

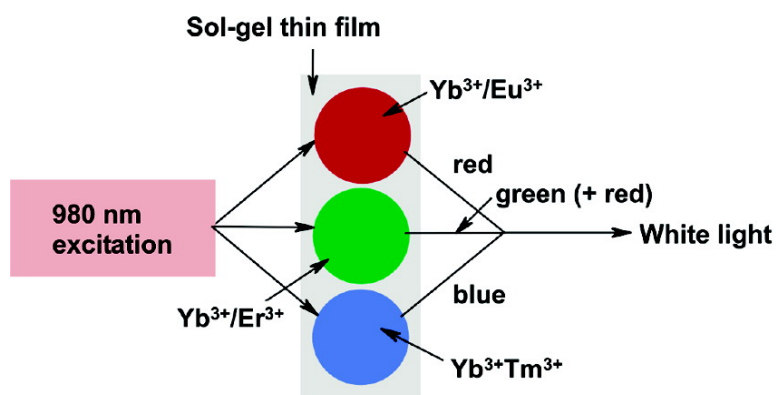
Communication

Bright White Light through Up-Conversion of a Single NIR Source from Sol-Gel-Derived Thin Film Made with Ln-Doped LaF Nanoparticles

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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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There is a large interest in cheap, efficient generation of (white) light sources for a variety of purposes, such as displays, liquid crystal display, back light, and alternatives to general lighting (incandescent light bulb).^{1–3} Approaches are (i) the conversion of electricity, (ii) the conversion of light, either by down-conversion or up-conversion, and (iii) thermal radiation in the incandescent lamp. Electricity is exploited in light-emitting diodes with some major recent advances in OLEDs^{4–7} and PLEDs.^{8–10} White light sources are challenging because (1) blue and white light emitters are not as efficient as green and red emitters,^{11,12} (2) energy down-conversion in the case of multilayer devices, by reabsorption and subsequent emission of lower-energy photons, (3) bias dependent color variation,¹³ (4) multilayer devices lead to high manufacturing cost,¹⁴ and (5) long-term stability of emitters remains an issue.¹⁵ Down-conversion is the conversion of UV into visible light and is widely exploited in phosphors.¹⁶ The up-conversion process converts near-infrared photons via multiphoton processes into visible photons (details below).¹⁷ The incandescent light bulb produces light by heating and is one of the oldest devices, but the efficiency is still very low (10–12%).¹⁸

The up-conversion process is based on sequential absorption and energy transfer steps. This event is different from multiphoton absorption processes, requiring high excitation densities. Lanthanide ions are suitable candidates for up-conversion processes because of their energy levels.^{17,19,20} To achieve an efficient, cost-effective and durable white light source we need (i) stable photocycle, (ii) cheap excitation (e.g., 980 nm CW laser) and efficient absorption, (iii) control over the intensity of red, green, and blue emission, and (iv) easy and cost-effective device fabrication.

Here, we report a simple method to produce white light from sol–gel matrices, such as SiO₂ and ZrO₂, made with Ln³⁺-doped LaF₃ nanoparticles co-doped with Yb³⁺ ions. Up-conversion with lanthanide ions in Y₂O₃,^{21,22} Gd₂O₃,²³ ZrO₂,^{24,25} and SiO₂²⁶ is known; however, white light generation has not been reported. The co-doping with Yb³⁺ ions makes it possible to excite with 980 nm light only. Red, green, and blue emission was generated from three different lanthanide ions, that is, Er³⁺ (red as well as green), Eu³⁺ (red), and Tm³⁺ (blue) ions. We have achieved the following: (1) the CIE coordinates of the resulting light can easily be adjusted by controlling the concentration of lanthanide ions in the nanoparticles^{27–31} as well as the concentration of nanoparticles (Ln³⁺ doped) in the sol–gel thin layer; (2) internal energy transfer between Eu³⁺, Er³⁺, and Tm³⁺ ions is avoided by their spatial isolation. The sol–gel process is simple, gives robust layers, and allows tuning of the properties.³² These films are potential candidates for making planar waveguides, flat panel display, and fiber amplifiers.

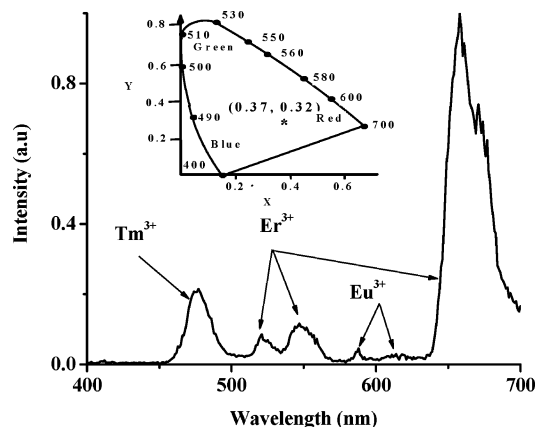


Figure 1. Up-conversion emission spectrum of silica thin film prepared at 800 °C made with La_{0.45}Yb_{0.5}Er_{0.05}F₃, La_{0.75}Yb_{0.2}Tm_{0.05}F₃, and Yb_{0.75}La_{0.2}-Eu_{0.05}F₃ nanoparticles under 300 mW 980 nm CW laser excitation (the insets show the CIE color coordinates of the resulting white light).

This work profits from our route to improve the NIR emission of Ln³⁺ ions in sol–gel-derived thin films.^{33,34}

La_{0.45}Yb_{0.5}Er_{0.05}F₃, La_{0.75}Yb_{0.2}Tm_{0.05}F₃, and Yb_{0.75}La_{0.2}Eu_{0.05}F₃ nanoparticles were prepared by the co-precipitation technique. The sol–gel made with nanoparticles was prepared by acid hydrolysis, and the sol was spin coated on a quartz plate (see Supporting Information for details). Figure 1 shows the up-conversion emission spectra of silica films made with three different nanoparticles. Emission peaks at red, green, and blue region can clearly be seen. The calculated color coordinates are 0.37 and 0.32.^{35,36} These fall within the white region of the 1931 CIE diagram.³⁷ This white light was bright and can be seen by our naked eye even at a laser pump power of only 200 mW. There is no change in the color coordinates of the white light with a change in excitation power. The weak emissions from the Eu³⁺ ions are necessary because, otherwise, the color coordinates move toward the green region (0.30, 0.41).

A control silica thin film with the same concentrations of La³⁺, Er³⁺, Tm³⁺, Eu³⁺, and Yb³⁺ ions by direct incorporation only showed green and red emission from Er³⁺ ions (Figure 2). This clearly demonstrates that a single silica thin film prepared with three different Ln³⁺/Yb³⁺-doped nanoparticles is necessary to produce white light. An emission band of Tm³⁺ ions at 790 nm was also observed (Figure S1). The intensity ratio of red to green emission from Er³⁺ ions can be tuned by changing the concentration of Yb³⁺ ions in the Gd₂O₃ nanoparticle.²³ We also found similar green-to-red ratio dependence by changing the Yb³⁺ concentration in the nanoparticle. We also observed very weak blue emission at 490 nm, compared that of Tm³⁺, from a silica film made only with Yb_{0.8}La_{0.15}Eu_{0.05}F₃ nanoparticles, which results from cooperative up-conversion of two Yb³⁺ ions. The blue emission is not from

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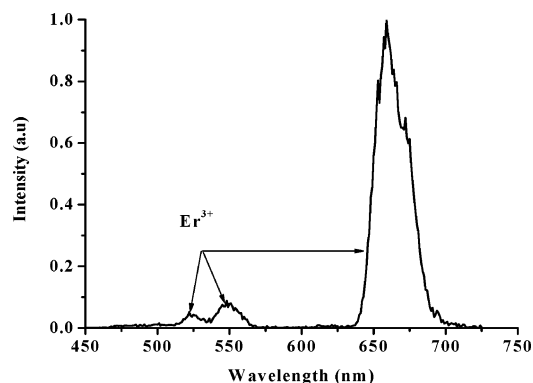


Figure 2. Up-conversion emission spectrum of Ln^{3+} (Er^{3+} , Tm^{3+} , and Eu^{3+}) and Yb^{3+} ions directly incorporated in one silica film prepared at 800 °C as control sample under 300 mW 980 nm CW laser excitation.

Eu^{3+} ions because no blue emission at 490 nm was observed when the Eu^{3+} was excited directly at 418 or 464 nm. Maciel et al.²⁶ have reported this cooperative up-converted emission mechanism in silica glasses. There was no blue emission from Er^{3+} ions, due to a three-photon process, and no UV emission from Tm^{3+} ions, either. It is obvious that blue, green, and red emission can be produced separately as well.

Control films with Tm^{3+} and Eu^{3+} each co-doped with Yb^{3+} ions did not show any up-conversion. The up-conversion luminescence can likely be improved by using $\text{LaF}_3:\text{Ln}^{3+}$ core-shell nanoparticles (the doped LaF_3 core is surrounded by an undoped shell of LaF_3).³³ Possible mechanisms for the up-conversion processes are photoavalanche (PA), excited-state absorption (ESA), and energy transfer (ET).¹⁷ Figure S2 shows the dependence of the up-conversion emission intensity on the excitation power, showing the blue emission from Tm^{3+} ions is a three-photon process, the green and red emission from Er^{3+} and Ho^{3+} ions are two-photon processes. All of the three up-conversion processes are not due to photoavalanche process because there is no appearance of threshold in the power dependence graph, and no s-shaped curves are observed. Up-conversion from Tm^{3+} and Eu^{3+} ions is due to energy transfer processes because both ions have no ground or excited-state absorption that matches the 980 nm photon. Green and red emission from Er^{3+} ions is predominantly due to energy transfer processes, and little contribution is from Er^{3+} excited-state absorption, as can be seen from a silica thin film made with $\text{La}_{0.45}\text{Yb}_{0.5}\text{Er}_{0.05}\text{F}_3$ nanoparticles that showed intense luminescence when compared to a silica thin film made with $\text{La}_{0.95}\text{Er}_{0.05}\text{F}_3$ nanoparticles (Figure S3).

Similar to SiO_2 matrix, white light was observed with CIE coordinates of 0.37 and 0.31 when ZrO_2 films were made with the above $\text{Yb}^{3+}/\text{Eu}^{3+}$, $\text{Yb}^{3+}/\text{Er}^{3+}$, and $\text{Yb}^{3+}/\text{Tm}^{3+}$ nanoparticles (Figure S4). A ZrO_2 thin film prepared with the same concentrations of La^{3+} , Er^{3+} , Tm^{3+} , and Eu^{3+} ions with Yb^{3+} ions by direct incorporation only showed green and red emission from Er^{3+} ions, which substantiates the importance of the role of three different nanoparticles. A lanthanum silicate phase ($\text{La}_{0.31}\text{Si}_{6.24}\text{O}_{26}$) along with the expected LaF_3 phase was observed by X-ray diffraction (XRD) on a silica thin film sample. XRD studies on ZrO_2 thin films made with nanoparticles showed the presence of lanthanum zirconate ($\text{La}_2\text{Zr}_2\text{O}_7$), but no LaF_3 (Figure S5). We conclude that the nanoparticles have reacted with OH groups present in the ZrO_2 sol-gel to form Ln^{3+} -doped lanthanum zirconate. Despite the formation of lanthanum zirconate, the three pairs of Ln^{3+} ions are spatially isolated in the sol-gel layer made with nanoparticles, which is unlikely in the case of direct incorporation of Ln^{3+} ions.

So, effectively, the pairs of Ln^{3+} ions are still in a nanoparticle that has very low phonon energy ($\sim 300\text{ cm}^{-1}$).

In conclusion, white light can easily be generated from SiO_2 , ZrO_2 sol-gel thin film made with Ln^{3+} -doped nanoparticles co-doped with Yb^{3+} ions. Our control experiments prove the need for Ln^{3+} -doped nanoparticles rather than Ln^{3+} ion directly incorporated in SiO_2 and ZrO_2 thin films.

Acknowledgment. NSERC (Canada) support is gratefully acknowledged.

Supporting Information Available: Emission spectra, decay curve, energy transfer diagrams, power dependence upconversion graph, and XRD of the prepared thin films. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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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 - 2θ 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.

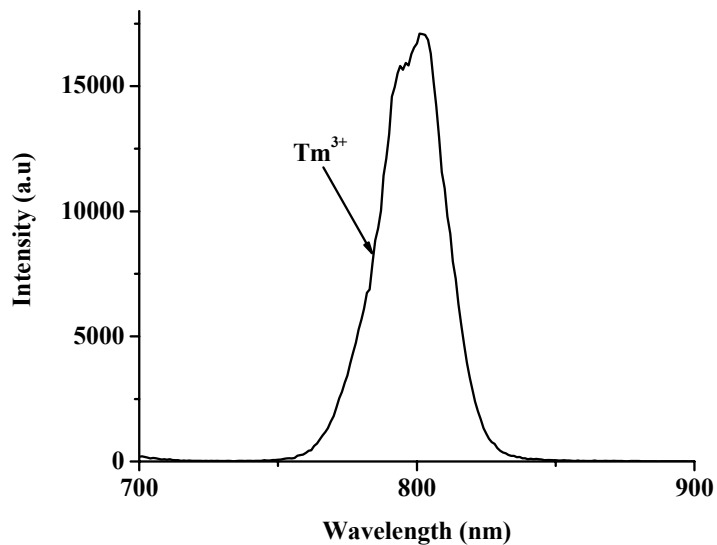


Figure S1. Up-conversion emission spectra of silica thin film prepared at 800°C made with $\text{La}_{0.75}\text{Yb}_{0.2}\text{Tm}_{0.05}\text{F}_3$ nanoparticles under 300 mW 980 nm CW laser excitation.

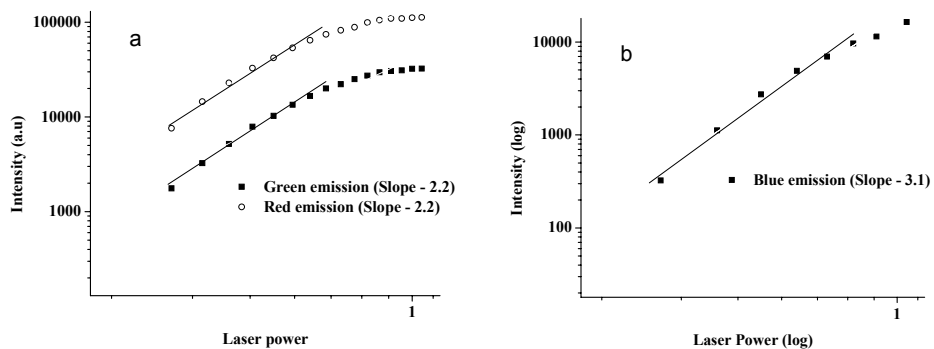


Figure S2. Dependence of the up-conversion emission intensity on the excitation power in different samples a) $\text{La}_{0.45}\text{Yb}_{0.5}\text{Er}_{0.05}\text{F}_3$, b) $\text{La}_{0.75}\text{Yb}_{0.2}\text{Tm}_{0.05}\text{F}_3$ nanoparticles individually incorporated in silica films and heated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

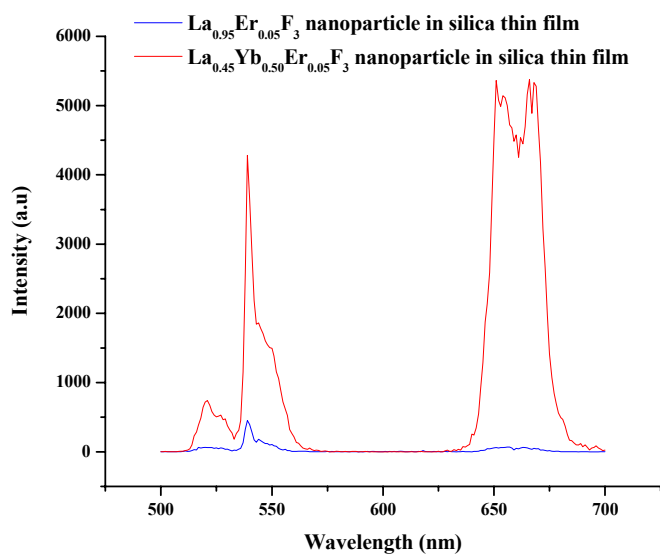


Figure S3. Up-conversion emission spectra of silica thin film individually incorporated with $\text{La}_{0.45}\text{Yb}_{0.50}\text{Er}_{0.05}\text{F}_3$ and $\text{La}_{0.95}\text{Er}_{0.05}\text{F}_3$ nanoparticles, heated at 800 °C under 300 mW 980 nm CW laser excitation.

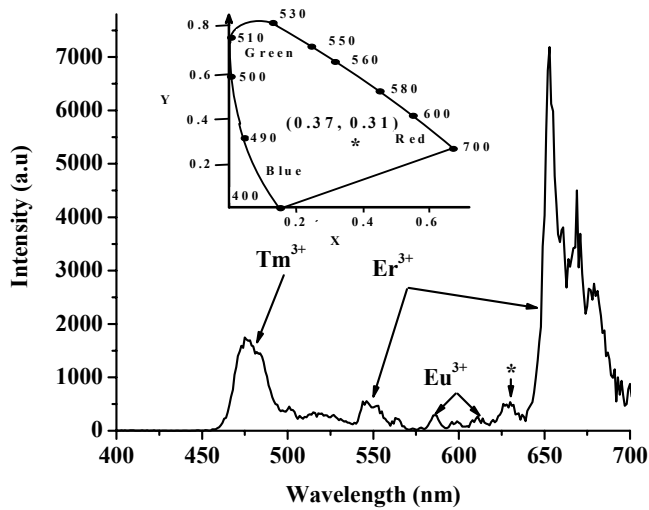


Figure S4. Up-conversion emission spectra of ZrO₂ thin film prepared at 800 °C made with La_{0.45}Yb_{0.5}Er_{0.05}F₃, La_{0.75}Yb_{0.2}Tm_{0.05}F₃, and Yb_{0.75}La_{0.2}Eu_{0.05}F₃ nanoparticles under 300 mW 980 nm CW laser excitation (the insets show the CIE colour coordinates of the resulting white light). * The origin of the emission at 630 nm is not entirely clear. Work is in progress to unravel this issue.

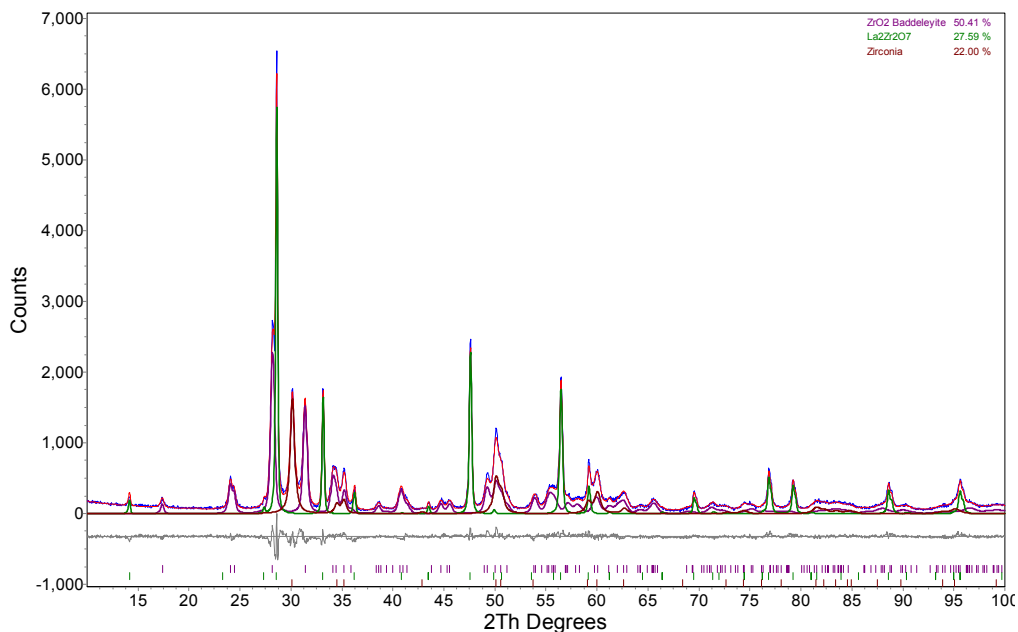


Figure S5. XRD pattern (Rietveld refinement plot) of a silica film prepared at 800 °C made with 25 weight % of $\text{La}_{0.45}\text{Yb}_{0.52}\text{Er}_{0.05}\text{F}_3$ nanoparticles. Green lines: $\text{La}_2\text{Zr}_2\text{O}_7$ phase, Violet lines: ZrO_2 Baddeleyite phase, Red lines: ZrO_2 Zirconia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

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