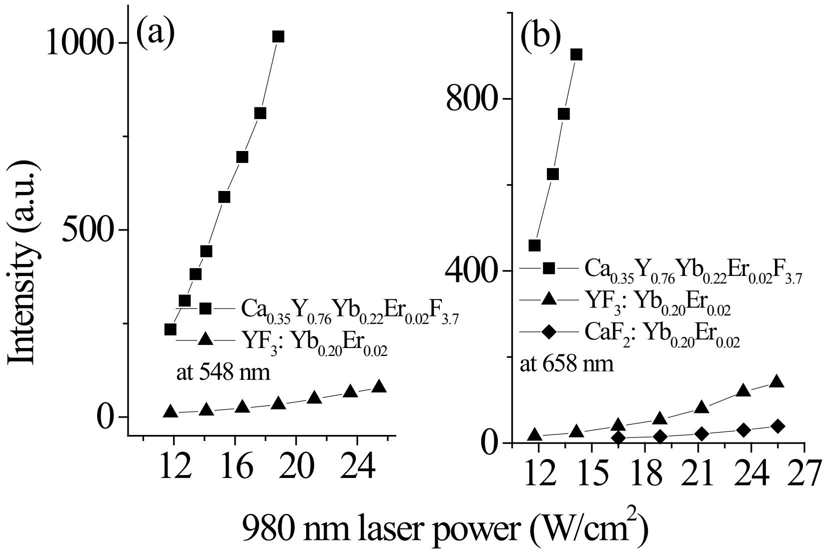

Figure S11. The relative UC mission intensities for $Ca_{0.35}Y_{0.76}Yb_{0.22}Er_{0.02}F_{3.7}$, YF_3:$Yb_{0.20}Er_{0.02}$ and CaF_2:$Yb_{0.20}Er_{0.02}$ at 548 nm and 658 nm respectively

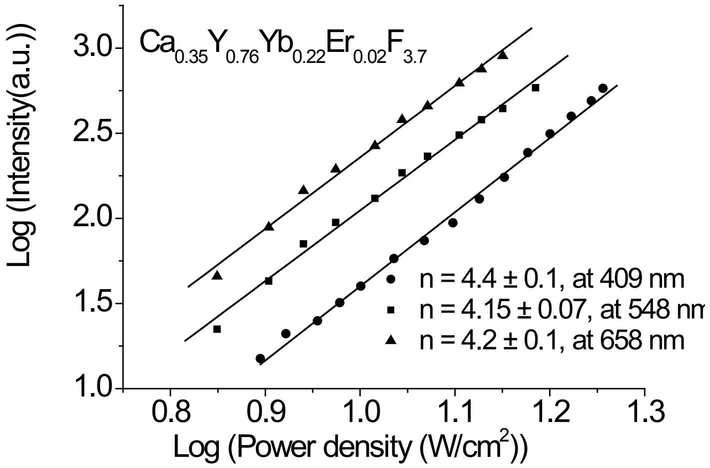

Figure S12. The Log-Log curves of the UC emission intensities versus the excitation power density for $Ca_{0.35}Y_{0.76}Yb_{0.22}Er_{0.02}F_{3.7}$

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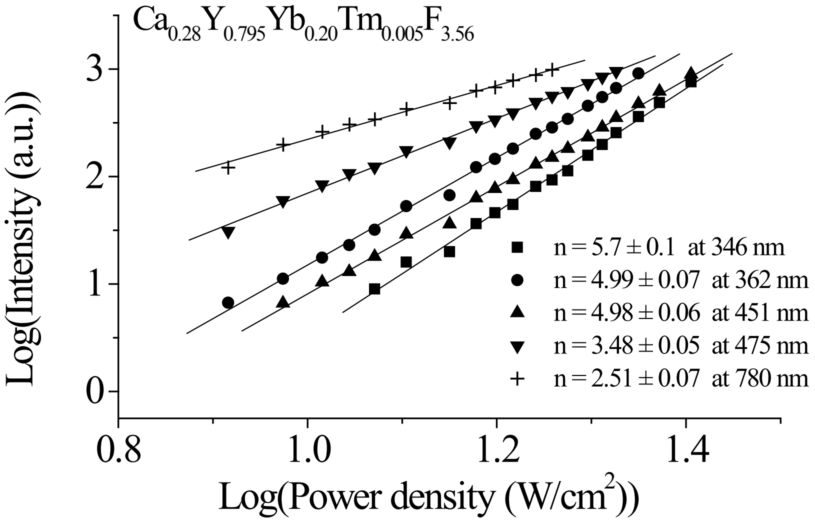

Figure S13. The Log-Log curves of the UC emission intensities versus the excitation power density for $Ca_{0.236}Y_{0.769}Yb_{0.226}Tm_{0.005}F_{3.472}$

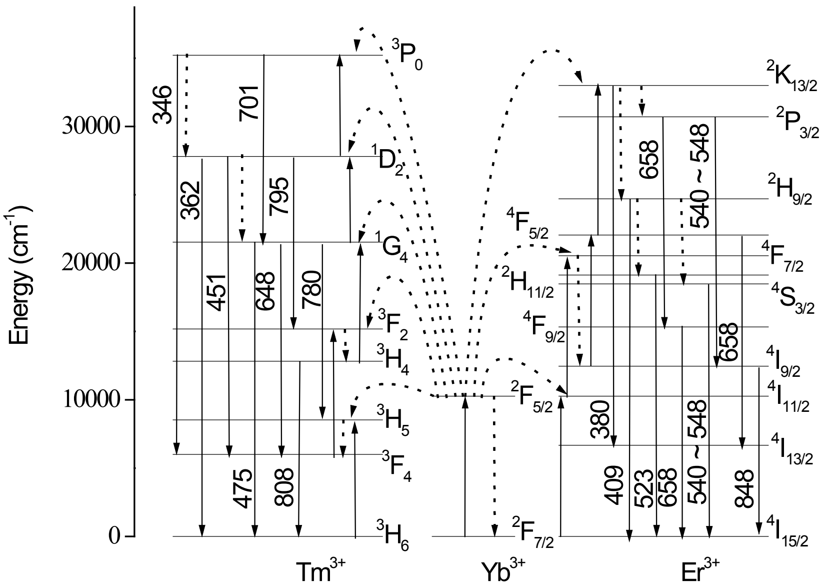

Figure S14. UC excitation and emission schemes for the Yb^{3+}-sensitized Er^{3+} and Tm^{3+} microcrystals,