Supplementary Information

Scaling Down the Size of the $BaLnF_5$ (Ln = La, Gd, and Lu) Nanocrystals with the Ln^{3+} Size

Shyam Sarkar,[a] Chanchal Hazra,[a] and Venkataramanan Mahalingam[a*]

[a] *Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER), Kolkata, Mohanpur, West Bengal, India.*

Experimental section

Chemicals and materials:

All the chemicals used in this work lanthanum oxide (La_2O_3, 99.99%), gadolinium oxide (Gd_2O_3, 99.99%), lutetium oxide (Lu_2O_3, 99.99%), ytterbium oxide (Yb_2O_3, 99.99%), erbium oxide (Er_2O_3, 99.99%), trifluoroacetic acid (CF_3COOH, 99%), oleic acid (90%), 1-octadecene (90%) and barium acetylacetonate [$Ba(acac)_2$, 99.99%], absolute ethanol were purchased from Sigma Aldrich. All the materials were used without further purification.

Preparation of $BaLnF_5$:Yb^{3+}(20%)/Er^{3+} (2%)(Ln=La, Gd and Lu) nanocrystals:

Barium lanthanide fluoride, $BaLnF_5$ (Ln=La, Gd and Lu) nanocrystals doped with Yb^{3+}(20%)/Er^{3+}(2%)-ions were prepared by thermal decomposition method using oleic acid as capping agent and 1-octadecene as high boiling point solvent. Briefly, lanthanide trifluoroacetates were first prepared by refluxing stoichiometric amounts of corresponding lanthanide oxides (0.78 mmol of Ln_2O_3, Ln=La, Gd, Lu; 0.20 mmol of Yb_2O_3 and 0.02 mmol of Er_2O_3) with 1:1 trifluoroacetic acid and water at 85^0C and then evaporated at 65^0C until dried completely. Then 2 mmol of $Ba(acac)_2$, oleic acid (20 mL) and 1-octadecene (20 mL) were added to this dried precursors. Then the resulting mixture was first heated to 120°C under vacuum. After 15 minutes, the temperature of the mixture was raised to 330°C under an Argon flow. After leaving the reaction at this temperature for 2 h, the mixture was cooled to room temperature. Finally the nanocrystals were precipitated with absolute ethanol. The nanocrystals were separated by centrifugation and further purified by dispersing them with hexane followed by precipitation again with absolute ethanol. A 1 wt% colloidal dispersion was made by dispersing approximately 100 mg in roughly 10 mL of toluene.

Characterization techniques:

The crystallinity and phase purity of the as prepared $BaLnF_5$ (Ln=La, Gd, Lu) nanocrystals have been carried out by powder X-ray diffraction (XRD) measurements, using Rigaku-smartlab diffractometer with Cu Kα operating at 200kV and 45mA at a scanning rate of 1º min^{-1} in the 2θ range from 20º to 90º. The morphology of the nanocrystals were characterized by transmission electron microscopy (TEM), using JEOL 2100 instrument. Thermogravimetric analysis (TGA) were done using Mettler Toledo TGA 851 instrument under N_2 atmosphere at heating rate 10° min^{-1}. The FTIR spectra were recorded using Perkin Elmer Spectrum RX1 spectrophotometer with the KBr disk technique in the range of 400-4000cm^{-1}. The upconversion emission (UC) spectra were taken exciting the toluene dispersion of the nanocrystals using a 980 nm diode laser source from RGB Lase LLC, which was coupled with a fibre with core diameter of 100 µm, was used to excite the samples. The output signal was measured with the Jobin Yvon Fluoromax-4 spectrometer.

Table-1: Structural parameters of Yb^{3+}(20%)/Er^{3+}(2%)-doped $BaLnF_5$ (Ln = La, Gd and Lu) nanocrystals.

Nanocrystals	Crystalline phase	Crystallite size from XRD(nm)	Average size from TEM(nm)	Lattice constant (Å)
$BaLaF_5:Yb^{3+}/Er^{3+}$	Cubic	12.56	~12	a = b = c = 11.0750 PDF card No-00-046-0039
$BaGdF_5:Yb^{3+}/Er^{3+}$	Cubic	8.62	~8	a = b = c = 6.9557 PDF card No-00-024-0098
$BaLuF_5:Yb^{3+}/Er^{3+}$	Cubic	2.54	~3	a = b = c = 6.0230 PDF card No-01-072-3546

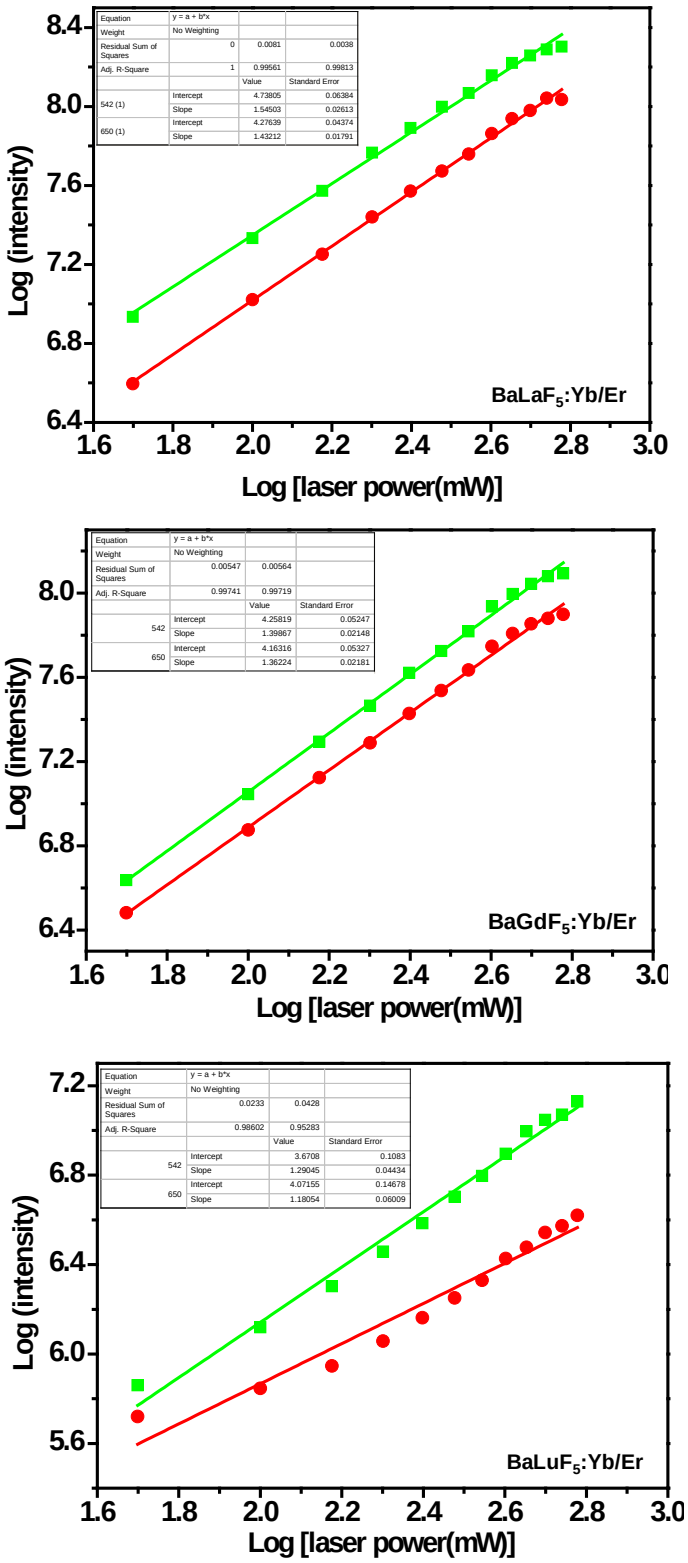

Fig. S1: The logarithmic plots of upconversion emission intensity verses the laser power of Yb^{3+}(20%)/Er^{3+}(2%)-doped $BaLnF_5$ (Ln = La, Gd, Lu) for 545 nm and 650 nm emissions.

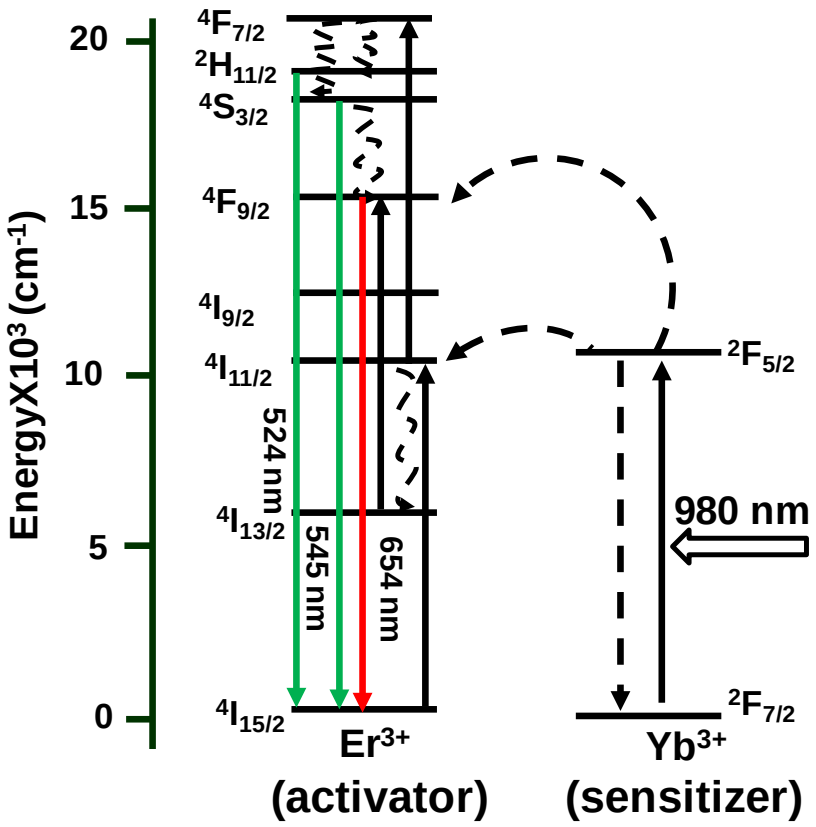

Fig. S2: Probable energy transfer mechanism between Yb^{3+} and Er^{3+} via the upconversion processes.

In the above mechanism, Yb^{3+} ions act as a sensitizer and Er^{3+} ion as an activator in the upconversion process. Under the 980 nm laser excitation electron transferred from the ground state ($^2F_{7/2}$) of Yb^{3+} ion to its excited state, $^2F_{5/2}$,and the subsequently this energy transfer is transferred from Yb^{3+}($^2F_{5/2}$) to Er^{3+}($^4I_{11/2}$) energy level. This happens as these levels are closer in energy. A further excitation of electron from Er^{3+}($^4I_{11/2}$) to the Er^{3+}($^4F_{7/2}$) occurs via second energy transfer from Yb^{3+}($^2F_{5/2}$) level. The excited electrons decay first non-radiatively to $^2H_{11/2}$, $^4S_{3/2}$ and $^4F_{9/2}$ energy levels and then radiatively decay to the ground state ($^4I_{15/2}$) of Er^{3+} ion releasing green and red emissions, respectively.