Energy-transfer from Gd(III) to Tb(III) in (Gd,Yb,Tb)PO₄ Nanocrystals

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Supplementary Information



Fig.S1 Powder XRD patterns of : (A) as-synthesized hexagonal $Gd_{90-x}Yb_{0.10}Tb_xPO_4.2.5H_2O$ nanocrystals with x = 0.005 (a), x = 0.03 (b) and x = 0.05 (c); (B) the corresponding monoclinic $Gd_{90-x}Yb_{0.10}Tb_xPO_4$ phase obtained after calcination of the as-synthesized nanocrystals at 900 °C for 3 hours. The vertical red lines in each figure represent the reference PDF numbers.



Fig. S2 Room-temperature emission spectra of monoclinic $Gd_{0.895}Yb_{0.10}Tb_{0.005}PO_4$ nanocrystals excited at different wavelengths.



Fig. S3 Room-temperature emission decay curves of the nanocrystals: (A) $Gd_{0.87}Yb_{0.10}Tb_{0.03}PO_4$ (red squares) and $Gd_{0.85}Yb_{0.10}Tb_{0.05}PO_4$ (black squares): monitoring the ${}^{5}D_4 \rightarrow {}^{7}F_5$ (Tb³⁺) emissions while exciting at 272 nm; (B) and (C) $Gd_{0.895}Yb_{0.10}Tb_{0.005}PO_4$ (green squares), $Gd_{0.87}Yb_{0.10}Tb_{0.03}PO_4$ (red squares) and $Gd_{0.85}Yb_{0.10}Tb_{0.05}PO_4$ (blue squares) monitoring the ${}^{5}D_4 \rightarrow {}^{7}F_5$ (Tb³⁺) emissions while exciting at 377 and 367 nm, respectively.



Fig. S4 Plots of residuals *vs.* independent variable for better judgment of the fittings curves of the emission decay curves (a) ${}^{6}P_{7/2} \rightarrow {}^{8}S_{7/2}$ (Gd³⁺), (b) ${}^{5}D_{3} \rightarrow {}^{7}F_{6}$ (Tb³⁺), (d) ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ (Tb³⁺), exciting at 272 nm, and (c) ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ (Tb³⁺), exciting at 367 nm, for Gd_{0.895}Yb_{0.10}Tb_{0.005}PO₄ nanocrystals.



Fig. S5 Room-temperature emission decay curves of $(Gd,Tb)PO_4$ nanocrystals with and without Yb^{3+} : monitoring the emissions at (A) 543 nm, (B) 380 nm and (C) 311 nm while exciting at 272 nm. The symbols represent the experimental data while the solid lines are the fitting curves.



Fig. S6 Room-temperature excitation spectra (A) monitoring the emission at 543 nm and emission spectra (B) exciting at 272 nm, of $Gd_{0.895}Yb_{0.10}Tb_{0.005}PO_4$ (black lines) and $Gd_{0.995}Tb_{0.005}PO_4$ (red lines).



Fig. S7 Room-temperature excitation and near infrared emission spectra of Yb^{3+} in monoclinic $Gd_{0.85}Yb_{0.10}Tb_{0.05}PO_4$ nanocrystals: (A) monitoring the emission at 1031.5 nm and (B) exciting at distinct wavelengths that correspond to the peaks in the excitation spectra, showing in the region of the ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}(Yb^{3+})$ transition. The inset in (A) magnifies the spectral region of the ${}^{8}S_{7/2} \rightarrow {}^{6}P_{7/2-3/2}$, ${}^{6}I_{7/2-17/2}$ (Gd³⁺) and ${}^{7}F_{6} \rightarrow {}^{5}D_{1-2}$, ${}^{5}G_{6-2}$, ${}^{5}D_{1-2}$, ${}^{5}L_{10-6}$, ${}^{5}H_{7}$ (Tb³⁺) transition lines and the spectrum was recorded with wider emission slits for acquiring better signal.