

Supplementary Materials

Bright white light through up-conversion of a single NIR source from sol-gel derived thin film made with Ln³⁺ doped LaF₃ nanoparticles

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Experimental Section

General

All chemicals were obtained from Aldrich and used without further purification. The source of water used consisted of distilled water.

Preparation of citrate stabilized lanthanide doped nanoparticles

Around 2 g of citric acid (99.9%) and 0.126 g NaF (99+%) was dissolved in 40 ml of water. The pH of the solution was adjusted to 6 by adding NH_4OH (30% w/v) and the solution was heated to 75 °C. Stoichiometric amounts of the nitrate salts of lanthanide ions (99.99%) were dissolved in 2 ml of methanol and added drop wise. A clear solution was obtained and after two hours of reaction, the resulting solution was mixed with 70 ml of ethanol to precipitate the nanoparticles. These particles were collected by centrifuge at 3000 rpm, washed with ethanol, and dried under vacuum. After drying the particles can easily be dispersed in water. $\text{La}_{0.45}\text{Yb}_{0.50}\text{Er}_{0.05}\text{F}_3$: ^1H NMR [Bruker AC 300] (D_2O) δ 2.45 - 2.60 (broad, $\text{CH}_2\text{COOH} - \text{COH}(\text{COOH}) - \text{CH}_2\text{COOH}$). This is fully consistent with previous work.¹ This work showed particle sizes in the range 5-6 nm as determined by AFM (Thermo microscope AFM scanner having a silicon nitride tip (model MLCT-EXMT-A) supplied by Veeco Instruments). The 5% doping level of lanthanide ion was decided based on our earlier report.² Above this concentration, concentration quenching occurs.

Preparation of Sol-gel thin films

50 mg of Ln^{3+} doped LaF_3 nanoparticles were dissolved in 2 ml water, which was then mixed with 3 ml of tetraethoxyorthosilane (TEOS) (99.999%) and 7.8 ml of absolute

ethanol. The pH of the solution was adjusted to 2 by adding a few drops of 0.1 N HCl and the solution was stirred for 24 hours to get a clear sol. The sol was then spin coated on a quartz substrate at 2500 rpm and heated to 400°C from 25°C in 1.40 hr, staying at 400°C for 30 min and then heated to 800 °C in 2 hr and staying at 800 °C for 12 hr under ambient environment. 1 mg of $\text{La}_{0.45}\text{Yb}_{0.5}\text{Er}_{0.05}\text{F}_3$, 100 mg of $\text{La}_{0.75}\text{Yb}_{0.2}\text{Tm}_{0.05}\text{F}_3$, and 150 mg of $\text{Yb}_{0.75}\text{La}_{0.2}\text{Eu}_{0.05}\text{F}_3$ in 4 ml water were used for the material which gave white light emission. This optimum ratio of nanoparticles was determined after 4 trial runs.

Characterization

All up-conversion fluorescence analyses were done using an Edinburgh Instruments FLS 920 fluorescence system. The excitation source used was a Coherent 2-pin 980 nm CW semiconductor diode laser with $P_{\text{max}} = 800$ mW at 1000 mA. The fiber was coupled to a 100 μm (core) fiber. A red-sensitive peltier-cooled Hamamatsu R955 photomultiplier tube (PMT), with a photon-counting interface, was used for analyses between 200-850 nm. All up-conversion emission analyses in the visible region were measured with a 2 nm resolution. The direct excitation of Eu^{3+} at 418 and 464 nm was done by exciting the samples with a 10 Hz Q-Switched Quantel Brilliant, pumped by a Nd:YAG laser, attached with an optical parametric oscillator (OPO) with an optical range from 410-2400 nm.

XRD analysis: Approximately 20-25 mg of the sample was powdered in an alumina mortar to break up lumps. The powder was smeared on to a zero-diffraction quartz plate using ethanol. Step-scan X-ray powder-diffraction data were collected over the 2θ range 3 - 100° with $\text{CuK}\alpha$ (40 kV, 40 mA) radiation on a Siemens D5000 Bragg-Brentano θ -2 θ diffractometer equipped with a diffracted-beam graphite monochromator crystal, 2 mm

(1°) divergence and anti-scatter slits, 0.6 mm receiving slit, and incident beam Soller slit. The scanning step size was $0.04^\circ 2\theta$ with a counting time of 2 s/step. X-ray powder-diffraction data for different phases were refined with the Rietveld program Topas 2.1 from Bruker using the fundamental parameters approach.

Assignment of the emission peaks in Figures 1, 2, S1, and S3:

The emission band around 470 nm is assigned to the 1G_4 to 3H_6 transition of Tm^{3+} ions and the emission at 790 nm is assigned to the 3H_4 to 3H_6 . Er^{3+} gave emission peaks around 515, 540, and 645 nm which are assigned to the $^2H_{11/2}$ to $^4I_{15/2}$, $^4S_{3/2}$ to $^4I_{15/2}$, $^4F_{9/2}$ to $^4I_{15/2}$ transitions, respectively. The emission bands around 590 nm and 612 nm are assigned to the 5D_0 to 7F_1 and 5D_0 to 7F_2 transitions of Eu^{3+} ions, respectively.

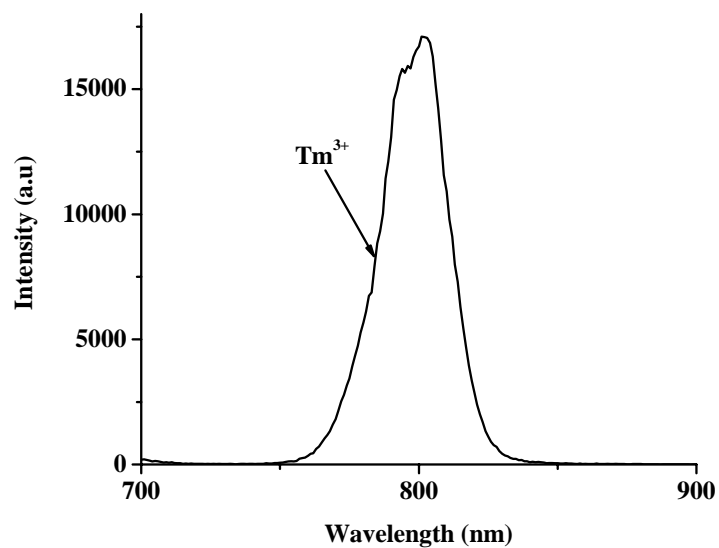


Figure S1. Up-conversion emission spectra of silica thin film prepared at 800°C made with $\text{La}_{0.75}\text{Yb}_{0.2}\text{Tm}_{0.05}\text{F}_3$ nanoparticles under 300 mW 980 nm CW laser excitation.

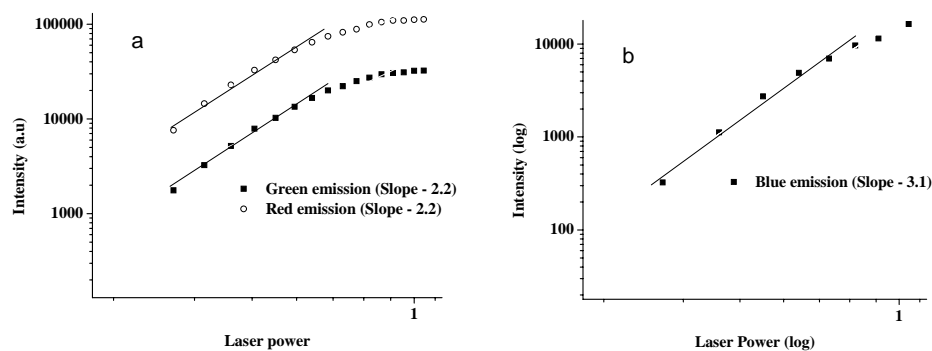


Figure S2. Dependence of the up-conversion emission intensity on the excitation power in different samples a) $\text{La}_{0.45}\text{Yb}_{0.5}\text{Er}_{0.05}\text{F}_3$, b) $\text{La}_{0.75}\text{Yb}_{0.2}\text{Tm}_{0.05}\text{F}_3$ nanoparticles individually incorporated in silica films and heated at 800 °C under 980 nm laser excitation. Errors in the fitting the slope were estimated to be 5% based on duplicate measurements.

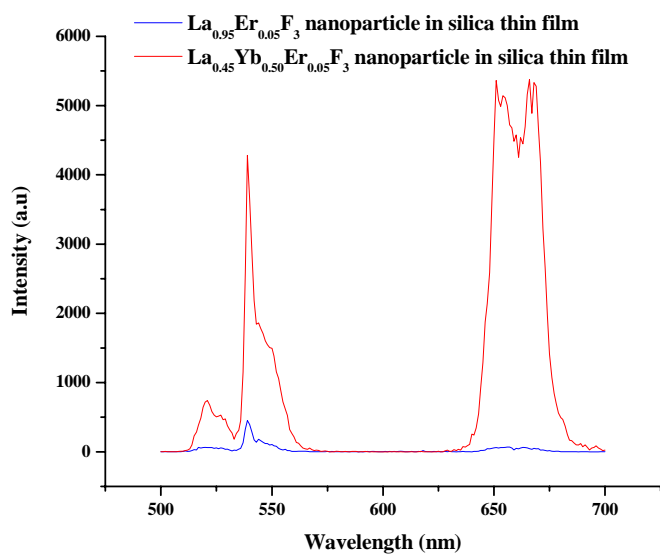


Figure S3. Up-conversion emission spectra of silica thin film individually incorporated with $\text{La}_{0.45}\text{Yb}_{0.50}\text{Er}_{0.05}\text{F}_3$ and $\text{La}_{0.95}\text{Er}_{0.05}\text{F}_3$ nanoparticles, heated at 800 °C under 300 mW 980 nm CW laser excitation.

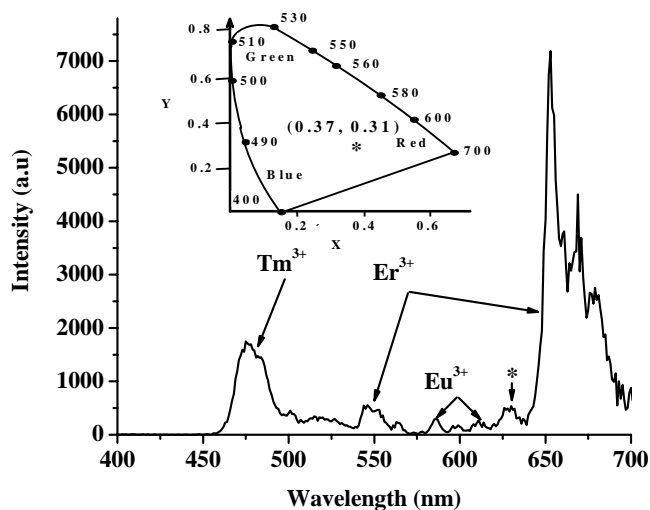


Figure S4. Up-conversion emission spectra of ZrO_2 thin film prepared at 800°C made with $\text{La}_{0.45}\text{Yb}_{0.5}\text{Er}_{0.05}\text{F}_3$, $\text{La}_{0.75}\text{Yb}_{0.2}\text{Tm}_{0.05}\text{F}_3$, and $\text{Yb}_{0.75}\text{La}_{0.2}\text{Eu}_{0.05}\text{F}_3$ nanoparticles under 300 mW 980 nm CW laser excitation (the insets show the CIE colour coordinates of the resulting white light). * The origin of the emission at 630 nm is not entirely clear. Work is in progress to unravel this issue.

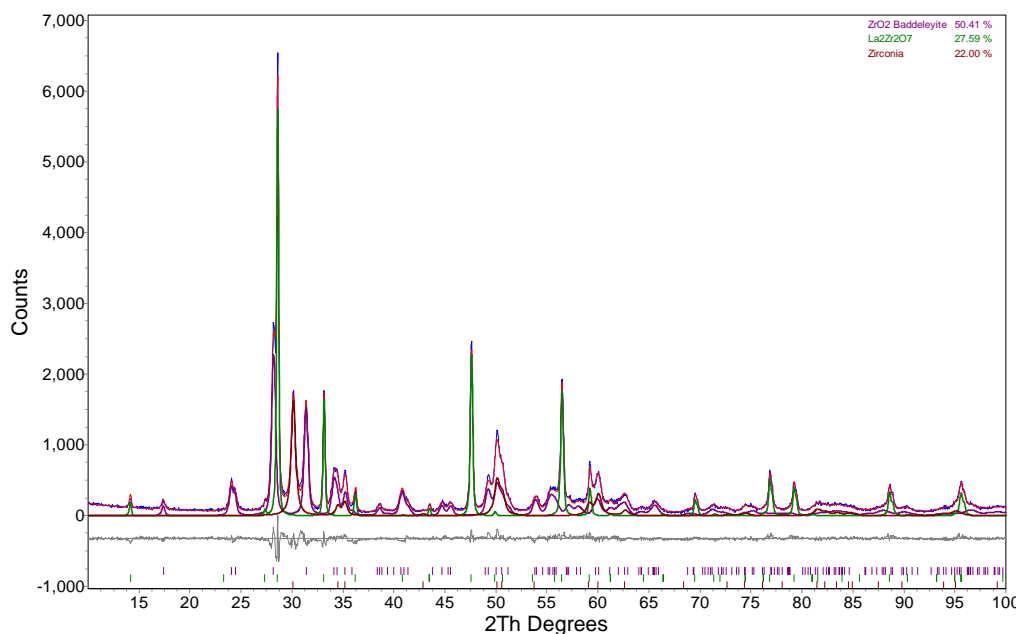


Figure S5. XRD pattern (Rietveld refinement plot) of a silica film prepared at 800 °C made with 25 weight % of $\text{La}_{0.45}\text{Yb}_{0.52}\text{Er}_{0.05}\text{F}_3$ nanoparticles. Green lines: $\text{La}_2\text{Zr}_2\text{O}_7$ phase, Violet lines: ZrO_2 Baddeleyite phase, Red lines: ZrO_2 Zirconia phase.

¹ Sudarsan, V.; Sri Sivakumar, van Veggel, F. C. J. M.; Raudsepp, M. submitted.

² Stouwdam J. W.; van Veggel, F. C. J. M. *Nano Lett.* **2002**, 2, 733.

³ Bruker AXS 2003: Topas V2.1: General Profile and Structure Analysis Software for Powder Diffraction Data - User's Manual. Bruker AXS, Karlsruhe, Germany.