

## Electronic Supplementary Information for

# Pure-phase $\text{La}_2(\text{WO}_4)_3$ : $\text{Eu}^{3+}$ Nanocrystals and Spindle-like $\text{NaLa}(\text{WO}_4)_2$ : $\text{Yb}^{3+}/\text{Er}^{3+}$ Nano-/microcrystals: Selective Synthesis, Morphologies and Photoluminescent Properties

Xiaolin Liu<sup>a</sup>, Wenhua Hou<sup>\*a,b</sup>, Xiaoyan Yang<sup>a,b</sup>, Qingming Shen<sup>c</sup>

<sup>a</sup>*Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, P. R. China*

<sup>b</sup>*Nanjing University-Yangzhou Institute of Chemistry and Chemical Engineering, Yangzhou 211400, P. R. China*

<sup>c</sup>*Key Laboratory of Organic Electronics and Information Displays, Institute of Advanced Materials, Nanjing University of Posts and Telecommunications, Nanjing 210046, P. R. China.*

\* Corresponding author. E-mail: [whou@nju.edu.cn](mailto:whou@nju.edu.cn)

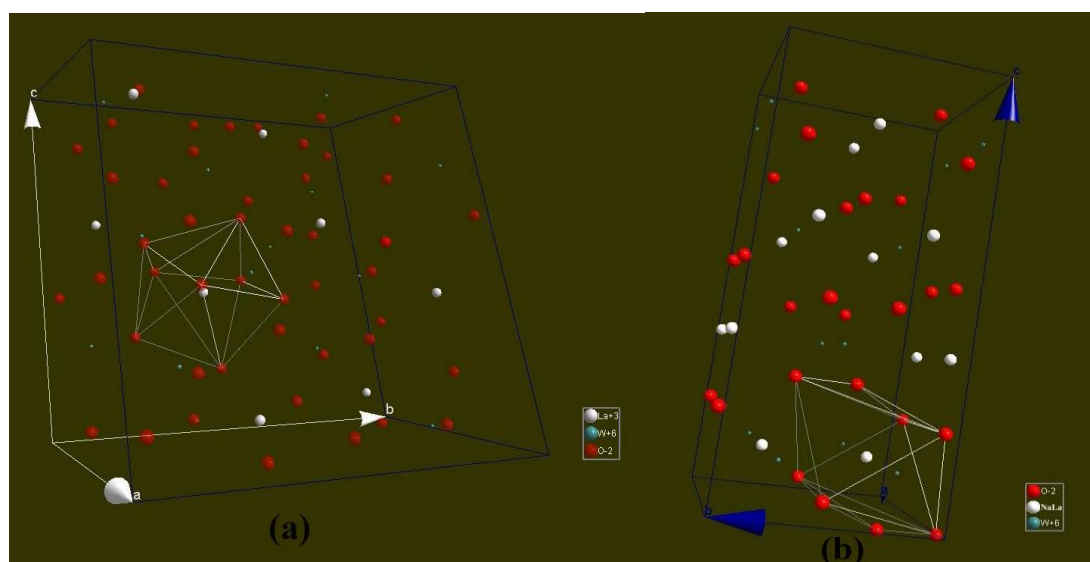


Figure S1. Simulated crystal structures of (a) monoclinic  $\text{La}_2(\text{WO}_4)_3$ , and (b) tetragonal  $\text{NaLa}(\text{WO}_4)_2$ . (White polyhedrons denote  $\text{LaO}_8$ )

**Synthesis of  $\text{La}_2(\text{WO}_4)_3$  through a conventional process:**  $\text{Na}_2\text{WO}_4$  stock solution was prepared by dissolving  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (1.319 g, 4 mmol) in 40 mL distilled water. The obtained  $\text{Na}_2\text{WO}_4$  stock solution was then added dropwise into a well-stirred solution of  $\text{La}(\text{NO}_3)_3$  (2 mmol, 10 mL) at room temperature. The resulting milky suspension was allowed to stir for another 30 min. The as-synthesized precursor of  $\text{La}_2(\text{WO}_4)_3$  was collected by centrifugation, washed with distilled water for several times, and then dried at 60 °C for 24 h. The precursor was calcined at 600 °C in air for 2 h with a heating rate of 5 °C/min, giving rise to  $\text{La}_2(\text{WO}_4)_3$ .

Thermogravimetric-differential thermal analysis (TG-DTA) was performed to study the thermal behavior of  $\text{La}_2(\text{WO}_4)_3$  precursor synthesized through a conventional process. As shown in Figure S2, there is only one distinct weight loss step between 20-400 °C with a broad endothermic peak in the corresponding DTA curve, indicating the evaporation of the adsorbed water. In addition, there is an obvious exothermic peak in the DTA curve with little weight loss around 580 °C, which can be attributed to the crystallization process of  $\text{La}_2(\text{WO}_4)_3$ .

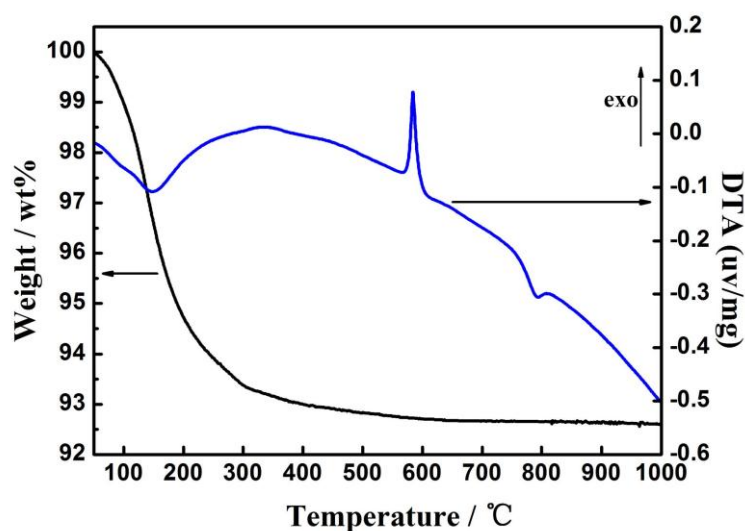


Figure S2. Thermogravimetric (TG, black line) and differential thermal analysis (DTA, blue line) of  $\text{La}_2(\text{WO}_4)_3$  precursor synthesized through a conventional process.

As shown in Figure S3, after calcination of the precursor at 500 °C for 2 h, the resultant product was still amorphous, being consistent with the result of TG-DTA.

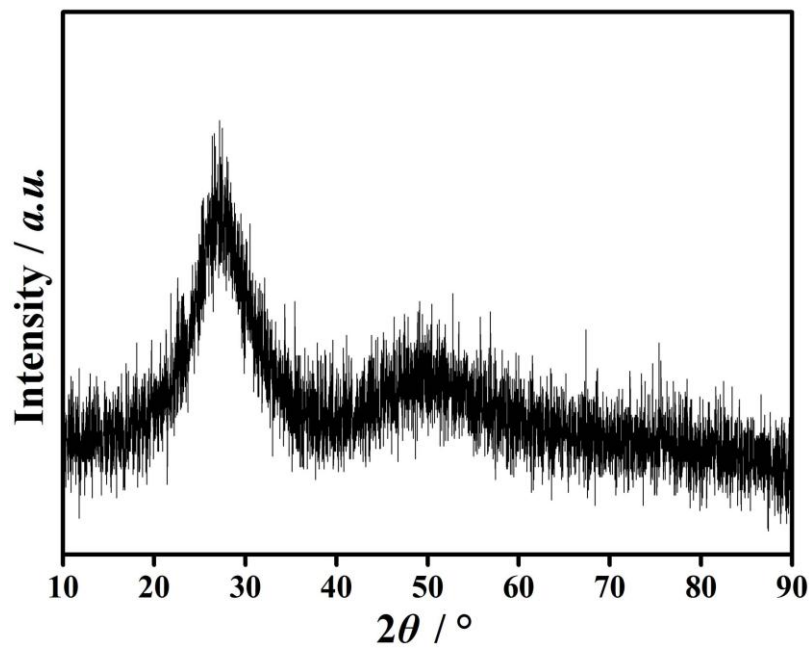


Figure S3. XRD pattern of  $\text{La}_2(\text{WO}_4)_3$  precursor after calcination at 500 °C for 2 h.

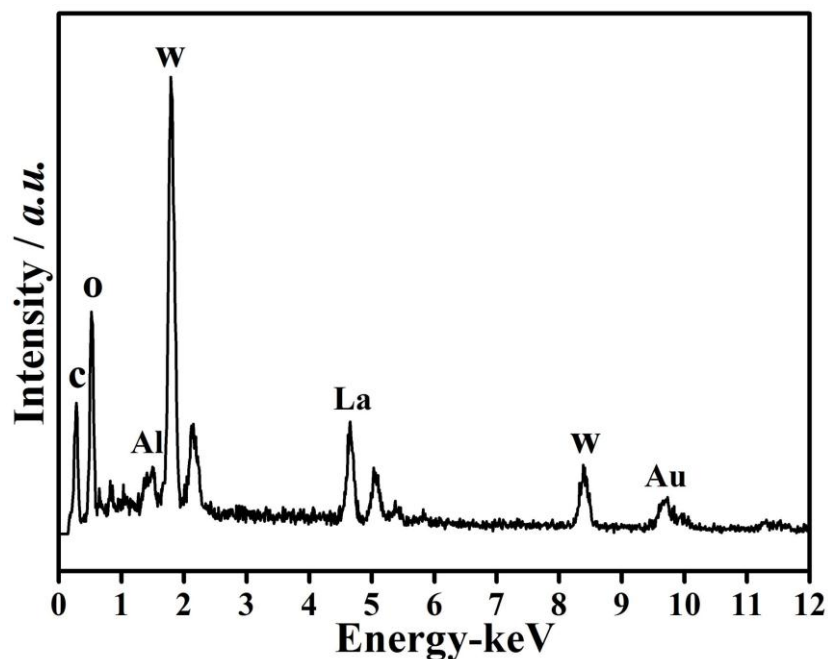


Figure S4. Energy-dispersive spectrum (EDS) of  $\text{La}_2(\text{WO}_4)_3$  precursor synthesized through a conventional process.

Energy-dispersive spectrum (EDS) was recorded to detect the chemical composition of  $\text{La}_2(\text{WO}_4)_3$  precursor synthesized through a conventional process. As shown in Figure S4, the precursor only contains O, W and La (C, Al, Au are from the testing facilities), demonstrating that the white precipitate does not contain Na element and  $\text{NaNO}_3$  can be washed away from the white suspension (the white suspension was immediately produced when  $\text{Na}_2\text{WO}_4$  stock solution was added into the solution of  $\text{La}(\text{NO}_3)_3$ ).

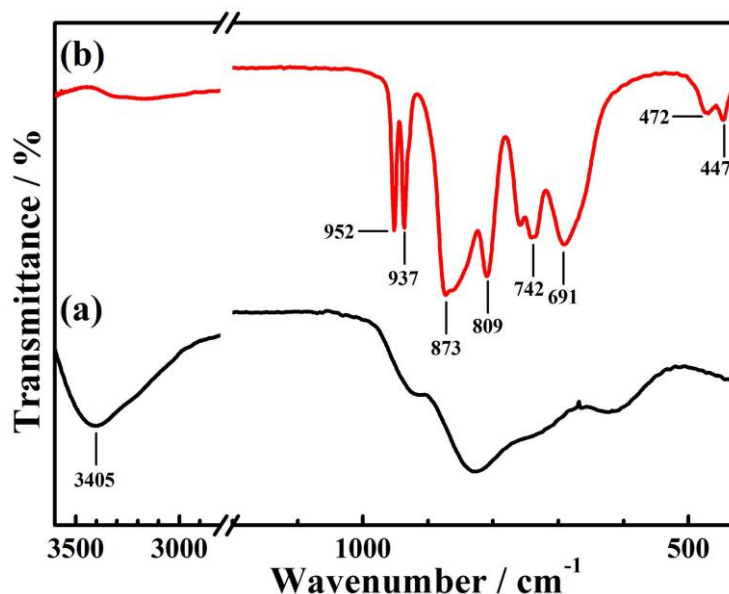


Figure S5. FT-IR spectra of (a)  $\text{La}_2(\text{WO}_4)_3$  precursor, and (b) calcined product synthesized through a conventional process.

To investigate the surface property and to determine the composition of  $\text{La}_2(\text{WO}_4)_3$  precursor synthesized through a conventional process, the FT-IR absorption spectra of the precursor and calcined product were measured. As shown in Figure S5, a strong broad absorption band around  $3405\text{ cm}^{-1}$  is attributed to the stretching and bending vibrations of O-H, respectively, indicating that the O-H group is from the adsorbed water. After the sample was calcined at  $600\text{ }^\circ\text{C}$  for 2 h, these two bands disappeared, suggesting the successful removal of the adsorbed water. As shown in Figure S4b, the bands at  $952\text{ cm}^{-1}$ ,  $937\text{ cm}^{-1}$ ,  $873\text{ cm}^{-1}$ ,  $809\text{ cm}^{-1}$ ,  $742\text{ cm}^{-1}$  and  $691\text{ cm}^{-1}$  are related to the symmetric and anti-symmetric stretching vibrations of  $\text{WO}_4$  units, while those at  $472\text{ cm}^{-1}$  and  $447\text{ cm}^{-1}$  can be assigned to the bending vibrations of  $\text{WO}_4$  units<sup>[1]</sup>. With careful observation, it could be found that the precursor has the similar profile with that of the calcined product ranging from  $1000\text{ cm}^{-1}$ - $400\text{ cm}^{-1}$ . The main difference is that there are not apparent split peaks in the spectrum of the precursor, which may be attributed to the amorphous state of the precursor.

Combined with the above-mentioned TG-DTA, XRD and EDS results, it can be concluded that the amorphous  $\text{La}_2(\text{WO}_4)_3$  with adsorbed water is the precursor for the final crystalline  $\text{La}_2(\text{WO}_4)_3$ .

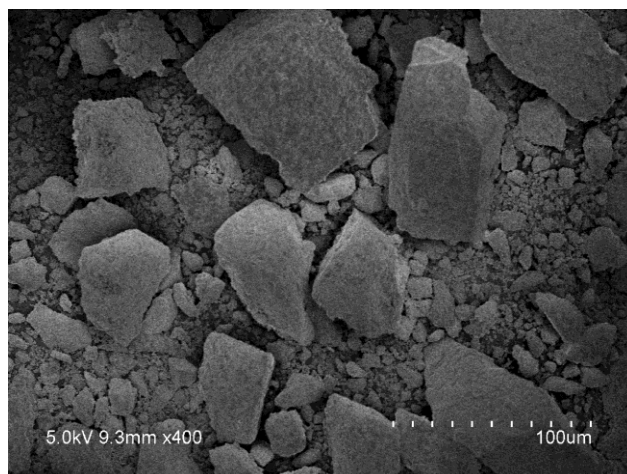


Figure S6. SEM image of  $\text{La}_2(\text{WO}_4)_3$  synthesized through a conventional process.

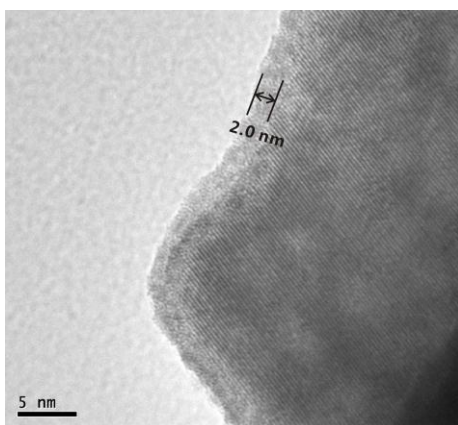


Figure S7. HRTEM image of spindle-like  $\text{NaLa}(\text{WO}_4)_2$  microcrystal.

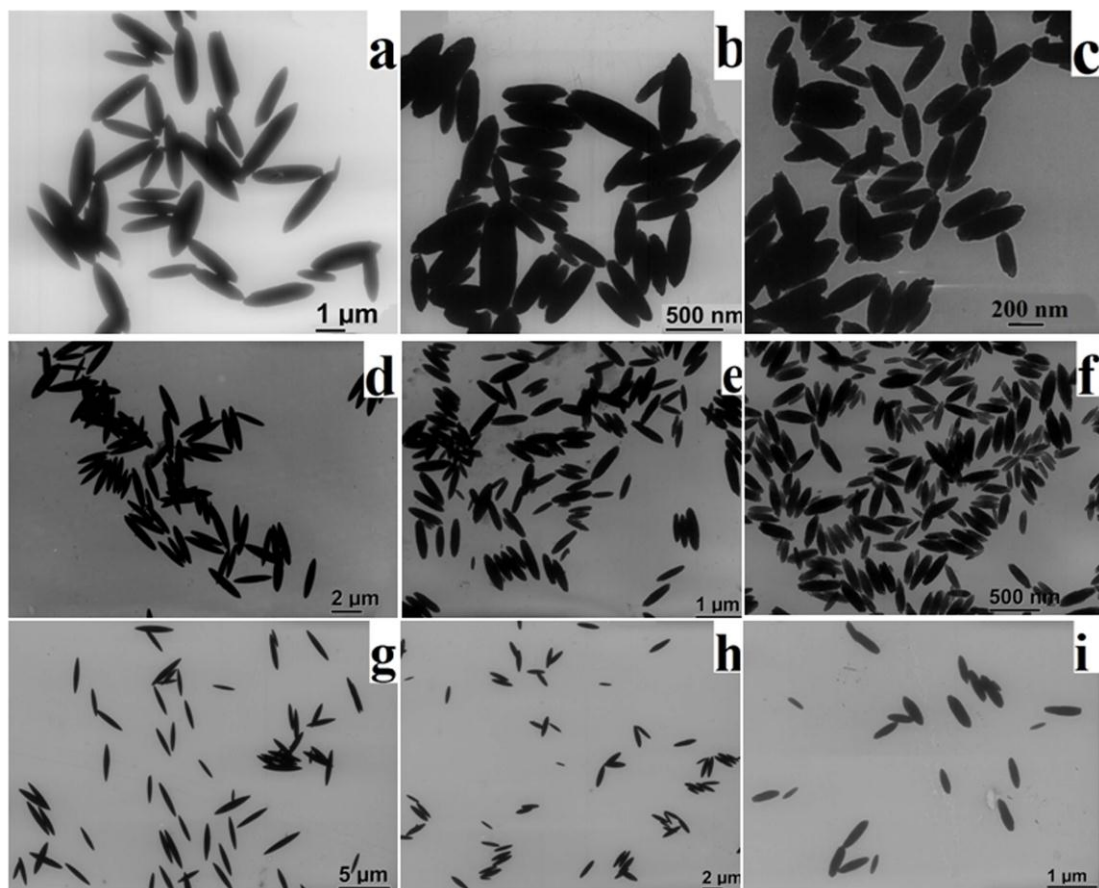


Figure S8. TEM images of NaLa(WO<sub>4</sub>)<sub>2</sub> synthesized at different temperatures for 24 h in the presence of different amounts of glycerine: (a) 160 °C, 10 mL; (b) 160 °C, 15 mL; (c) 160 °C, 20 mL; (d) 180 °C, 10 mL; (e) 180 °C, 15 mL; (f) 180 °C, 20 mL; (g) 200 °C, 10 mL; (h) 200 °C, 15 mL; (i) 200 °C, 20 mL.



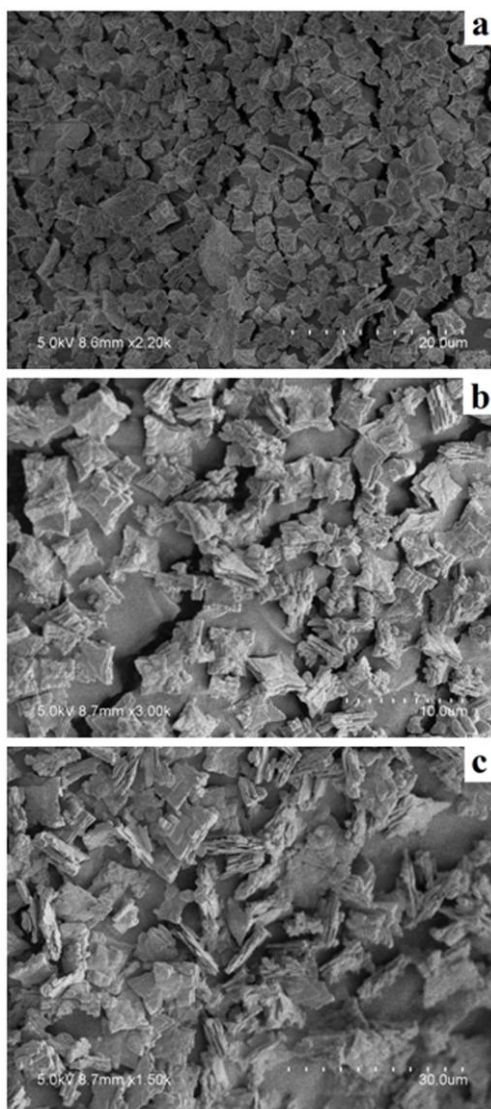


Figure S9. SEM images of NaLa(WO<sub>4</sub>)<sub>2</sub> synthesized at 180 °C for 24 h in the presence of different additives: (a) no additive, (b) 10 mL DEG, (c) 10 mL PEG-200.

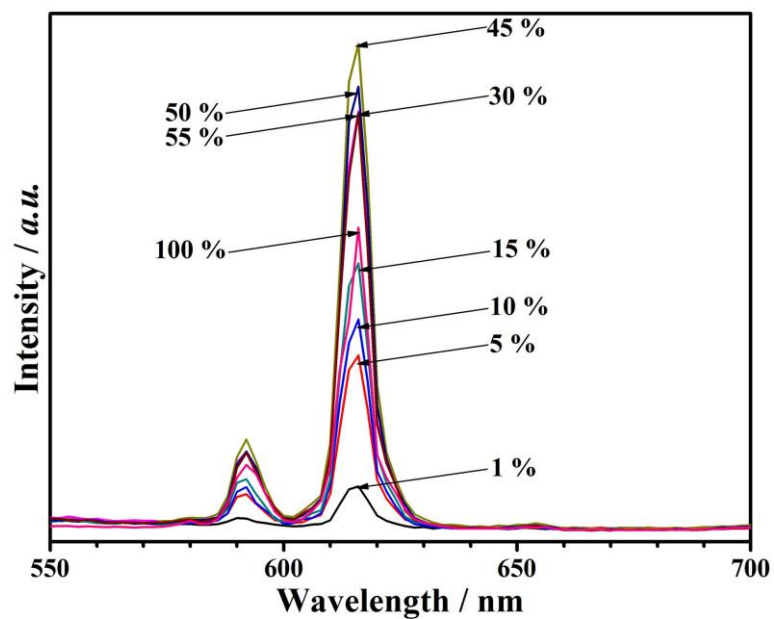


Figure S10. Emission ( $\lambda_{\text{ex}} = 467 \text{ nm}$ ) spectra of  $\text{La}_2(\text{WO}_4)_3: x \text{ mol\% Eu}^{3+}$  nanocrystals ( $x=1, 5, 10, 15, 30, 45, 50, 55, 100$ ).

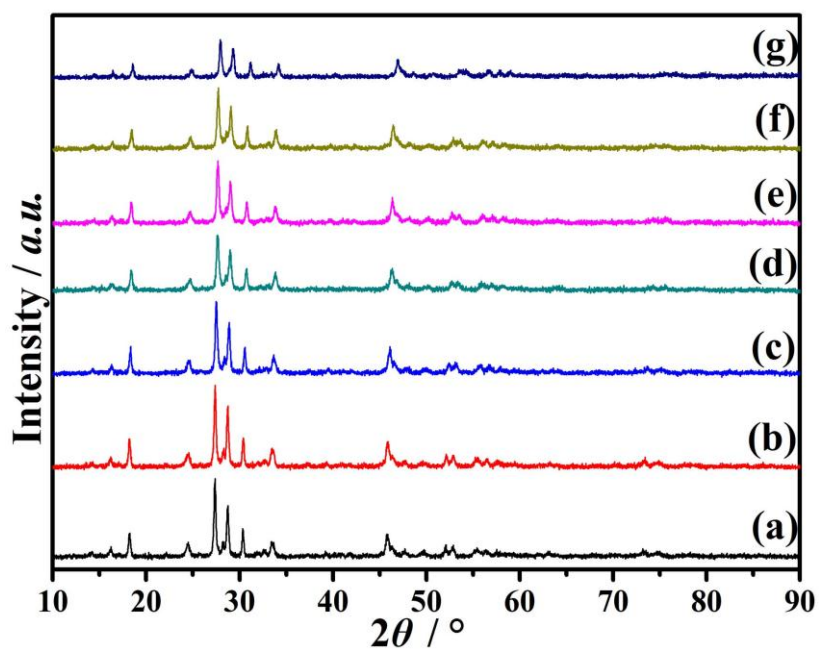


Figure S11. XRD patterns of  $\text{La}_2(\text{WO}_4)_3: x \text{ mol\% Eu}^{3+}$ , (a)  $x=10$ ; (b) 15; (c) 30; (d) 45; (e) 50; (f) 55; (g) 100.

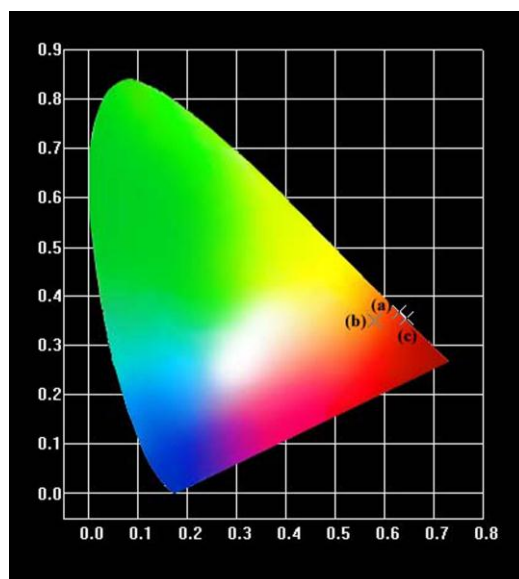


Figure S12. Commission Internationale de L'Eclairage (CIE) chromaticity coordinate diagram of (a) NaLa(WO<sub>4</sub>)<sub>2</sub>: 5 mol% Eu<sup>3+</sup>; (b) LuBO<sub>3</sub>: 6 mol% Eu<sup>3+</sup>; (c) La<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub>: 5 mol% Eu<sup>3+</sup>.

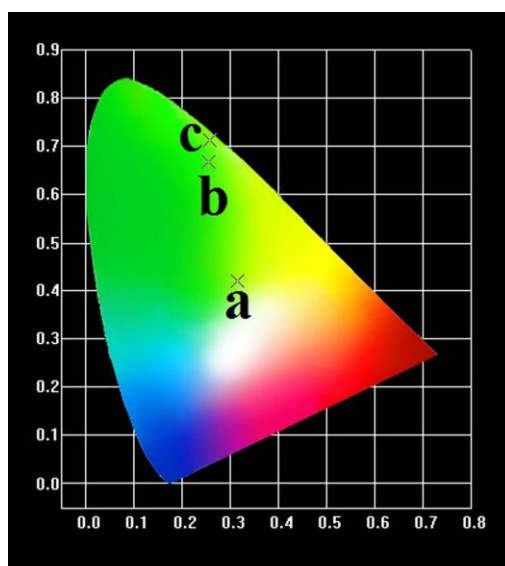


Figure S13. Commission Internationale de L'Eclairage (CIE) chromaticity coordinate diagram of NaLa(WO<sub>4</sub>)<sub>2</sub>: *x* mol% Yb<sup>3+</sup>/3 mol% Er<sup>3+</sup>, (a) *x*=5; (b) *x*=30; (c) *x*=40.

## References:

- [1] I. E. W. Loyd J. Burcham, *Spectrochim. Acta A* **1998**, 1355–1368.